The behaviour of bulk nanomaterials and metallic glasses under dynamic loadings
INDUSTRIAL AND ENVIRONMENTAL ISSUES OF NANOMATERIALS

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Abstract. In many domains of materials-oriented industries, the need for nanostructured materials has become ever more evident. In fact, it is well accepted, and in some cases well demonstrated that properties of materials, such as electrical, magnetic, and mechanical are dictated by the size of the elementary crystallites, notably when these sizes are significantly less than 0.1 μm (<100 nm). The emergence of nanostructured materials possessing more performance-enhanced property gave rise to many investigations during the past decade. Previous work has shown the importance of microstructure control (not only grain size, but also stoichiometry, impurities, the nature of the interfaces, and the nature of the defects) to attain reproducibility and hence the true benefits of the nanostructure and, whatever the method of preparation of such nanomaterials.

1. INTRODUCTION

The nanometric scale (10⁻⁹ m) is intrinsic to all what nature object, inert or living. Observed for a long date in terms of infinitely small, this nanometric scale emerged with forces - since the years 90 - in the technology domains, biology, electronics, surfaces and materials ... for the control of new properties and for the creation of new objects or new systems [1-9].

The main goal of many groups is to build on the experience and knowledge to produce the most advanced nanostructured materials in close collaboration with interested industries. They plan on the applied point of view to reach the control of fabrication processes in order to produce dense nanomaterials having a nanostructure and a level of densification perfectly controlled and, on the fundamental point of view to understand the evolution of properties as a function of the grain size [1,9].

Processing materials via powders has the potential of controlling the material microstructure at a nanoscale. The process begins with the synthesis of powders. It is now possible to synthesize powders with a grain size in the nanorange (1 to 100 nm) for a wide range of ceramic and metallic compounds from three different ways: (i) physical route such as evaporation-condensation processes, laser pyrolysis ... [10-17] or (ii) chemical route including soft chemistry, sol-gel methods, hydrothermal synthesis which can be extend to supercritical conditions [18-21] and (iii) the mechanical route in which powders are “nanostructured” (as opposed to than “nanosized”) e.g. powders of metallic alloys with a nano-distribution of phases within each particle, can be obtained by mechanical alloying [22-26].

The emergence of nanostructured materials possessing more performance-enhanced property gave rise to many investigations during the past decade [9]. In this paper only processes leading to the production of dense metallic materials will be exposed. All processes relative to the formation of thin films, multilayers, and surface... will be excluded.

2. GENERALITIES

2.1. Two classes of nanomaterials [1,9].

Since one forty of years, one went counts that the properties of certain materials could be modified, improved, adapted, if, during the elaboration process of the material, one arranged that the dimension of grains constituting the material itself are very small, of some nanometers to the hundred of nanometers. The first “nanomaterials” had been born. Since a little less than time, about around fifteen years, this term “nanomaterials” is also, sometimes, used to describe the matter in which the atoms constitute assemblies of which the dimensions are also on the order of some nanometers. These assemblies known under the names of clusters of aggregates have not a priori practically anything in common with nanomaterials previously defined. These new materials, on the contrary to previous ones, are not conceivable, by nature, which to the nanometric scale. Solid architectures constituted of atoms of carbon can help to specify the distinction between these two families of nanomaterials: (i) to the solid state, carbon is known under two crystalline forms, graphite and diamond. It is possible, for the one as for the other of these two varieties, to produce
them to the state of very small grains of some nanometers. (ii) Besides, since around fifteen years, one knows to synthesize sorts of molecules of fullerenes, of which the most famous one is constituted of 60 atoms of carbon, the C60 [1].

Conceptually, it seems therefore that two families of nanomaterials coexist and, therefore two communities of researchers that evolved regardless the one of the other (figure 1). These two communities distinguish themselves (i) by the nature and the spirit of the basic research that they develop and, (ii) by the applications that are conventional for the first community, on the contrary new for the second family of nanomaterials.

![Figure 1. Communities of researchers working in the nano-world](image)

2.2. Two classes of granulo-dependent properties

The term “nanomaterials” is usually used for nanostructured or nanophased materials, in which the dimension of grains is ranged from 1 to 100 nanometers, which have specific characteristics due to the modification of the surface / volume ratio. Two different effects are usually observed:

- The nanograin behaves as a "box" inside which the property can or cannot exist. Underneath a certain critical dimension, characteristics of the property depend on the dimension of the grain. One talks about the effect of confinement. The evolution of these characteristics according to the dimensions is often not monotonic while presenting an extremum [27].

- In the nanograin, the constitution of atomic layer close to the surface plays a role more and more important in the global behavior of the material when the dimension of the grains decreases. This is the surface energy that has a larger contribution. The evolution of such a property according to the grain dimensions is monotonic. This is the case of all properties led to thermodynamic [27].

However, if many examples in literature can easily illustrate these effects in electronics, magnetic recording, cosmetics, catalysis, ... it very difficult to classify the evolution of mechanical properties versus the grain size. The relative dearth of experimental data on mechanical properties of nanomaterials has been attributed to the difficulty in preparing dense bodies [28].

Nevertheless, some examples presented figure 2 showed clearly that the improvement of mechanical properties of metals and alloys has been led historically to the diminution of microstructure.

![Figure 2. Many transformations have been developed for controlling the cooling rate in order to refine the microstructure and, consequently to increase mechanical properties.](image)
In addition the decreasing of the grain size increases the yield strength and most often the toughness according to Hall-Petch law [29-31]. The development of the substructure in order to limit the dislocation motions via the precipitation – creation of dislocation cells (10-200nm) and, consequently to reinforce the compromise between elasticity and ductility and, the development of a texture implying oriented properties [32]. As an example, figure 3, showed that the control of the microstructure, in the case of tungsten alloys prepared by powder metallurgy and thermal-transformation allowed increasing by two orders of magnitude of strength resistance and, simultaneously, increasing by 6 their toughness [33].

![Image](https://via.placeholder.com/150)

**Figure 3.** Microstructure of W-Ni-Fe-Co alloys which are composed of two phases α-γ. a) Stacking faults observed in the γ-phase. b) Precipitates present in the γ-phase (40-80nm) and c) Polygonisation of α phase (70-150nm).

2. FABRICATION OF NANOSTRUCTURED METALLIC COMPOUNDS

2.1. Amorphisation - Annealing.

Via high cooling rates from $10^4$ to $10^6$ K/s, it is possible to solidify metals without nucleation and growth of crystallites for confined volumes having very low thickness. In addition, starting from complex alloys getting eutectics with a large effect of sur-melting, it is possible to reduce the cooling rates up to 10 – 100 K/s allowing the formation of component with significative volume. The figure 4 shows the position of these materials in reference with classical ones [34]. Finally from amorphous structures, some heat treatments at low temperature can be performed leading to the demixion of sur-saturated elements of alloys. Consequently, several soft magnetic materials have been prepared such as Fe,Si,B,Cu,Nb or Fe,Ta,N [35]. This elaboration route implies to identify some alloys which are able to support the amorphous process at low cooling rate.
2.2. Severe Plastic Deformation.

The hyper-work hardening by intense plastic deformation of metals is the route which has been largely used during the last fifteen years for producing ultra fine grained materials. Several types of processes have been developed. By rolling of piling up of bands, laminated products in aluminium were prepared with grain sizes ranged from 100 to 700 nm [36]. But also by sequenced hammering, bars in alloys of tungsten having bi-phased structure were prepared with a nanometric sub-structure of 80 to 200 nm for the phase allowing to a same basic alloy to attain limits of elasticity of 1700 MPa comparatively to the 900 MPa obtained by conventional way [33,37]. These transformations by work hardening are always accompanied of a crystallographic texture with most often the development of internal stresses. However, this is the technique of the extrusion of an ingot in an angled canal (ECAP, figure 5) with several passages that nevertheless was the object of the biggest number of publications (Al, Cu, Ni,... [38,39]).

Developed by Valiev [38,39], this extrusion technique allowed with materials to weak energy of plastic deformation to develop microstructures to ultra fine grains. In addition, these grains which have complex crystallographic textures get improved mechanical properties such as the yield strength. On the contrary, the ductility depends on the metallic system as be shown in figures 6 and 7 [41,42].

Figure 4. Classification of glassy alloys in comparison with other materials [35].

Figure 5. Severe plastic deformation by Equal Channel Angular Pressing [40].

Figure 6. Comparison of mechanical properties for Cu and Ti between cold rolling and extrusion by ECAP [40].
Figure 7. Comparison of mechanical properties (tensile strength and limit of fatigue) in the cases of Invar Fe-Ni alloy and Al-Mg 5056 between cold rolling and extrusion by ECAP for different cycles and temperatures used [41].

For an industrial point of view, it will be necessary to take into account the level of power for a couple product / material. The product itself should be machined to acquire the final geometry and surface state.

2.2. Powder Metallurgy Processes.

Determination of the macroscopic properties of nanostructured materials has been difficult because of the limited quantities of nanomaterials produced by many of the processing techniques. One technique for producing significant quantities of nanomaterials is ball milling. In this and other techniques, the desire is to process the materials under “far from equilibrium” conditions [43]. According to simple calculations, mechanical activation (including ball milling) has the second highest departure from equilibrium conditions, with a typical ΔG value of 30kJ.mol⁻¹ [43]. This relatively large degree of departure from equilibrium makes this process quite attractive for such goals as extension of solubility limit, synthesis of amorphous phases, formation of non-equilibrium alloys and solid solutions, initiation of chemical reactions at low temperatures, and, of course formation of nanopowders. Ball milling has been used to reduce grain size to the nanometric range in numerous studies [22,23,44].

Products and materials with nanometer-scale crystals are formed from nanometer-scale particles in processes than entail first forming the particles of the desired chemistry and size scale, combining the particles into a green body and, then densifying the particles. However, in each case, it is necessary to add a consolidation step to obtain fully dense materials. Different processes have been developed to consolidate nanoparticles [45-48]. Rawers [48] has recently reviewed the main methods to densify nanomaterials and discussed the advantages and disadvantages. All the methods are based on the application of high pressure and high temperature to affect densification through particle deformation and mass transport in order to achieve pore removal. One promising technique is the hot-pressing of mechanically milled powders, in which the careful control of processing parameters (time, temperature and pressure) makes possible the fabrication of fully dense nanostructured samples [47-48]. However, this high temperature treatment can lead to significant grain coarsening (Oswald ripening). Decreasing the temperature to ameliorate the problem of grain growth necessitates the use of very high pressure (4 GPa in some cases) to plastically deform the nanometric grains [50]. An alternative route to enhance densification and avoid excessive grain growth is the so-called fast firing method [51]. The aim of this method is to reduce the time of exposure to high temperatures. An example is given on the figure 8 in the case of W-9% Y nanopowders prepared by ball milling and, then sintering in vacuum [49].
Figure 8. Evolution of the hardness and density of tungsten ODS alloy as a function of milling time [49].

One promising technique was the combination of mechanical and field activations. A few years ago, the simultaneous effect of an electrical field combined with an applied pressure during the combustion, using the Field-Activated Pressure-Assisted Synthesis (FAPAS) process was found to be suitable to produce good quality dense intermetallic compounds in a one step process [52,53]. Consequently, the application of this technique on mechanically activated powders was undertaken in order to investigate a new route hereafter called MAAPAS process [54,55]. With this approach, several dense nanostructured materials have been fabricated including intermetallics, ceramics and composites [55-59]. A process which also relies on field activation, called Spark Plasma Sintering (SPS), has been also developed and has received increased attention [60,61] (figure 9).

Figure 9. General view of SPS chamber [60].

The combination of mechanical activation and the SPS, hereafter called the MASPS process, has been shown to be suitable for the production of materials having nanostructure and a controlled consolidation level [62]. In fact, the SPS process is a newly developed synthesis and sintering process that, it is claimed uses microscopic electric discharges between the particles under pressure [63]. This has been acknowledged to reduce significantly the synthesis and densification temperatures limiting the grain growth. This process is similar to conventional hot pressing, in that the precursors are loaded in a die (typically graphite) and a uniaxial pressure is applied during the synthesis or the sintering. However, instead of using external heating source, a pulsed DC current is allowed to pass through the sample and also through the electrically conducting pressure die.
As examples, we present results on the sequential use of mechanical and field (SPS) activations to 
(i) synthesize and simultaneously densify nanostructured intermetallics (i.e. MoSi$_2$ by reactive 
sintering including an SHS reaction [64,66]). Solid reactants (Mo and Si) in a stoichiometric ratio are pre-
milled to particle sizes in the nanometer range (mechanical activation), then compacted into a green body. 
The green body is then exposed to sufficient pulsed DC current to a temperature at which the reaction 
occurs, and to a uniaxial pressure to consolidate the product. Thus, the control of SPS processing 
parameters allowed obtaining dense nano-organized MoSi$_2$ compounds, with a relative density of 96 %. 
TEM analyses had revealed that the nano-organization, especially the nanosize of the coherently diffracting 
domain size, was due to dislocation networks (figure 10) [65]. MoSi$_2$ is brittle at room temperature. In this study, the dense nano-organized MoSi$_2$ produced at 1573 K 
reveals excellent mechanical properties: a Vickers hardness of 13± 0.5 GPa, and a fracture toughness of 
5.8± 0.2 MPa m$^{1/2}$. Especially the $K_I$ exhibited a considerably high value. A commercial dense material 
MoSi$_2$ (SuperKanthal 1800), presents a lower Vickers hardness (9.9± 0.6 GPa) and a lower fracture 
toughness (4.4± 0.2 MPa m$^{1/2}$). In addition, an increasing of the density coupled to a nano-organization 
enhanced the resistance to the "pest" phenomenon. This deceleration could be due to the formation of a 
silica layer which partially protected the sample surface and which could be formed thanks to the nano-
organization of the MoSi$_2$ substrate. In addition, our samples preserved their physical integrity, even after 
an oxidation at 673 K in air under the atmospheric pressure during 3 years whereas the micrometer sample 
was destroyed after one week in the same conditions [65].

(ii) consolidate different nanopowders of alloys for enhanced mechanical properties. Mechanical 
activation was accomplished by high energy planetary milling and field activation was made through the 
use of the SPS process. The powder was produced by CEA-DTEN (Grenoble, France). An initial step of 
atomization was used to produce powder with the following nominal composition Fe-40Al (at.%). A small 
amount of Zr and B were added for improving grain boundary strength [66]. The type of drum mill that has 
been used has a maximal production capacity of 10 Kg per batch. Y$_2$O$_3$ was added during the milling stage 
to introduce fine yttria dispersion [67-69]. The SPS material has a heterogeneous grain size distribution. 
Small grains are of the order of 150-300 nm (figure 11, [70-72]). Large grains can however reach a size of 
about several micrometers. Fine oxide particles were also visible within the large grains. They usually have 
a size of 10-40 nm or may sometimes have a larger size (about 200 nm). In addition, it seems that such a 
microstructure (especially the nanostructure) led to a modification of the properties of materials prepared 
via classical routes. Indeed, the Vickers hardness ($HV_{300}$) at 298K of MASPS sample is greater (450Hv) 
than the Fe-Al40 compound prepared by conventional extrusion (350Hv) starting from the similar milled 
powder as precursor.
However, SPS complementary experiments should be performed in order to understand the role of the current stimulation. In particular, it will be essential to compare both sintering processes with different conducting materials (e.g., nano-intermetallics prepared by ball milling) and insulating (e.g., nano-ceramics prepared via chemical routes). Such a study should allow us to understand the role of the electric stimulation on the sintering mechanisms (grain growth and consolidation steps). Such experiments are in progress. Thus, these local differences result from an heterogeneous microstructure of the end-products. Some numerical calculations should be developed simultaneously in order to establish correlation between SPS processing parameters and final microstructure of materials [74].

3. CONCLUSION

The objective of this paper was to demonstrate the effectiveness of different techniques in forming a variety of highly dense nanostructured materials. Unfortunately, some efforts are still necessary to control such processes. In fact, different processes have emerged during the ten last years and allow today to attain metallic materials having an ultra fine grains and/or a nanometric structure. What they be produced by severe deformation plastic (SPD) or by consolidation of nanostructured agglomerate powders, these materials necessitate a more precise control of the process since the final microstructure is nanometric. It is not sufficient to have the label "nano" for that, implicitly, the physic-chemical properties obtained from metallic models such as copper, iron, aluminum and nickel, according to very specific protocols and-mostly non-available to industry— to be universal and applicable to other any system. In addition, if the powder consolidation methods lead to isotropic materials, other processes such as the ECAE imply strong crystallographic textures. For applications in the short one run, this is therefore more an approach in the continuity of the processes and materials already existing than it are necessary to consider the new applications in the domains of nanometals and alloys.

The production of pieces with microstructures to evolved properties is possible with costs and investments in terms of technology and process control. The figure 12 gives a schematic evaluation of the maturity for an industrial transfer of existing processes. One will keep that the way of consolidation of nanostructured powders via SPS is the one of the more mature for an industrial application.
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**References**


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**Figure 12.** Schematic evaluation of the maturity for an industrial transfer of existing processes.
DYNAMIC BEHAVIOR OF NANOMATERIALS

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Abstract. The deformation mechanisms in nanomaterials are examined from both theoretical and experimental viewpoints, with a view to understanding grain size effects and size effects. The fundamental deformation mechanisms in bcc, fcc and hcp metals are considered first. On the basis of simple constitutive modeling, it is shown that the response of these metals to reductions in grain size can be significantly different. These simple constitutive models do, however, break down at very small grain sizes. At the very small sizes associated with such breakdowns, molecular dynamics and atomistic results are used to indicate some potential behaviors (only some of which have been observed experimentally). These theoretical and computational results are then compared with the results of a variety of experimental techniques (including high-rate deformations and microscale testing) that have been used to examine a variety of nanostructured metals.

I. SUMMARY

Although experiments employing strain rate changes are very useful in revealing deformation mechanisms, there is very limited experimental data on the strain-rate sensitive mechanical properties of nc/UFG metals. The primary material parameter of interest is the strain rate sensitivity. The available data indicate a substantial increase in rate-sensitivity when the grain size of fcc metals is reduced into the UFG and nc regime, regardless of the technique used to process the material. This behavior was summarized in the work of Wei et al. [1], showing the change in the rate sensitivity of copper over a wide range of grain sizes. Similar behavior is observed in other fcc metals, such as nickel and gold. Note that all of these rate-sensitivities are for deformations that are at nominal strain rates from $10^{-4}$ to $10^3$ s⁻¹. There is no clear explanation for this at present, but one plausible explanation is that the evolution of dislocation substructure (which is known to be important in fcc metals) is controlling the behavior. For coarse-grained fcc metals, the primary obstacles to the motion of glissile dislocations are known to be forest dislocations, leading to the rate dependence of flow stress through thermal activation. Wei et al. showed that when the grain size is refined into the UFG/nc regime, the rate sensitivity should increase with reduced grain size [1]. Further, as the grain size is reduced to below a transition size, the forest dislocation density in the grain interior may become very low, whereas the obstacle density associated with grain boundaries becomes very high. It is thus plausible that the controlling obstacles are the grain (or subgrain) boundaries.

Very different rate-dependent behavior is observed in nanostructured bcc metals. In these materials it is observed that the effective rate-sensitivity decreases with decreasing grain size. Such a decrease has been observed in iron, tantalum, tungsten and vanadium, and a summary of this data is presented in [1]. The source of this behavior is the deformation mechanism that dominates bcc metal plasticity, that of kink nucleation and propagation, and is discussed in detail in the next chapter. In brief, the explanation is that the plastic deformation of nanocrystalline bcc metals is controlled by the Peierls-Nabarro stress and the temperature- and rate-insensitive grain boundary controlled Hall-Petch mechanism, and for the very high-strength nanocrystalline bcc metals these terms are much larger than the rate-dependent terms, resulting in a reduction in the effective rate-sensitivity.

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References
ULTRAFINE-GRAINED MATERIALS PROCESSED FROM NANOPOWDERS: MICROSTRUCTURES AND MECHANICAL PROPERTIES

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Abstract. Bulk ultrafine-grained materials (Al, Fe, Ni) have been processed either by Hot Isostatic Pressing (HIP), Spark Plasma Sintering (SPS) or combined HIP and dynamic severe plastic deformation (DSPF). The resulting microstructures (grain/crystallite sizes, grain size distribution, crystallographic texture, defects) depend on the processing route and are characterised by means of X-ray diffraction line profile analysis and transmission electron microscopy. The influence of the microstructure on the mechanical behaviour is studied by quasi-static compression tests at room temperature. The observed macroscopic behaviour especially the flow softening during the quasi-static compression test is discussed in relation with the initial microstructure and its evolution during straining.

1. INTRODUCTION

The processing of materials with ultrafine grains strongly expanded in the recent years since the pioneering work of Gleiter [1]. The unique behaviour of these materials opens promising perspectives of their applications in various fields. Nevertheless, it is clear that the strategy for the choice of a material results in a compromise between optimal physical performances for the foreseen application and the capacities of shaping and mechanical strength required. Metals and metallic alloys are the fundamental structural materials. Their properties are strongly dependent not only on the chemical nature of the material, but also on the initial microstructure and on its possible subsequent evolutions under assigned loading or any exterior conditions to face. Consequently, it is of prior importance to control the elaboration process with a deep understanding of the effect of processing conditions on the microstructure and the relationship between the microstructure and the properties of final material.

Among the several ways to process bulk materials with ultrafine-grained (ufg) microstructures, the compaction of powders has a fundamental place because of its versatility to tailor microstructures. This type of process allows obtaining fully or near fully dense materials with grain sizes spanning the nanocrystalline (nc, 30-100 nm), the ufg (100 - 1000 nm) and the microcrystalline regimes. nc materials have so far demonstrated excellent physical-chemical properties and improved mechanical characteristics, e.g. high strength [2,3]. Other properties such as ductility which is a key parameter in forming processes are still to be confirmed [4-6]. Indeed, the lack of usable ductility and toughness has slowed down the potential use of these materials in structural components. At the same time, ufg materials processed either by powder metallurgy (PM) methods or severe plastic deformation (SPD) processes or their combination draw an increasing interest as they offer the ways to offset some of the drawbacks exhibited by nc materials [2,3,4-8]. The present work reports on the influence of processing routes on the macroscopic behaviour of bulk ufg materials produced from nanopowders by use of PM methods \textit{per se} or in combination with a SPD process.

2. EXPERIMENTAL PROCEDURES

2.1. Processing routes

\textit{Hot Isostatic Pressing (HIP)} processing provides a method for producing components from diverse powdered materials, including metals and ceramics. During the HIP process, a powder is placed in a container, typically steel can. The container is subjected to moderate temperature and a very high vacuum to remove air and moisture from the powder. The container is then sealed and HIPed. The application of high inert gas pressures and elevated temperatures results in the removal of internal voids and creates a strong metallurgical bond throughout the material. Fully dense bulk ultrafine-grained aluminium and iron
samples have been processed [9,10] using an instrumented HIP setup. Our HIP device can operate at 1200°C and produces a pressure up to about 300 MPa using Argon as inert gas. The compaction device used in this study has a special expansion cell within the hot press, allowing the measurement of the capsule height or width during compaction, and gives in steady-state information on the sample density. It should be noted that HIP is a time-consuming process, particularly with nanopowders as the time needed for removing the gas introduced during the filling step can exceed 1 week for a cylindrical container of 15 mm in diameter and 20 mm height.

Spark Plasma Sintering (SPS) processing has been carried out at the CNRS facilities at Toulouse. The principle of SPS is based on the application of a uni-axial pressure and pulses of high current density to raw powders in a graphite die. The physics of the compaction process is not fully understood, but its main characteristic is an ultra-fast compaction at much lower temperatures than the classical techniques, thus preventing grain growth [11]. In the study reported here, the starting materials were pure Ni nanopowders (80 nm in particle size). The resulting bulk materials have an average grain size of about 300 nm. Nevertheless, microstructure heterogeneity, contamination of the powder or incomplete particles bonding have been reported as shown later on.

Dynamic Severe Plastic Deformation (DSPD) is a peculiar process of severe plastic deformation in the dynamic regime. Dynamic loading offers a remarkable method as a new grain refinement process [12]. Bulk materials produced from coarser powder particles by HIP are subsequently processed using a dynamic drop mass bench with a maximum impact velocity of 10 m/s and of a maximum kinetic energy of 2.5 kJ. The set up apparatus located at L3M (Tremblay Institute of Technology) is equipped with a dynamic load cell, an accelerometer, and a laser beam displacement transducer. In the present study cylindrical pre-Hipel commercial purity (99 %) Al samples have been impacted at a strain rate of $300 \text{s}^{-1}$. The height reduction was about 70%.

2.2. Mechanical Testing and Microstructure Characterisation

After processing, the resulting materials were subsequently tested by compression at different strain rate in quasi-static regime. The as-processed microstructure and its evolution after compression test were studied by scanning electron microscopy (SEM) coupled with electron backscattering diffraction (EBSD) analysis, transmission electron microscopy (TEM) and X-ray diffraction line profile analysis. The TEM investigation was carried out using a JEOL-2011 operating at 200 kV and the samples were thinned mechanically first to about 50 μm and finally with Ar+ ions until perforation. The X-ray line profiles are measured by a high-resolution rotating anode diffractometer (Nonius, FR591) using CuKα radiation. The scattered X-rays were detected by imaging plates with the angular resolution of 0.005° in 2θ, where θ is the angle of diffraction. The line profiles are evaluated using the extended Convolutional Multiplicative Whole Profile (eCMWP) fitting procedure described in detail in other reports [13,14]. This method gives the dislocation density and the twin-fault probability with good statistics.

3. RESULTS

HIP-processed materials. Figures 1 and 2 illustrate the microstructure and the mechanical behaviour in the case of Al and Fe ubf materials. The Al samples were processed from a powder having mean particle size of 70 nm. Figure 1a shows that HIP resulted in a fully dense bulk material with a composite-like microstructure consisting of micron-sized grains embedded in an ubf matrix with an average grain size of 150 nm and a random crystallographic texture as it is expected from HIP [9]. In Figure 1b the mechanical behaviour during quasi-static compression at a strain rate of about $10^{-3} \text{s}^{-1}$ is compared to the behaviour of a conventional Al sample (with the mean grain size of 120 μm) also processed by HIP. A net gain in the yield stress is observed in the case of ubf Al as shown in Figure 1b. It is noticed that after a short plateau, the flow stress slowly decrease ending with a rupture after about 18% plastic deformation. The AFM micrograph presented in Figure 1c shows that the deformation mechanism occurs mainly by multiple events of grain alignments within macroscopic deformation bands homogeneously distributed on the surface of the sample. XRD investigation shown in Figure 1d illustrates the presence of γ-Al₂O₃ particles within the microstructure. The contribution of the oxide phase on the level of yield strength has been evaluated elsewhere [15]. A rough estimation of the amount of the alumina oxide has given about 3% [9].
Figure 1. Different aspects of the microstructure and mechanical behaviour of commercial purity Al processed by HIP. (a): the microstructure of the as-processed bulk material; (b): mechanical behaviour of the UFG material compared to a standard coarse-grained Al; (c): grain alignment during deformation; (d): XRD analysis showing the composite nature of the as-processed material.

Figure 2a shows a comparison of the mechanical behaviour under quasi-static compression of UFG iron samples with different mean grain sizes ranging between 250-1000 nm and a conventional specimen having an average grain size of 5 µm. The jumps in the stress-strain curves are related to strain rate change experiments. The striking feature displayed on the figure is a clear transition occurring at about 500 nm from hardening to softening.

Figure 2b obtained by EBSD experiment shows the microstructure for UFG iron having a mean grain size of 500 nm after the compression test. It is clear that the deformation in the investigated volume mainly occurs in a shear band (SB) located between the two red lines. In this area of Figure 2b, the fraction of small angle grain boundaries is much higher than in its surroundings which indicates a lattice dislocation activity in the SB. The figure also shows the crystallographic texture evolution inside and outside the SB. It can be noticed that while outside the SB the crystallographic texture keeps almost random, a \{111\} fiber-like texture develops within the SB as a consequence of an intense plasticity.
Figure 2. Mechanical behaviour under quasi-static compression tests of ufg iron processed by HIP (a) and selected microstructure details after compression test for a sample having an average grain size of about 500nm (b). The crystallographic textures inside and outside the SB are shown in the bottom and upper parts of the figure, respectively.

SPS-processed materials. The microstructural features and deformation characteristics of samples processed by SPS (at a pressure and temperature of 150 MPa and 500°C respectively, applied during 1
minutes) are shown in Figure 3. The average grain size is about 294 nm, however the microstructure is heterogeneous in the sense that it contains ufg/nc grains as well as micron-sized grains. TEM images show that a fraction of grains contains grown twins which has an average probability of 0.3% in the whole sample as determined by X-ray line profile analysis. For comparison, another sample was consolidated from the same powder by HIP method. Before HIP processing, the powder was heat-treated in a glove box under controlled hydrogen flux at 400°C and subsequently encapsulated and sealed under inert gas (Ar) for preventing oxidation. During HIP method, the capsule was subjected to a pressure of 140 MPa at 700 °C for 150 min. In the case of SPS, the powder has been processed in air before the sintering which results in a two times higher oxide content compared with the HIP-processed sample as revealed by XRD investigation (not shown here). The average grain size in the case of HIP-processed sample is higher (403 nm) than that for the specimen produced by SPS due to the longer time and higher temperature of HIP processing. The twin probabilities and dislocation densities (5-6×10¹⁸ m⁻²) are the same in the two materials within the experimental errors. The higher oxide content and the smaller grain size of the SPS-processed sample result in a higher compressive yield strength. X-ray analysis revealed that the dislocation density increased while the twin-probability decreased during compression test indicating dislocation activity during deformation. The decay of twins are also confirmed by TEM. In Figure 3b the arrows indicate locations of incomplete particle bonding in the vicinity of a coarse grain in the SPS-processed sample.

As for the mechanical behaviour, Figure 3c reveals that during compression of the SPS-sample a plateau occurs after a short hardening stage that is immediately followed by a flow softening regime till the failure of the sample. The inset in Figure 3c is a SEM observation showing that the ufg matrix deforms by grain alignment in multiple deformation band events. In addition, cracks are created at the interfaces between large and ufg grains. Contrary to the SPS-processed Ni sample, flow softening and cracks were not observed for the sample produced from the same initial powder by HIP.

DSPD-processed materials. In this case samples are first prepared by HIP from conventional coarse-grained powders. The resulting grain size in the as-HIPed material was about 2 μm. After the DSPD step the grain size decreases down to about 500 nm as measured by TEM while X-ray line profile analysis gives a dislocation density of about 1.4±0.2×10¹⁸ m⁻². This microstructure has been also found to be stable after 3 months storage at room temperature. Figure 4a shows the microstructure of the HIP-processed sample before and after crash test. After DSPD step the material exhibited a strong (111) fiber-like texture parallel to the impact load axis [12]. Figure 4b illustrates the effect of a strain path change during subsequent quasi-static compression tests conducted parallel to the impact axis (ND) and perpendicular to the impact axis (TD). It is observed that while a long hardening stage is observed when the sample is tested along ND, in the case of TD testing a maximum in the flow stress has been reached at small strains which was followed by a rapid flow softening.

4. DISCUSSION

In this study different ufg materials have been processed using different PM procedures. In spite of the differences in the resulting microstructures, the compression behaviour of all materials can be characterized by a short initial hardening at the very beginning of the deformation which is followed by a lack of hardening or even flow softening. In the following section we are discussing only the apparent softening exhibited by the macroscopic compression behaviour of the processed materials.

Both in the cases of iron and nickel it was found that for large grain size (>500 nm) the samples harden during compression test while for small grains flow softening occurs. Due to the Hall-Petch relation, smaller the grain size, higher the stresses needed for plastic deformation. The higher stress level during deformation results in a larger probability of debonding in the grain boundaries during straining. The resulting cracks may yield to strain localization and flow softening with increasing strain. Moreover, as the smaller grain size of the sintered specimens is usually resulted from smaller initial powder particle size, these samples contain higher oxide content. The higher volume fraction of oxide dispersoids causes an additional increase of the flow stress which may increase the probability of cracking at grain boundaries. Furthermore, the oxide on the interfaces may reduce the grain boundary strength resulting in easier cracking [16]. In the case of Ni processed by SPS, the powder processing in air further increased the oxide content in the sintered sample. Moreover, in this sample there are incomplete particle bonding (see Figure 3b) which may also contribute to cracking during deformation. This explains the different behaviour of Ni samples processed from the same powder by SPS and HIP.
Figure 3. (a): BF TEM image of the starting nanopowder showing a skeleton of NiO on the surface of Ni particles; (b): a typical TEM view of the as processed material. The arrows indicate incomplete particle bonding around a coarser grain; (c): macroscopic behaviour showing a flow softening as a consequence of deformation incompatibility between coarser grains and the ufg matrix.

It is found here that in the face centered cubic (FCC) materials processed by SPS and HIP, the macroscopic deformation of the ufg matrix occurs mostly by grain alignment within thin deformation bands oriented at about 40-45° with the loading axis. These bands are more or less homogeneously distributed. The perfect-like behaviour observed in the case of Al may be explained by the occurrence of these multiple events of grain alignments within deformation bands. It has been reported that the strain rate sensitivity of the flow stress of FCC metals increases with decreasing grain size [17]. It is thus expected that despite the operation of the deformation band hardening is maintained. Therefore, the rapid decrease of the flow stress observed in the case of SPS processed sample are to be linked to damages nucleated at the interfaces between grains as discussed above.

In the case of DSPD processed samples, a clear strain path change effect is observed. In particular, a marked flow softening is observed during the subsequent quasi-static deformation along TD. This effect has been reported many times in conventional materials [18] and appears to be due to a dynamic destabilization of the microstructure formed during HIP previously. The texture most probably also affects on the
orientation-dependence of compression behaviour. Additional investigations are needed for the full description and understanding of such a behaviour.

Figure 4. (a): The microstructure of HIP-processed Al before and after crash-test. (b): mechanical behaviour of the HIP (Crash processed material when the compression axis is parallel (ND) or perpendicular (TD) to the impact direction, simulating the effect of a strain path change.

It should be noted that the transition of the mechanical behaviour from hardening to softening in body centered cubic (BCC) iron has been reported previously [19] following either quasi-static or dynamic compression test. This transition is accompanied by shear band formation that localises the deformation as a consequence of the diminishing strain rate sensitivity of the flow stress with decreasing grain size [17].
5. CONCLUSIONS

In this study the focus has been given on the flow softening observed during quasi-static compression at room temperature conducted on in situ materials processed by different PM routes. It is found that this behaviour is resulted from different origins such as crack nucleation and propagation in the as-sintered samples, or the destabilisation of the sintered microstructures during Dynamic Severe Plastic Deformation or diminishing strain rate sensitivity in the case of iron. Usually the flow softening has been observed for samples having small grain size (<300-500 nm) but the occurrence of this phenomenon is also affected by the oxide content and the incomplete bonding in the as-processed materials.

Acknowledgments

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References

BEHAVIOUR OF NANO NICKEL BASED COMPOSITES AND NANO NICKEL UNDER HIGH LOADING RATE

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Abstract. Gleiter made the visionary argument that metals and alloys, if made nanocrystalline, would have a number of appealing mechanical characteristics of potential significance for structural applications. In many applications, like crash-worthiness and aeronautics, materials are loaded dynamically. In this work it is aimed to study the dynamic compressive behaviour of nano Ni and nano Ni based composites. The grain size dependence is also taken into consideration for non reinforced Ni. A Hall-Petch plot shows that the compressive flow stress strongly depends on grain sizes and composition of the electrolytical plating bath, too. All samples up to a grain size of 1 μm were produced by electro deposition. The results of compression tests have been compared to a coarse grained pure Ni with a grain size of about 100 μm. Nano particles of Al₂O₃ have been used to reinforce nano Ni. The resolved flow stress and hardness are strongly influenced by the additive used during electro-deposition. It is possible to increase the flow stress by reinforcing considerably.

1. INTRODUCTION

Ultra fine grain structure materials (nano materials) with unique properties were firstly introduced by Gleiter [1]. Nano materials offer the possibility to improve mechanical properties like hardness, tensile and compression strength and wear resistance only due their small grain sizes. Numerous practical applications for nano materials are based on this opportunity. Since mechanical properties of metallic alloys are very sensitive to their grain size Ni with different grain size has been studied [2, 3]. The fraction of amorphous phase in the interphase increases drastically with decreasing grain size. It is aimed in this work to investigate the reinforcement of nano Ni by nano Al₂O₃ particles in order to achieve a high strength Ni with larger grains and a lower amount of amorphous phase in the microstructure.

2. INVESTIGATED NICKEL MATERIALS

Ni has been studied with four nominal grain size: 20 nm (fig. 1), 100 nm, 1000 nm and 100 μm. The Ni with the grain sizes of 20 nm, 100 nm and 1000 nm, prepared by electrochemical deposition, have been purchased from Integran, Toronto [4, 5] in order to have the same production condition for the material. These materials were compared to a commercially available coarse-grained Ni with grain sizes of about 100 μm.

Figure 1. SEM micrograph of the nano Ni
The nano Ni based composites were produced in the laboratory of Saarland University of Saarbrücken. The composites (fig. 2) have been electrochemically deposited by pulsed electro-deposition (PED) from a Watts type electrolyte with an amount of alumina powder (Baikalox – Ultra-High Purity Alumina by Baikowski, Annecy, with a medium diameter of 45 nm according to the manufacturer) of 120 g/L. The sodium salt of saccharine (3.54 g/L) and the trisodium salt of naphthalene-trisulfonic acid (7.5 g/L) have been used in order to investigate their influence on the particle content, hardness and flow stress of the composites.

Figure 2. SEM micrograph of the cross-section, no additives

The SEM element mapping of the cross section (fig. 3) of the Ni/Al₂O₃ composite approve the successful embedding of alumina particles into the nano Ni matrix by PED.

Figure 3. SEM element mapping, cross-section
3. EXPERIMENTAL RESULTS

3.1 Hardness Measurements

Hardness measurements for the electro-deposited material are shown in figure 4. The hardness increases with degreasing grain size as it is expected.

![Figure 4. Vickers hardness vs grain size of electrodeposited Ni](image)

The hardness measurement of the nano composite was performed on thin layers. Hence, only the micro hardness $(HV0.1)$ could be determined. The micro hardness of the nano Ni with the grain size of 20 nm was determined for comparison to that of the nano Ni composite. All results are compiled in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>n-Ni (20 nm, fig. 4) Na-saccharine</th>
<th>n-Ni (67 nm)</th>
<th>n-Ni /Al$_2$O$_3$ + Na-saccharine (49 nm) (56 nm, 14.8 vol.-%)</th>
<th>n-Ni /Al$_2$O$_3$ + Na-saccharine (58 nm, 5.1 vol.-%)</th>
<th>n-Ni /Al$_2$O$_3$ + Na-naphthalene-trisulfonic acid (49 nm, 15.5 vol.-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro hardness</td>
<td>504 HV0.1</td>
<td>200 HV0.1</td>
<td>244 HV0.1</td>
<td>406 HV0.1</td>
<td>285 HV0.1</td>
</tr>
</tbody>
</table>

The micro hardness of nano Ni and nano Ni based composites are strongly depending on the additives of the electrolytic bath due to their effect on grain size and particle content in the composites, respectively. Since the composition of the plating bath to produce the Ni shown in figure 4 is not known it is not possible to discuss its influence on the mechanical behaviour. The results show that Na-saccharine increases the micro hardness of the pure Nickel due to the decreasing grain size, but it has no effect on the grain size in the the nano Ni composite and due to the reduced alumina content it decreases the micro hardness of the nano Ni composite. Na-naphthalene-trisulfonic acid acts as grain refiner in the nano Ni composite also and increases slightly the particle content. So there is an increased micro hardness.
3.2 Quasistatic and Dynamic Compression Tests

Dynamic compression tests at strain-rates ranging from $1 \times 10^3$ s$^{-1}$ to $5 \times 10^3$ s$^{-1}$ were conducted at ambient temperature using a split-Hopkinson-pressure-bar (SHPB) [6, 7]. Compression test specimens (2 mm in diameter and 2 mm in length) were cut from the Ni plates using electro-discharge machine. The specimens were lubricated with ball bearing grease prior to testing. For comparison quasistatic compression tests were performed on an universal testing machine at a strain-rate of about $5 \times 10^3$ s$^{-1}$.

In figure 5 the flow curves of quasistatic compression tests with Ni of different grain sizes are summarized. It shows clearly the influence of the grain size on the mechanical behaviour. The 0.2%-offset stress is strongly increased only due to the grain size.

![Figure 5. Quasistatic compression tests with Ni of different grain sizes.](image)

Figure 6 shows a quasistatic and a dynamic compression test with nano Ni. The nano Ni is slightly strain-rate sensitive, but it can easily be seen that the dynamic flow curves are strongly decreased due to the adiabatic heating compared to the quasistatic flow curve. From a deformation of $\varepsilon = 0.3$ the dynamic flow curve decreases stronger, which might be due to the onset of microcracking.

![Figure 6. Quasistatic and dynamic compression test with nano Ni (grain size 20 nm).](image)
Figure 7 and 8 show the quasistatic and dynamic flow curves of nano Ni (grain size 49 nm) and nano Ni/Al$_2$O$_3$ composites deposited with Na-saccharine, Na-naphthalene-trisulfonic acid and without any additive.

Figure 7. Quasistatic compression test with nano Ni (grain size 49 nm) and nano Ni composites

Figure 7 shows that there is a correlation between flow stress and particle content and hardness, respectively. The 0.2%-offset stress is strongly increased due to decreasing grain size of the Ni matrix and increasing particle content of the nano Ni composites respectively. From a deformation of $\varepsilon = 0.45$ the flow curve of Ni/Al$_2$O$_3$ with Na-naphthalene-trisulfonic acid decreases which is caused by a fracture of this sample.

Figure 8. Dynamic compression test with nano Ni (grain size 49 nm) and nano Ni composites

Figure 8 shows the dynamic compression curves of the same samples. There is a slight strain rate sensitivity for pure nano Ni and nano Ni composite with Na-saccharine and there is a strong strain rate sensitivity for the nano Ni composites without additive and with Na-naphthalene-trisulfonic acid, i.e., for the two composites with the high particle content. Both composites show a strong decrease in the dynamic flow curve due to adiabatic heating. The adiabatic heating in the composites is caused by internal friction at the particles.
3.3 Hall-Petch Equation

The diagram in figure 9 shows a Hall-Petch plot of the quasistatic compression tests.

The results show, that the flow stress of the electro-deposited pure Ni is half the 0.2%-offset stress according to the Hall-Petch-relation of the Ni by Integran. That is caused by higher contaminations in the pure nano Ni and nano Ni composites. But the two nano Ni composites with a particle content of about 15 vol.-% show higher 0.2%-offset stresses as aspected by Hall-Petch. The 0.2%-offset stress is equal to pure nano Ni with a grain size of 20 nm or even better. The advantage of the composites compared to pure nano Ni (grain size 20 nm) is the highly decreased amount of amorphous phase in the microstructure. While nano Ni with a grain size of 20 nm has about 40% of this glassy phase, a Ni matrix with a grain size of approximated 55 nm has only 5-50% of amorphous phase. Less of the amorphous phase increases the thermal and electrical conductivity and improves the collapse behaviour in ballistic tests.

4. CONCLUSION

In summary, this study shows that the grain refinement of Ni has an effect on the mechanical properties particularly on the yield stress. Moreover we observed that if the nano Ni is slightly strain rate sensitive, the dynamic flow curve strongly decreased due to the adiabatic heating. The advantage of the composites compared to pure nano Ni (grain size 20 nm) is the highly decreased amount of amorphous phase in the microstructure. The highest compression strength was measured on the composite.

References
DYNAMIC RESPONSE OF SEVERE PLASTIC DEFORMATION PROCESSED 1070 ALUMINUM AT VARIOUS TEMPERATURES

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Abstract. The properties of materials are directly related to their microstructure, one quantitative measure of which is the average grain size. Most of the strength properties of crystalline materials are improved with diminishing grain size, and therefore new technologies have been developed to produce also bulk metals with nanocrystalline or ultra-fine grain sizes. In this paper, we report the results of compression experiments on ultrafine-grained 1070 aluminum produced by different routes of equal-channel angular pressing (ECAP). The compression tests were conducted at different strain rates and temperatures using a servo-hydraulic materials testing machine and the Split Hopkinson Pressure bar technique. The results show that both increasing strain rate and decreasing temperature increase the work hardening capability of ultrafine-grained aluminum, thus enhancing the ductility of the material. The strain rate dependence of ultrafine-grained aluminum is also higher than that of the coarse-grained material, which implies that there are also differences in the active deformation mechanisms of these two different types of materials.

1. INTRODUCTION

Many of the properties of crystalline materials depend on grain size, and therefore controlling and adjusting the grain size is of both great scientific as well as technological interest and importance. Some properties benefit from large grain size, such as the creep resistance of high temperature materials, but more often small grain size is found to enhance the properties, such as the yield and tensile strength, of the material. By conventional processing techniques, such as alloying and heat treatments, the smallest obtainable grain sizes of bulk materials have usually been limited to the micrometer level, but various new methods have made it possible to produce grain sizes in the sub-micrometer or even nanometer scales.

One of the ways to prepare bulk materials with decreased grain size is the so-called severe plastic deformation (SPD), which can be accomplished by several different techniques. The most common of these techniques is the equal-channel angular pressing (ECAP), where an initially coarse-grained bulk sample is repeatedly forced through a die making a large (typically 90°) angle between its inlet and outlet. As the inlet and outlet of the die have the same cross-section, the sample can basically be processed as many times as desired. Depending on the number of passes as well as the way of rotating the sample between the passes, different microstructures with different properties can be produced. A summary of the currently available SPD techniques can be found for example in [1,2].

The mechanisms of plastic deformation in bulk nanocrystalline (NC) and ultra-fine grained (UFG) metals have been subject to intensive studies during the last two decades. During this time, it has become evident that there are some fundamental differences between the deformation behaviors of fine-grained bulk metals and their coarse-grained (CG) counterparts. For example, the strength of NC and UFG metals can be several times higher than that of the same coarse-grained metals, but this usually is achieved at the expense of ductility, which often limits the usefulness of these materials. There is also clear experimental evidence that the strain rate sensitivity of nanocrystalline and ultra-fine grained metals and alloys differs from that of the corresponding coarse-grained materials [e.g., 3-6]. Most of these studies, however, have been conducted at low or intermediate strain rates, and quite little is still known about the effects of strain rate on the deformation behavior of nanocrystalline and ultra-fine grained materials at higher strain rates. At low strain rates the proposed deformation mechanisms often involve diffusion, which at ambient or low temperatures cannot be operative at high strain rates. On the other hand, due to the high initial dislocation densities of severely deformed materials, motion, multiplication, and storage of dislocations is impeded, which leads to
limited tensile ductility due to the lack of strain hardening. In compression, however, these materials usually exhibit almost ideally plastic deformation behavior and can be easily deformed to very large strains.

2. MATERIALS AND EXPERIMENTAL TECHNIQUES

In this work, we studied the mechanical response and microstructures of ultrafine-grained and coarse-grained commercially pure aluminum AA1070 (99.7 wt-% Al) at different strains, strain rates, and temperatures. UFG grades were fabricated using 2-turn and 3-turn equal-channel angular pressing (ECAP) dies at the Warsaw University of Technology (WUT) and at the University of Strathclyde (UOS) in Glasgow, respectively. Coarse-grained AA1070 was used in as-received condition as the initial material for both ECAP processes. The 2-turn die, shown in Figure 1a, has two co-planar 90° turns between the 8x8 mm square-shaped input and output channels so that one pass through the die is equivalent to two passes through a 1-turn classical ECAP die of route C. The 3-turn die, shown in Figure 1b, consists of three 90° turns between the 8x8 mm input and output channels so that one pass in the 3-turn die is equivalent to three passes in a 1-turn classical die using route B.

Three different UFG materials were selected for this study, one material fabricated using the 3-turn die with 3 passes, designated as UFG 1, and two materials fabricated using the 2-turn die with 4 or 5 passes, designated as UFG 2 and UFG 3, respectively. The billets used in the fabrication of materials UFG 2 and UFG 3 were rotated 90° after each pass so that effectively the route was C+B₂. Additional material information is given in Table I. The average grain sizes of the UFG materials, as determined from TEM micrographs, were ~500 nm for UFG 1 and ~750 nm for UFG 2 and UFG 3, and ~200 μm for the initial coarse-grained material, as determined from optical micrographs. As the TEM micrographs presented later in this paper show, there is quite a large variation in the size of individual grains, some being smaller than 100 nm (i.e., 'nanocrystals') and some on the order of 1 μm. This has at least two implications: on one hand the material properties tend to vary as a function of location, which leads to somewhat increased scatter in the measured mechanical properties, but on the other hand it enhances the ductility of the material, as the larger grains are generally more capable of strain hardening and thus resisting necking during tensile deformation. This, in fact, is one possible way to overcome the problems caused by the limited ductility of ultra-fine grained and nanocrystalline materials, but it of course sacrifices some of the high strength of these materials [e.g., 7,8]. The problem, at least at the moment, is that accurate control of the size and spatial distributions of grains in the ECAP process is quite difficult.

![Figure 1. ECAP dies used to manufacture the UFG aluminum billets, a) 2-turn die b) 3-turn die.](image)

<table>
<thead>
<tr>
<th>Material designation</th>
<th>UFG 1</th>
<th>UFG 2</th>
<th>UFG 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECAP processing sequence</td>
<td>3 passes in 3-turn die, 90°, B₂</td>
<td>4 passes in 2-turn die, 90°, C+B₂</td>
<td>5 passes in 2-turn die, 90°, C+B₂</td>
</tr>
<tr>
<td>Equivalent plastic strain</td>
<td>10.35</td>
<td>9.20</td>
<td>11.50</td>
</tr>
<tr>
<td>Billet dimensions</td>
<td>8x8x25mm</td>
<td>8x8x38mm</td>
<td>8x8x37mm</td>
</tr>
</tbody>
</table>
The ECAP billets were fine-turned to a diameter of 7.5 mm, cut to specimens with thickness-to-diameter ratios between 0.47-0.88, and ground and polished to flatness of 0.01 mm or less. Although only the center parts of the ECAP billets were used, the experimental scatter in the UFG results was somewhat larger than in the coarse-grained material, obviously at least partly because of the reasons discussed above.

The UFG and coarse-grained materials were tested in compression from quasi-static to intermediate strain rates using a conventional servo-hydraulic materials testing machine and at strain rates of around 100 s⁻¹ and 500-5000 s⁻¹ at Purdue University and Tampere University of Technology, respectively, using the Split Hopkinson Pressure Bar (SHPB) technique. The SHPB equipment used at TUT to conduct the high strain rate compression tests at different temperatures is shown in Figure 2. To obtain strain rates on the order of 100 s⁻¹, the SHPB device at Purdue University uses extra long aluminum pressure bars and strikers [9]. The tests discussed in this paper were conducted using a 2500 mm long striker bar, which produces an incident pulse of ca. 1 ms in duration.

![Figure 2. Hopkinson equipment with a cooling chamber at TUT.](image)

### 3. RESULTS AND DISCUSSION

The compression stress-strain curves at different strain rates and temperatures for the three UFG and the coarse-grained aluminum are shown in Figure 3. The tests at strain rates of ca. 100 s⁻¹ with the long-bar SHPB device could be conducted only up to relatively small strains (because still \( \dot{\varepsilon} = \varepsilon \cdot \Delta t \)), but the curves fit very nicely between the quasi-static and the high strain rate results obtained with a ‘conventional’ SHPB device. The ‘notch’ in the long-bar SHPB results is caused by slightly loosened thread joints in the pressure bars and is not related to the material behavior. However, the obvious ‘waviness’ of the high strain rate UFG curves, compared with the coarse-grained curves, is believed to be due to real material behavior and related to the inhomogeneties in the material microstructures and to the subsequent less stable and/or uneven mechanical response of the material. It should also be noted that the SHPB devices used in this study are known to produce extremely repeatable and smooth strain hardening curves for ‘ordinary’ (metallic) materials.
To further demonstrate the different behaviors of SPD processed UFG and coarse-grained materials, strain hardening rates ($\theta = da/d\varepsilon$) were determined for UFG 2 and the coarse-grained aluminum. For the high strain rate tests, the strain hardening rates were obtained by derivating a function first fitted to the raw test data. As Figure 4b shows, for the coarse-grained material the strain hardening rate increases as the strain rate is increased and/or temperature is decreased. The behavior of the ultra-fine grained material is much more complex. At the lowest strain rate of $10^{-4}$ s$^{-1}$, the UFG material starts to strain harden after yielding although the strain hardening rate is very low. On the other hand, at the strain rates of $10^{-3}$ s$^{-1}$ and $10^{-1}$ s$^{-1}$ (Figures 4a and 3b), the material starts to strain soften almost immediately after yielding and the hardening rate stays negative till the end of the test. As the strain rate is increased to ca. 100 s$^{-1}$, the material again shows slight strain hardening, and when the strain rate is increased even more, strain hardening becomes quite evident. Lowering the temperature enhances strain hardening even more, as the results at 2200 s$^{-1}$ at -100 °C show. Using the Considère’s criterion ($da/d\varepsilon = \sigma$), one could expect to obtain uniform elongations $\varepsilon_u$ of around 2-4 % for UFG 2 in tension under the same test conditions. Compared with the coarse-grained material, these values are still very low but demonstrate some of the effects of strain rate and temperature on the behavior of commercially pure fcc SPD-UFG materials. Same kind of strain hardening behavior as discussed above has been observed, for example, by Miyamoto et al. [10] in tension.
 Generally speaking, the flow stress \(\sigma\) of a material is a function of strain \(\varepsilon\), strain rate \(\dot{\varepsilon}\), temperature \(T\), and structure or deformation history \(s\), i.e., \(\sigma = f(\varepsilon, \dot{\varepsilon}, T, s)\). Evidently the microstructures of CG and UFG materials are quite different, which basically explains the observed large differences in the strength and tensile elongation values of these two types of materials. On the other hand, numerous authors have reported significant differences in the strain rate sensitivities, defined as \(m = \frac{\partial \log \sigma}{\partial \log \dot{\varepsilon}}\), of various ultra-fine grained and coarse-grained metals [11-14], which implies that there are also differences in the actual deformation mechanisms of fine-grained and coarse-grained materials. May et al. [5], for example, measured the strain rate sensitivity of 99.5\% pure aluminum using strain rate jump tests in compression at quasi-static strain rates and obtained a value of 0.014 for the UFG material and 0.004 for the CG material. These values compare well with our values determined using 3\% true flow stress at quasi-static and intermediate strain rates. When the strain rate sensitivity determination range is extended to about 1000 s\(^{-1}\), the values for the ultra-fine grained grades tend to decrease slightly. For both determination ranges the \(m\) values for UFG materials are, however, clearly higher than those for the coarse grained material. At low strain rates this could be explained by diffusion controlled deformation mechanisms, possibly similar to those observed in superplastic deformation of certain metals and alloys, but at higher strain rates this is evidently not possible. At higher strain rates and/or lower temperatures the increasing strain hardening capability of UFG materials could be explained by reducing recovery (annihilation of dislocations) and increasing capability of the material to store dislocations, for example because of the decreasing time scale and reducing thermal activation. There are also reports [e.g., 15] that when the grain size becomes small enough, even in aluminum mechanical twinning could take place at high strain rates and low temperatures despite the material’s high stacking fault energy, which normally does not favor twinning. Especially in true nanocrystalline materials it is also possible that under certain conditions completely new types of deformation mechanisms come into play instead, or in addition, to the currently known ones, i.e., dislocation glide, twinning, diffusion, and phase transformations.

Figure 4. True stress–true strain and strain hardening curves for a) UFG 2 and b) coarse-grained aluminum.
The temperature dependence $d\sigma/dT$ of the flow stress of the studied materials at $\sim 2000$ s$^{-1}$ is shown in Figure 6 at two different amounts of strain. At 3% of plastic strain, the temperature dependence of the UFG material seems to be slightly higher than that of the coarse grained material, but at 15% the situation is clearly the opposite. This is probably related to the limited strain hardening capability of the UFG material even at subzero temperatures and high strain rates, but this result must be verified by tests at lower strain rates at different temperatures.

Figure 7 shows the microstructures of UFG 2 and coarse-grained aluminum before and after compression testing to 15% of plastic strain at different strain rates. Because of the very large deformations during processing (Table I), the average dislocation densities in the ECAP materials are high but vary locally from the very high density cell walls (high-angle as well as low-angle boundaries) to almost dislocation free cell/grain interiors [5,10]. However, the post-mortem dislocation structures revealed by TEM, especially for materials with high stacking fault energies such as aluminum, do not always fully correspond to the dislocation structures of the bulk material due to easy dislocation cross slide and annihilation by image forces during thin foil preparation. What is, however, evident from the images of Figure 7 is that the effective grain size of ECAP aluminum is much smaller than that of the original material, even though there is quite a wide distribution of grain sizes in the ECAP processed material. The grain size obtained from TEM images is usually much larger than that obtained by x-ray diffraction techniques [16], because the contrast conditions in TEM do not always reveal all grains. This applies in particular to the lower angle sub-grain boundaries, which are often invisible or poorly visible in TEM images but accounted as individual grains in x-ray measurements. The magnification in the TEM images of Figure 7 varies, which to some extent makes their comparison more difficult, but some general observation are quite obvious. First, deformation at low strain rates does not cause any notable changes in the microstructure of UFG aluminum.

Figure 5. Strain rate sensitivity values determined for different strain rate ranges for a) UFG 1, b) UFG 2, c) UFG 3, d) CG aluminum.

Figure 6. Flow stress of UFG and CG aluminum as a function of temperature at a strain rate of $\sim 2000$ s$^{-1}$.
(Figures 7a-c), which is consistent with the stress-strain curves shown in Figure 3. In the coarse-grained material, instead, the dislocation density clearly increases because of strain hardening (Figures 7h-i). Secondly, even at higher strain rates the UFG material's microstructure does not show much of a change at room temperature (Figure 7d), but at a low temperature and a high strain rate (Figures 7e-g), clear storage of dislocations and new cell formation inside the grains can be observed in the microstructure. Also all these observations are consistent with the mechanical stress-strain response of these materials.

Figure 7. TEM-images of undeformed and 15 % deformed ultra-fine grained (a-g) and coarse-grained (h and i) aluminum. a) UFG 2 undeformed b) UFG 2 after deformation at $10^3 \text{s}^{-1}$ c) a large grain in UFG 2 after deformation at $10^3 \text{s}^{-1}$ d) UFG 2 after deformation at $1000 \text{s}^{-1}$ e-g) UFG 2 after deformation at $1800 \text{s}^{-1}$ at -100 °C, h) coarse grained undeformed aluminum i) coarse-grained aluminum after deformation at 1000 \text{s}^{-1}.
4. CONCLUSIONS

Ultrafine-grained 1070 aluminum billets with average grain sizes of 500 nm and 750 nm were fabricated by equal-channel angular pressing (ECAP) using 2-turn and 3-turn 8x8 mm square cross-section dies. Fine-
turned cylindrical specimens with length-to-diameter ratios from 0.47 to 0.88 were tested in compression at
strain rates ranging from quasi-static to about 5000 s⁻¹ using a servo-hydraulic materials testing machine
and two different Split Hopkinson Pressure Bar devices. Some of the high strain tests were conducted at
sub-zero temperatures down to -100 °C. The results show that the strain hardening capability of ultrafine-
grained aluminum depends both on strain rate and temperature. At the lowest strain rate of 10⁻⁴ s⁻¹, the UFG
materials show slight strain hardening, but between 10⁻³ s⁻¹ and 10⁻¹ s⁻¹ the materials strain soften almost
immediately after initial ‘yield peak’. At increasing strain rates, the UFG materials show again increasing
strain hardening capability, especially at sub-zero temperatures. The strain rate sensitivity of UFG
aluminum is higher than that of the coarse-grained material, suggesting that there are differences also in the
deformation and strain hardening mechanisms of these two different types of materials. Transmission
electron micrographs taken before and after compression to 15 % of plastic strain also support the observed
mechanical behavior of the tested materials.

Acknowledgments

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MECHANICAL PROPERTIES OF A Mg-9Li ALLOY TREATED BY
SEVERE PLASTIC DEFORMATION UNDER DYNAMIC LOADING

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Abstract. Sabots are necessary to guide sub caliber projectiles in a cannon tube. Their function is fulfilled if the cannon tube is left and no interaction with the projectile outside the tube occurred. Sabots are regarded as ballast and for that reason their mass has to be minimized. It is possible to reduce the mass of a sabot considerably if Al alloys are replaced by Mg alloys. A further reduction is possible by the application of Mg-Li alloys. It has been shown that the fracture toughness of Mg alloys was too small. In this work it is aimed to increase the fracture toughness of a Mg-9Li alloy by a treatment with the ECAP process. The fracture toughness of some Mg alloys were characterized by the Charpy test. It is shown that the fracture energy could be increased about the 18 fold by the ECAP process. An investigation by XRD shows a strong fibre texture of the ECAP treated alloys.

1. INTRODUCTION

Every KE rod requires for the acceleration in a cannon tube a sabot for guiding. It should open after leaving the cannon tube without interact with the W rod and its function is finished. There is no contribution to any interaction to a target and therefore a sabot is regarded as ballast. For that the mass of a sabot has to be minimized in order to avoid a loss on energy for accelerating the rod. A typical push-pull sabot is shown in Fig. 1 a) [1]. Al based alloys are in use as standard materials. The application of Mg alloys would reduce the density from 2.7 g/cm³ to 1.8 g/cm³. Mg alloys are brittle and of minor strength. A reinforcement by C-short fibres was used to improve the mechanical behaviour of the Mg alloy AZ91. The result of a ballistic test is shown in fig. 1 b) [1]. The sabot breaks when leaving the cannon tube and interacts with the W rod. This result shows that the fracture toughness of an alloy has a major influence on the functioning of a sabot. In a next step a Mg-8Li alloy was studied. Also this alloy was breaking when accelerated by a pressure exceeding 320 MPa.

![Figure 1 a) and b)](image)

Figure 1 a) and b). A sabot consisting of three parts a), a sabot consisting of Mg-C-short fibre composite after leaving the cannon tube [1].
This work is aimed to improve the fracture toughness of a Mg-9Li alloy by using a treatment by the ECAP process [2-7] and subsequent extrusion. The advantage of alloying Mg with Li allows a considerable reduction of the density from 1.8 g/cm$^3$ to 1.6 g/cm$^3$.

2. MATERIALS AND THERMOMECHANICAL TREATMENT

First ballistic tests were performed with sabots consisting of a Mg-8Li alloy. Fig. 2 shows a micrograph of the microstructure of an extruded billet of the wrought alloy. The darker phase is the Li-rich phase and the white etching phase is enriched by Mg. For the ECAP process a Mg-9Li alloy was used. The slightly increased Li content to 9% does not influence significantly the macroscopic mechanical behaviour [8].

The Mg-9Li alloy was studied in order to find out its mechanical properties after a thermo mechanical treatment. Billets of the alloy, 100 mm long and 33.8 mm in diameter, were held at 250 °C for 10 min and the ECAP tool was preheated to 300 °C. The billets had been extruded through the ECAP channel 4 times at 100 mm/min extrusion speed. Before each extrusion the billets and the ECAP channel were lubricated by spray of dry lubricant for high temperature. After each pass the billets were reheated to 250 °C for 10 min and rotated by 90 ° around the axis.

Then the resulting billets of 65 mm in length and 33.5 mm in diameter were held at 260 °C for 20 min for stress relieving. The extrusion tool was preheated to 300 °C and lubricated with the same dry lubricant T-50 as the specimen prior to extrusion. To produce tensile, compression and Charpy specimens the billets had been extruded to round and square cross sections, respectively.

The fine grained structure due to the ECAP process will slightly coarsen during the heat treatment. A subsequent extrusion has elongating the grains to a ribbon like micro structure.

Fig. 3 a) and b) show the microstructure after the thermo mechanical treatment by ECAP and extrusion in the axial directions (a)) and the cross-section (b)), respectively.

The white etching phase of the microstructure is elongated along the axis of the specimens as shown in fig. 3 a). Whereas the shape of this phase is of thin lamellae in the cross-section (fig. 3 b)). The microstructure may be assumed as consisting of elongated thin ribbons along the axis of the extruded specimens.
The investigation of a Mg-9Li specimen treated in the ECAP process and subsequently extruded by XRD reveals an extremely strong fibre texture in the (100) direction. Fig. 4 illustrates the results.

3. MECHANICAL PROPERTIES

3.1 Charpy test

The Charpy test was used to investigate the fracture toughness of Mg alloys used for sabots. Reference [9] describes the alloys and the tests. Fig. 5 summarizes the results of Charpy tests. The values for the fracture energy in the diagram of fig. 5 represent the mean value of 5 Charpy tests.

The Mg C-short fibre composite possess the smallest fracture energy of 0.1 J. It behaves very brittlely as the fractured sabot in fig. 1 b) confirmed. This work is focused on the ECAP Mg-9Li. The fracture energy after ECAP and subsequent extrusion is increased to 23.9 J compared to 1.42 J of the un-ECAPed Mg-8Li alloy. The fracture energy of the two Mg alloys RS66A and RS66B was large enough to prevent breaking, as it is shown in fig. 1 b).
Fig. 5 shows the result of a metallographic investigation of the microstructure near the fractured zone. The white etching layers show clearly that this zone is strongly bent. Charpy impacts perpendicular to the layered microstructure reveal the high toughness. In fig. 6 the fracture of a white etching phase surrounded by the darker phase is shown. An increased density of dimples reveals that the white etching phase behaves more ductilely under impact loading in the Charpy test.
3.2 Tensile and compression tests

The quasistatic compression tests in fig. 7 show clearly a strong Bauschinger effect, which is mainly due to the subsequent extrusion after the ECAP process. The quasistatic compression strength is increased compared to that of the Mg-8Li alloy reported in reference [9], but the 0.2%-offset compressive stress is considerably lower due to the Bauschinger effect.
Fig. 8 summarizes three quasistatic tensile tests. The tensile loading acts in the same direction as the ECAP and extrusion process. Therefore the strain to fracture is relatively high, but the necking is relatively moderate as shown in fig. 9. The shape of the specimen ends indicates brittle fracture. Micro cracks are in the white phases (Mg-rich phase) of the microstructure, which have been strongly elongated by extrusion and loaded in the same direction during the tensile test.

Fig. 9 shows the results of dynamic compression tests. The dynamic compression strength is also increased compared to the Mg-8Li alloy without a treatment by the ECAP process [10]. The dynamic compression strength shown in fig. 10 is also increased compared to the quasistatic compression strength shown in fig. 7 due to the strain-rate sensitivity of the alloy.

The texture plotted in fig. 11 has completely changed compared to that in fig. 4 due to the compression test. The investigation by XRD reveals a strong fibre texture in (001) direction.
Figure 10. Dynamic compression tests conducted on Mg-9Li specimen

Figure 11. XRD investigation of a dynamically compressed specimen. Fibre texture in (001) direction

PF 001

Fig. 12 shows details of the microstructure of a dynamically compressed specimen. It shows clearly that the elongated white phases are deformed by the upsetting test. Micro cracks can be found only in the white phases, which is the Mg rich phase.
4. CONCLUSION

Mg alloyed with Li is a powerful alloy to reduce the mass of structural components as it is important for a sabot, because its function is accomplished when a KE rod emerges from the cannon tube. Mg alloyed with 8 or 9% Li crystallizes still in the hcp structure and behaves in a relatively brittle manner. A treatment to increase the toughness is necessary. For that reason a Mg-9Li alloy was treated by ECAP, heat treated and subsequently extruded. ECAP leads to a fine grained structure, which will slightly coarsen by the heat treatment and then elongated by extrusion. This thermo mechanical treatment results in a strongly increased fracture toughness perpendicular to the length axis as Charpy tests show. The quasistatic and dynamic compression strength is increased compared to the un-ECAP Mg-Li alloy, but the 0.2%-offset compressive strength is lower due to a Bauschinger effect.

References

HIGH STRAIN RATE RESPONSE OF NANOSTRUCTURED AND MICROSTRUCTURED NICKELS SINTERED BY SPS

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Abstract. The ductility of nanostructured and microstructured nickel have been evaluated under dynamic compression with strain rates ranging from \(10^4\) to \(10^5\) s\(^{-1}\). The materials were sintered with an electrical field activated process involving direct current pulses called the Spark Plasma Sintering process. This process provides fast heating permitting sintering of bulk nanostructured conducting and non-conducting materials. Thermally activated and viscous regimes characterizing the dynamic behaviour of metallic materials have been identified and compared to conventional microstructured nickels made by electrodeposition. Preliminary results reveal that the hardening characteristics and the strain rate threshold delimiting the two regimes are independent of the nickel microstructure.

1. INTRODUCTION

One mean to make bulk nanostructured materials is through electrical field activated processes. These processes, consisting of the consolidation of material powders by mean of a high electrical current, provide fast heating, which minimizes the growth of powders. Electrical field activated processes either involved direct current pulses like the Spark Plasma Sintering process (SPS) or alternate current pulses like the Field Activated Pressure Assisted Synthesis process (FAPAS) [1].

In the present work, the SPS technology was applied to nickel powders to generate microstructured and nanostructured nickel. The conditions of the SPS experiments are described along with a numerical simulation of the process providing information on the temperature homogeneity in the specimens during the entire heating cycle.

The mechanical properties of the nickel materials were obtained in compression under quasi-static and dynamic conditions and compared to data generated with a nickel made by electrodeposition [2]. Dynamic compression properties were generated at strain rates where microstructured nickels exhibit two types of strengthening. The first one, generated from quasi-static strain rates up to dynamic strain rates of \(10^3\) s\(^{-1}\), involves moderate strengthening of the material and is known as the thermally activated regime. The second one, occurring at strain rates greater than \(10^3\) s\(^{-1}\), is associated with high strengthening of the material via drag dislocation effects identified as the viscous regime [3,4].

2. MATERIALS

2.1. Microstructured and nanostructured nickels sintered by Spark Plasma Sintering

Nickel specimens were sintered using the SPS technique consisting in the consolidation of material powders embedded in graphite dies by mean of a high electrical current, see figure 1. For the microstructured nickel materials, original powders were 5 μm in size composed of 137 nm crystallites. Two nanostructured nickel materials were sintered starting from nanostructured powder 100-500 μm in size composed of 45 nm crystallites, which were obtained by a milling of the microstructured powder in a planetary ball mill for 4 hours and 16 hours [5].
The specimens were 15 mm in diameter and 10 mm in height and finished 5.3 mm and 5.8 mm in height after consolidation, for the microstructured and nanostructured specimens, respectively. The specimens were surrounded by a graphite die 30 mm in diameter and 30 mm in height and two graphite pistons 20 mm in length. An axial compression was applied to the pistons as to provide a pressure of 30 MPa to the specimens. Using die temperature measurements, the experiments were conducted with a heating rate of 50°C/min up to a temperature of 750°C. To minimize heating of the SPS setup, the graphite pistons are in contact with a graphite/Inconel spacer which is water-cooled.

To obtain the mechanical properties, compression specimens 6 mm in diameter and 3.3 mm in height were machined from the SPS specimens.

Because these processes involved components with variable electrical conductivities, non-homogeneous current intensities are generated implying different local heating rates [6]. Numerical simulations were conducted to examine the variation in temperature during the process of the nickel materials. These simulations were performed with the finite element numerical code ABAQUS (166 Valley Street, Providence RI 02909, USA). The temperature was calculated by solving the heat equation. The loss of heat by radiation was taken into account with an emissive coefficient of 0.8 and with an exterior temperature of 26°C. The numerical model used to simulate the SPS experiments incorporates quadrilateral elements of 0.5 mm in size. The SPS cycle was simulated by imposing the experimental current boundary conditions and estimating the temperature boundary conditions, see companion paper on the numerical simulation of the SPS in these proceedings. These temperature conditions were deduced from a specific set of experiments providing temperature data at several locations along the SPS setup to be reported.

Results of the numerical simulations reveal that for the present SPS cycles, 50°C/min average heating rate and initial specimen size of 15 mm in diameter and 10 mm in height, the difference in temperature within the specimen was only of 0.5% at the beginning (120s) of the heating phase, to reach 0.3% during the remainder of the heating phase, see figure 2. Metallurgical observations of specimens confirm that these small variations in temperature did not affect the structural homogeneity of the processed materials, see figure 3.

It is important to note that either for higher heating rates or for larger specimen sizes, greater temperature differences are encountered. Consequently, experimental-numerical investigations are required to provide engineering solutions, in term of die design and/or die material, so as to reduce such discontinuities.
Figure 2. Difference in temperature between the centre, T1, and the border T (T2, T3, T4) of the specimen during the heating phase and the constant temperature phase.

Figure 3. Optical image of the microstructured nickel sintered by SPS on the border (left) and on the centre (right) for the same specimen. Some twins and a grain size of 11 μm are observed for both parts of the sample confirming the temperature homogeneity inside the sample.

The materials generated by SPS were 11 μm in grain size for the microstructured nickel and 72 and 68 nm in crystallite sizes (determined by XRD methods [7]) for the nanostructured nickels sintered with the powders mill for 4 hours and 16 hours, respectively, see table 1.

In addition, we can notice that the micro-distortion level (including structural defects and stresses) increases when the ball milling duration is increased. In general, it is reported that microstructure (size, distortions, defects...) depends on the milling time and/or the power of shocks. Indeed, the lattice strain increases in the first stage of deformation, reaches a maximum and, then decreases upon further millings [8]. This behaviour has been attributed to strain release which can be observed during the milling [8], especially when the deformation mechanisms from plastic deformation via formation and movement of dislocations to grain boundary gliding. However, in spite of many research efforts, the mechanism of phase formation during ball milling is not well understood [9]. It is most often suggested that the ball milling process introduces a variety of defects (vacancies, dislocations, grain boundaries, stacking faults, twin defects ...) which raise the free energy of the system making it possible to produce metastable phases. Consequently, these modifications induced during the ball milling process can modify the reactivity of solids after a subsequent heat treatment [10].
Table 1. Metallurgical characteristics of the SPS nickel specimens. Crystallite size and micro-distorsion level were obtained by X-ray diffraction [7].

<table>
<thead>
<tr>
<th>Initial powder size (µm)</th>
<th>Initial crystallite size (nm) / micro-distorsion level (%)</th>
<th>Final crystallite size (nm) / micro-distorsion level (%)</th>
<th>Density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without milling = 5</td>
<td>137 / 0</td>
<td>not available / 0</td>
<td>95,0</td>
</tr>
<tr>
<td>4h milled = 500 – 1300</td>
<td>45 / 0,6</td>
<td>72 / 0</td>
<td>85,7</td>
</tr>
<tr>
<td>16h milled = 100-300</td>
<td>45 / 0,9</td>
<td>68 / 0,07</td>
<td>84,7</td>
</tr>
</tbody>
</table>

2.2. Microstructured nickel made by electrodeposition

In addition to the materials sintered by SPS, a reference microstructured nickel was evaluated. This nickel was made through electrodeposition (EL) and was optimized through a tempering heat treatment to reach a quasi-static yield strength of 220 MPa. The nickel has a 10 µm grain size, see Figure 4. Extended compressive and torsion data are available for this nickel, with compression tests conducted with 9 mm diameter specimens [2]. To establish if there is any size effect, with regard to the 6 mm diameter used with the SPS specimens, few tests were generated with EL specimens 6 mm in diameter.

![Figure 4. Microstructure of the electrodeposition nickel tempered to 220 MPa](image)

3. MECHANICAL TESTS

Compression tests were conducted with specimens of diameter to height ratio of 2 using two diameters 6 and 9 mm. Quasi-static compression tests were conducted at 10⁻² s⁻¹ with a conventional testing machine.

A direct impact compression test was used to generate data in the thermally activated and viscous regimes at strain rates ranging from 10⁷ to 10⁸ s⁻¹. The technique, originally introduced by Dharan [10], consists in a direct impact with a striker 20 mm in diameter and 90 mm in length of a specimen placed against a Hopkinson pressure bar, see Figure 5. The striker speed, \( V \), typically between 20 and 100 m/s, is recorded using two laser beams separated by 18 mm and positioned 30 mm apart prior to the impact. Both the striker and Hopkinson bar are made of tungsten alloys 17,5 g/cm³ in density and 1500 MPa in yield stress.

![Figure 5. Direct impact compression test.](image)
The true deformation is obtained from the specimen end displacements with the specimen/bar interface deduced from the strain history, \( \varepsilon_I(t) \), of the Hopkinson bar using strain gauges, and with the specimen/striker interface displacement rate equal to \( V \):

\[
\varepsilon(t) = Ln \left( 1 + \varepsilon_n(t) \right) = Ln \left( 1 + \left( V \cdot C_o \int_0^t \varepsilon_I(t) \, dt \right) / L_o \right)
\]

where \( L_o \) is the specimen length, and \( C_o \) is the velocity sound in the Hopkinson bar material. With the assumption that plastic deformation is isochoric, the axial stress is obtained from the strain history, \( \varepsilon_I(t) \), of the Hopkinson bar:

\[
\sigma_x(t) = \sigma_0(t) \left( 1 + \varepsilon_n(t) \right) = \rho \cdot C_o^2 \cdot \varepsilon_I(t) \cdot S_T/S_o \left( 1 + \varepsilon_n(t) \right)
\]

where \( \rho \) is the density of the Hopkinson bar, and \( S_T \) and \( S_o \) are the section area of the Hopkinson bar and specimen, respectively. Due to inertia, the radial and tangential stresses, \( \sigma_r(t) \) and \( \sigma_\theta(t) \), are:

\[
\sigma_r(t) - \sigma_\theta(t) = \rho \cdot C_o^2 \cdot \varepsilon_I(t) \cdot S_T/S_o \left( 1 + \varepsilon_n(t) \right) - \left( \frac{3}{8} \right) \rho \cdot (R_o \cdot V/L_o)^2 \left( 1 - \varepsilon_n(t) \right) \]

The equivalent stress is then derived:

\[
\sigma(t) = \sigma_x(t) - \sigma_r(t) = \rho \cdot C_o^2 \cdot \varepsilon_I(t) \cdot S_T/S_o \left( 1 + \varepsilon_n(t) \right) - \left( \frac{3}{8} \right) \rho \cdot (R_o \cdot V/L_o)^2 \left( 1 - \varepsilon_n(t) \right)
\]

### 4. QUASI-STATIC AND DYNAMIC COMPRESSIVE RESPONSES

The quasi-static and dynamic responses of the nickel materials are provided in figures 6 to 8. All tests were conducted to a plastic deformation of about 0.30. As expected, nanostructured nickels exhibit yield strengths several times greater than the two microstructured nickels. Insufficient data are available to establish if the strength of microstructured and nanostructured nickels increases with the inverse square root of the crystallite size as predicted by the Hall-Petch relation.

However, the nanostructured nickels reveal very little loss of the hardening capacities, indicating that the dislocation mechanisms still play a major role. To a lesser extent, the same trend is observed under dynamic conditions, see figure 8.

![Figure 6. Quasi-static compressive responses of the nickel materials.](image-url)
5. THERMALLY ACTIVATED AND VISCOUS REGIMES

The fact that dislocations mechanisms play a major role with the nanostructured nickel materials is confirmed when the strength at 0.05 and 0.3 plastic deformation is plotted as a function of strain rate, see figures 9 and 10. The strain rate limit of the thermally activated domains remains about $3 \times 10^4$ s$^{-1}$ for both microstructured and nanostructured nickel. A difference in strengthening between the materials can be noticed when plastic deformation is significant (0.3) with a reduced strengthening of the nanostructured nickels in the $10^4$-5 s$^{-1}$ strain rate regime. Further investigations are required with fully dense nickel specimens sintered by SPS to precise the observed strengthening in the $10^6$-5 s$^{-1}$ strain rate regime.

Figure 7. Quasi-static and dynamic compressive responses of microstructured nickel EL.

Figure 8. Quasi-static and dynamic compressive responses of nanostructured nickel SPS.
Figure 9. Thermally activated and viscous regimes of the microstructured and nanostructured nickel for a plastic deformation of 0.05.

Figure 10. Thermally activated and viscous regimes of the microstructured and nanostructured nickels for a plastic deformation of 0.3.
6. CONCLUSIONS

Nanostructured and microstructured nickels sintered with the Spark Plasma Sintering process along with a microstructured nickel made by electrodeposition were evaluated in compression up to a plastic deformation of 0.3 at strain rates ranging from $10^{-4}$ to $10^5$ s$^{-1}$. High yield stress along with significant remaining hardening capabilities are characterizing the nanostructured nickels, when compared to the microstructured nickels. The strengthening mechanisms encountered with strain rate were found to be similar with a transition between the thermally activated and viscous regimes of the order $3 \times 10^3$ s$^{-1}$.

Because the Spark Plasma Sintering materials were not fully densified, further investigations are required to understand fully the dynamic hardening characteristics of nanostructured nickels at low plastic deformation. Moreover, it will be essential to clearly control the ball milling parameters in order to control the grain size and the nature of defects of nanostructured agglomerated powders [12]. Then, the role of each parameter (grain size and structural defects) on the sintering mechanisms (grain growth and consolidation steps) will be determined for producing dense nanostructured metals having a nanostructure and a density perfectly controlled density.

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References

THE POTENTIAL OF NANO MATERIALS FOR DYNAMIC APPLICATIONS

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Abstract

It is becoming apparent that nature's bottom-up approach to functional nanostructures can be mimicked to produce artificial molecules with nano scaled dimensions and engineering properties.

This tremendous opportunity could lead to the development of hard protective coatings for high impact velocity, nano composites for shock absorbing, hard materials for transparent ceramics and nano fibers for armor applications.

Israel's nano initiative involves a wide range of nano materials R&D programs for high strain rate applications, starting from the process, new materials, physical and mechanical properties evaluation techniques and many more.

The programs include, developing of nano fibers, reinforcing materials by nano particles as well as developing of bulk ceramics based on nano to submicron powder.

From our preliminary results, we can conclude that in some cases at a low strain rate, the nano particles reinforcing polymer could increase the impact strength. Furthermore POSS nano particles embedded in specific coating could reduce the damage caused by high velocity impact. Another program includes the evaluation on nano ceramic particles reinforcing Mg alloy which show also strengthening affect.

In the presentation we will explore some of the recent activities related to nano materials with highlights on the potential for dynamic applications.
BALLISTIC PROTECTION CAPABILITY OF SUBMICRO AND NANO CERAMIC AGAINST KINETIC ENERGY PENETRATORS

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Abstract. Light-weight armour systems becoming still more important to ensure improved strategic mobility and tactical agility for future combat systems, while maintaining crew protection. It is necessary to airlift military vehicles to remote locations in under-developed regions this requires a large weight reduction in the armour system. An area of armour development is in the area of ceramics. Ceramics are effective because of their hardness, which is considerably greater than that of other material classes, and also they are much lighter than steel. In the recent three decades materials with extremely fine grains also in the area of ceramics have been developed. This work deals with sub micro and nano ceramics for ballistic protection. Kinetic energy projectiles have been used to investigate the protection capability. The ceramic materials were produced with different grain sizes, which influences the resulting hardness. It could be found that hardness of ceramic materials is directly related to the ballistic protection level.

1. INTRODUCTION

Future combat systems should possess improved strategic mobility and tactical agility, while maintaining overwhelming firepower and crew protection. Therefore, armoured vehicles have to be lighter, faster, and more agile than the cold war era main battle tanks. Tactical mobility involving airlift of vehicles requires a significant weight reduction. Since the 1950s the main alternatives to steel have been aluminium alloys, an alloy with reduced density. Light-weight metals have one disadvantage the reduced strength compared to steels. A solution for the lack in strength may be sub micro and nano materials possessing a fine grained micro structure which improves the mechanical behaviour enormously.

The aim of this work is to investigate the ballistic capabilities of sub micro and nano ceramics. It is well known that the hardness of conventional ceramics enables them to shatter bullets, allowing the kinetic energy transferred to be easily absorbed by the backing armour. The mechanical behaviour of nano ceramics expressed by the macro hardness offers an increased ballistic protection performance.

2. CERAMIC MATERIALS

2.1 Al₂O₃

High purity Al₂O₃ powders with different grain sizes were used to produce square shaped plates with a side of 100 mm and a thickness of 5 mm for terminal ballistic tests. Plates a, b and c in table 1 have been shaped by gel casting and plate d by pressing of spray granules. Then the plates have been pressure less sintered at different temperatures and for different holding times. The sinter temperature and holding time, grain sizes, density and mechanical properties are compiled in table 1. The plates have been purchased by Fraunhofer Institute for Ceramic Technologies and Systems, IKTS, of Dresden [1-5].

The objective was to test different hardnesses and strengths expressed as the 4-point bending strength, because the ballistic tests should provide information about what mechanical properties are important for ballistic protection capability. The hardness of ceramics is depending on the Hall-Petch equation as table 1 shows, whereas the bending strength is influenced by the process, which influences the residual faults and the inter-grain phases.
Table 1. Investigated Al₂O₃ ceramic with different grain sizes and mechanical properties

<table>
<thead>
<tr>
<th>Shaping method</th>
<th>Sintering temperature (°C (h))</th>
<th>Mean grain size (µm)</th>
<th>Density (g/cm³)</th>
<th>Hardness (HV10)</th>
<th>Bending strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>gel casting 1250 (2.5)</td>
<td>0.6</td>
<td>3.97</td>
<td>1977</td>
<td>557</td>
</tr>
<tr>
<td>b</td>
<td>&quot; 1550 (2.5)</td>
<td>3.76</td>
<td>3.96</td>
<td>1725</td>
<td>470</td>
</tr>
<tr>
<td>c</td>
<td>&quot; 1725 (5)</td>
<td>9.82</td>
<td>3.97</td>
<td>1543</td>
<td>350</td>
</tr>
<tr>
<td>d</td>
<td>pressing 1380 (2)</td>
<td>0.91</td>
<td>3.96</td>
<td>1908</td>
<td>345</td>
</tr>
</tbody>
</table>

A metallographic investigation was performed from all plates. The microstructure of the four different plates is shown in fig. 1 a) – d).

Figure 1a) – d). Microstructure of the Al₂O₃ plates investigated (table 1). The grain size is increasing from left to right: a) 0.6 µm, b) 3.76 µm, c) 9.82 µm and d) 0.91 µm.
For the hardness measurements in table 1 the Vickers hardness HV10 was used. The necessity to use the macro hardness indenter for determining the hardness is explained in reference [6]. It could be shown that the macro hardness for grain sizes smaller than 0.5 μm is decreasing significantly.

2.2 Si₃N₄

Si₃N₄ ceramic is well known for its mechanical properties and was taken in consideration as valve material for gasoline engines. In this work Si₃N₄ ceramic possessing a nano grained micro structure was investigated on their ballistic protection capability. A conventional Si₃N₄ ceramic in industrial use with grain sizes in the micrometer level was also investigated for comparison.

The nano Si₃N₄ was purchased by Fraunhofer Institut Keramische Technologien und Systeme, IKTS, of Dresden and the industrial Si₃N₄ by the company Sintec in Buching. Table 2 shows the chemical composition.

<table>
<thead>
<tr>
<th></th>
<th>Al₂O₃</th>
<th>Y₂O₃</th>
<th>Si₃N₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>nano Si₃N₄</td>
<td>8</td>
<td>6</td>
<td>bal.</td>
</tr>
<tr>
<td>conv. Si₃N₄</td>
<td>6</td>
<td>4</td>
<td>bal.</td>
</tr>
</tbody>
</table>

![Figure 2 a) and b)](image)

The Vickers hardness of the nano Si₃N₄ and the conventional Si₃N₄ measured at room temperature amounts to 1544 HV10 and 1353 HV10, respectively. KIC values were determined by the method of Ansits [7] to be for the nano Si₃N₄ and the conventional Si₃N₄ 2.5 MPam¹/² and 4.9 MPam¹/², respectively.

Depending on the columnar grain growth of the conventional ceramic is the KIC value twice of that of the nano ceramic. The nano ceramic was sintered at a significantly lower temperature than the conventional ceramic in order to avoid the anisotropic coarsening of the grains. A fine grained microstructure results in a higher hardness.

Contrary to the Al₂O₃ ceramic, which has been sintered in the solid state, the Si₃N₄ ceramic was produced by a liquid phase sintering process. In reference [8] it is shown that the increase in hardness for liquid
phase sintered ceramics is relatively small, because of the huge amount of amorphous grain interface phases.

![Graph](image)

**Figure 3.** Strength of Si$_3$N$_4$ ceramic investigated

The strength of the Si$_3$N$_4$ ceramic was tested by 'the ball on three balls test' developed of the University of Leoben [9-11]. Fig. 3 shows the results of the tests. The strength of the conventional ceramic is significantly higher.

### 3. BALLISTIC TESTS

#### 3.1 Experimental

The ballistic protection capability of the ceramics was investigated in DOP (Depth Of Penetration) tests using a W heavy metal rod with the following geometry: 4mm in diameter and 60 mm in length, respectively. The impact velocity amounts to 1660 m/s. Fig. 4 demonstrates schematically the design of the utilized target of NATO. An armour steel of medium tensile strength (1000 MPa) was chosen, because the Al$_2$O$_3$ ceramic plates were only 5 mm thick. Two of them have been used for the ballistic tests. The Si$_3$N$_4$ plates were 20 mm thick. From plates with this thickness only one was used for the DOP tests.

Flash X-ray photos have been taken from every test in order to control the yaw angle of the rod. The parameters for the evaluation are schematically presented in fig. 5. Reference target and backing consist of the same steel alloy. The abbreviations stand for $p_{ref} =$ density of backing and reference target, $p_{ref} =$ penetration in the reference target, $R_{pen} =$ penetration in the backing, $t_r$ and $p =$ thickness and density of materials investigated, respectively. They were used to evaluate the results using equations (1) – (3). In
these equations only the protective property of the studied material will be taken in consideration. Hence, the $F$ values are directly related to the materials investigated.

![Diagram](https://example.com/diagram1.png)

**Figure 4. Target configuration for testing the ceramics**

![Diagram](https://example.com/diagram2.png)

**Figure 5. Parameter for evaluation of the ballistic results**

\[
F_m = (P_{ref} - \rho_{res}) \cdot \rho_{ref} / \tau_z \cdot \rho \\
F_s = (P_{ref} - \rho_{res}) / \tau_z \\
F = F_m \cdot F_s
\]

(1) \hspace{2cm} (2) \hspace{2cm} (3)

### 3.2 Results of ballistic tests with $\text{Al}_2\text{O}_3$

The results evaluated from equations (1) – (3) are presented in fig. 6. All results are increase with increasing hardness or with decreasing grain size. This effect is strongest from a grain size of 0.91 $\mu$m to 0.6 $\mu$m. There is significantly no influence of the strength expressed in table 4 by the 4-point bending strength, as confirmed by plate d in table 1 having a high hardness but a very low strength. There were extraordinary high values.

The $F$ values for plate c in table 1 (1543 HV10) are a little too high. Controlling the flash X-ray had given that the rod exceeds the horizontal line of $1.3^\circ$. This increases slightly the ballistic result.
Following reference [6] will the macro hardness decrease for grain sizes smaller than 0.5 μm. Hence, it could be concluded from the experimental results, which are depending on the macro hardness, that the maximum ballistic protection capability is reached.

![Graph](image1)

**Figure 6.** Results of the ballistic tests on Al₂O₃ evaluated with equations (1) – (3)

![Micrographs](image2)

**Figure 7 a) and b).** SEM micrographs of fractured Al₂O₃, mean grain size a) 0.6 μm and b) 9.82 μm

Two micrographs of fracture surfaces are shown in fig. 7 a) and b). They are a feature of the smallest grain size a) and the biggest grain size b). It is clearly shown that the fine grained microstructure in fig. 7 a) generates more deflection of cracks due to the increased number of grain boundaries than the microstructure in fig. 7 b) does. But the influence of crack initiation and propagation is of negligible influence to the ballistic protection capability.
3.3 Results of ballistic tests on Si₃N₄

Fig. 8 presents the ballistic tests with Si₃N₄ graphically. The results confirm those received from the tests with Al₂O₃ shown in fig. 6 that the ballistic behaviour is directly related to the hardness. This is not a general statement, but valid for ceramic materials only.

The increase of the F values is not as strong as observed for the high purity Al₂O₃ ceramic. This is well understood and depends on the increased mass of inter grain phases due to the liquid phase sintering process, which causes a slightly increase in hardness only.

![Graph showing ballistic tests with Si₃N₄ possessing different hardness.](image)

Figure 8. Ballistic tests with Si₃N₄ possessing different hardness

Two micrographs of Si₃N₄ fracture surfaces are shown in fig. 9 a) and b). It is also clearly shown as in fig. 7 a) and b) that the fine grained microstructure must generate more deflection of cracks due to the increased grain boundaries. But the influence of crack initiation and propagation is of negligible influence to the ballistic protection capability.

Figure 9 a) and b). SEM micrographs of fractured Si₃N₄, mean grain size a) 0.9 µm and b) 6 µm
4. CONCLUSION

The ballistic results show clearly a strong dependency on the macro hardness assuming that a target configuration like in this investigation is used. The results show also that a ceramic material should be used, which could be sintered in the solid state, because liquid phase sintering increases the amorphous phases between the crystalline grains and is preventing a significant increase of the macro hardness.

For high purity Al₂O₃ ceramic the fracture of amorphous inter grain phases is becoming important if a certain grain size of the microstructure is exceeded. The Al₂O₃ ceramic investigated shows a significant decrease in hardness when decreasing the grain size from 0.5 μm on downwards. Since the ballistic protection capability is depending directly on the macro hardness as the results show it may be supposed that the ballistic protection decreases also if the grain size will be smaller than 0.5 μm.

References

STATIC AND DYNAMIC FRACTURE OF TRANSPARENT ALUMINA

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Abstract: Transparent polycrystalline alumina has a great potential to be a viable replacement for many conventional materials in highly demanding applications due to its superior mechanical properties, like hardness, wear resistance, strength or optical performances. These applications comprise missile radomes, armored windows, artificial joints and more. The present paper deals with static and dynamic fracture toughness of polycrystalline alumina with nanograin size for different loading rates. The specimens are all precracked with a sharp crack obtained by controlled bending tests of hardness microindentations. The preliminary results both of the static and dynamic fracture toughness are reported. The present paper is a part of ongoing research, so additional results including a statistical analysis will be added later. The present results show a marked increase in initiation toughness in the dynamic vs. quasi-static case.

1. INTRODUCTION

Recently CeraNova Corporation (MA, USA) has presented transparent PCA (Polycrystalline Alumina), using a powder processing method for green body forming, and a combination of sintering and hot isostatic pressing (HIP) to achieve almost 100% density and a fine-grained microstructure (average grain size <0.7 µm) [1]. The benefits of fine-grained microstructures with submicrometer grain size for obtaining improved mechanical properties (e.g. hardness [2], wear resistance [3], strength, or optical performance) are well known. Initial mechanical property measurements, according to CeraNova, indicate that CeraNova PCA has a toughness that is ~30% higher than standard alumina, 35-75% higher than sapphire, and hardness ~10% greater than that of sapphire. For applications where erosion resistance and thermal shock resistance are required, these improvements present significant advantages over other materials (e.g. sapphire). This fine-grained PCA is a viable replacement for many applications including those that require shapes obtained by powder processing, e.g. missile domes, armor vehicles windows, lamp envelopes [4] and artificial joints [5]. According to [1], CeraNova did not perform standard test to measure the fracture toughness (K₀), but performed Vickers indentation hardness tests to evaluate it. The Vickers indentation fracture toughness test, or IF, is addressed to estimate the fracture resistance, or K₁c of ceramics. According to [6], the IF test technique is fundamentally different than standard fracture toughness test [7], and suggested that IF technique is not appropriate for exact measurements of fracture toughness, K₁c, but rather may be used for approximate estimation of that property or to check out fracture toughness for materials for which this property is well known. Various methods to determine the fracture toughness of ceramic materials are described in the literature and even in a standard [7], but it is well known that different methods can produce different fracture toughness values for the same material, so the choice of a method should be done wisely, with respect to a material that under investigation and of course with respect to the specific abilities, e.g. specimen dimension, R-curve behavior or just availability of fixtures. The review of some of the existing methods versus standardized techniques, including a critical comparison can be found in [8-9]. It is well known, that some of the techniques for the determination of the fracture toughness are used less frequently, and some of them are more exact, for example the SEPB method recognized like the exact one [7], [10], but highly complicated and demanding special fixtures and equipment [11], and because of that are not widely used. In the SEPB method the precrack starts from a Vickers indentation, acknowledging the fact that Vickers indentations are less influenced by specimen surface flatness, parallelism, and surface finish. The forthcoming results were obtained with SEPB method and compared to the existing results from literature [1], [12].

In parallel, for some materials, it has been observed, that the dynamic fracture toughness increases markedly with the stress intensity rate. From [13], dynamic loading conditions produce values that are twice the quasi-static values, or it may even reach 3 times its quasi-static value [14]. This observation cannot be generalized to all the materials, since in certain cases the dynamic initiation toughness may sometimes be lower than its static counterpart or even remain unaffected by the rate of loading, as reported in the literature.
The purpose of this research is to measure the static fracture toughness, the dynamic fracture toughness and its dependency on stress intensity rate, to understand the influence of near-100% density and a fine-grained microstructure of the material on the above mentioned mechanical properties.

2. EXPERIMENTAL PROCEDURE

2.1 Materials and specimens.
Four nanograin alumina plates were prepared by CERANOVA and 6 x 8 x 45 mm bend bar specimens were cut from these plates. The properties of this material had been reported by the manufacturer as 100% dense, with a mean grain size of 0.7 µm, and a hardness of 2284±53 [kgf/mm²]. All faces were initially ground and edges were chamfered. The faces for the indents were polished to a mirror finish. Precracks were introduced following ASTM C 1431 “Standard Test for Determination of Fracture Toughness of Advanced Ceramics at Ambient Temperature” for precracked beam (pb) specimens from a Vickers indentation [7]. Precrack straightness was found to depend on surface roughness. The specimens were initially ground by the manufacturer, to a mean roughness of Ra 0.2 µm and then polished to Ra 0.1 µm or better. All roughness measurements were performed on a Wyko NT1100 interferometer. The specimens with Ra<0.1 µm tend to develop straighter precracks than specimens with greater Ra. A typical indent crack and precrack are shown in Figs 1 and 2, respectively. The same technique of sharp precracking was used for both static and dynamic tests. Concerning a dynamic tests, as far as we found, this is the one of the first times that ceramic specimens with a sharp precrack were used to evaluate the dynamic fracture toughness.

![Figure 1. Vickers indentation on polished PCA specimen. The cracks emanating from the corners of the indent can be clearly seen.](image1)

![Figure 2. A typical precrack on PCA specimen. The picture was taken with specimen through-lighting. Note the translucency of the specimen.](image2)

2.2 Static tests.
The specimens were fractured in three point bending with a span to width ratio of 5 at a loading rate of 0.0016 mm/sec in an Instron 4483 with 500N load cell, under displacement control. The fracture toughness was calculated from the maximum load and crack length measurements, according to standard recommendations [7]. There was no evidence of R-curve behavior for this material, as expected and the results for the fracture toughness are summarized in Table 1.

2.3 Dynamic tests.
The dynamic fracture toughness of a material is a key property when high rates of loading involved. By contrast with static fracture toughness measurements, there is no standardized technique to determine the dynamic fracture toughness. There are few techniques to determine the *K*<sub>IC</sub>, e.g. H-integral, [15], to relate the crack opening displacements, (COD), to corresponding stress intensity factor. For the dynamic experiments reported in this paper, a modified Split Hopkinson (Kolsky) Pressure Bar (SHPB) was used with one-point impact configuration technique. An overview of a method can be founded in Weisbrod
and Rittel [18]. Fracture gages were painted on the each side of the specimens near the crack tip using silver paint. The gages were wired to a power source and digital oscilloscope, so that crack propagation was detected during the impact test. A typical experimental record consists of incident and reflected pulses, collected from the strain gages mounted on the incident bar, as well as two fracture gages signals (fig. 3). All the signals were synchronized with the incident strain gage signal. Before testing the alumina specimens, preliminary tests and calculation routines were made on sharply notched PMMA specimens of the identical dimensions. The $K_{t}$ values for PMMA specimens, not reported here for the sake of brevity, were found to be in excellent agreement with previous results [16]. The 2D finite element model (Abaqus 6.5) was used to calculate stress intensity factor (SIF) for each specimen as a function of time using Irwin's formula which relates the crack opening displacement (COD) to the SIF. Numerical convergence was checked both for PMMA and PCA specimens. The fracture time was used to calculate $K_{fc}$, whose values are listed in first row of Table 2.

![Figure 3. A typical incident and reflected signal from one-point impact test with two fracture gages (Sp5 PCA).](image)

3. RESULTS AND DISCUSSION

Table 1 summarizes the static fracture toughness results of this study and compares these to the Indentation Toughness, $K_{Ic}$, results of similar materials. It can be seen that the SEPB results tend to be slightly lower as would be expected for a straight crack. Figure 4 clearly shows that the relative initial crack length does not affect the measured SEPB fracture toughness values.

Table 1. SEPB Fracture Toughness compared with Indentation Fracture toughness measurements of similar material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Test Method</th>
<th>$K_{fc}^{*}$ [MPa.m$^{1/2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeraNova PCA</td>
<td>SEPB</td>
<td>3.10±0.075</td>
</tr>
<tr>
<td>Sub-μm Al$_2$O$_3$ [12]</td>
<td>IF</td>
<td>-3.50</td>
</tr>
</tbody>
</table>
The dynamic fracture toughness values and comparison with static fracture toughness are summarized in Table 2. In this table one can find reference results for similar ceramic materials, [19-20]. The results for SiC-N by T. Weerasooriya et al., [19], shows clearly the same trend for the dynamic toughness values, but the stress intensity rate that reported by these authors is markedly lower. Additional results for Alumina with average grain size of 3 μm also summarized in Table 2, [20]. These results contradict the presented values and also whole trend that presented here. The reason for those discrepancies is that according to [20] maximum load was used to calculate the dynamic fracture toughness with no attempt to measure a true time to fracture. Also there is no evidence for dynamic equilibrium, whereas according to D. Rittel et al., [13], fracture typically happens beyond the maximum value of the force, as a result of inertial effects, so that the peak load cannot be identified as an indication of fracture, as illustrated in fig. (5).

Figure 4. Static fracture toughness (K_{lc}) versus non-dimensional crack length. There is no evidence of R-curve behavior

Table 2. Comparison of dynamic fracture toughness results.

<table>
<thead>
<tr>
<th>Material</th>
<th>$K_{lc}^d$ [MPa√m]</th>
<th>$K_{lc}$ [MPa√m]</th>
<th>$K_d$ [MPa · m^{0.5} · s^{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeraNova PCA</td>
<td>3.10±0.075</td>
<td>36.4±3.7</td>
<td>$&gt;10^6$</td>
</tr>
<tr>
<td>SiC-N [19]</td>
<td>4.75±0.25</td>
<td>5.5±9.5</td>
<td>$10^5$</td>
</tr>
<tr>
<td>$Al_2O_3$ [20]</td>
<td>2.70</td>
<td>3.5</td>
<td>$10^6$</td>
</tr>
</tbody>
</table>

Note the excellent agreement between two fracture gages readings. Both fracture times occur way after the maximum load, but still before that actual force drops to zero (see also [13]). For PCA Alumina typical fracture time was measured between 12 to 18 μs, and for PMMA specimens the fracture time was between 22 to 26 μs. As mentioned before, [13], the accurate timing of fracture is a critical issue. Comparison of dynamic and static fracture toughness values versus stress intensity factor rate is shown in fig. 6. The fracture toughness for polycrystalline alumina is apparently rate sensitive, in accord with [19].
Figure 5. True force acting on the specimen during impact and fracture times. Note the excellent agreement between two fracture gage times (Sp7 PMMA).

Figure 6. Comparison of dynamic and static fracture toughness versus stress intensity rate. Apparently fracture toughness for polycrystalline alumina is rate sensitive.
4. CONCLUSIONS

The static and dynamic fracture toughness of polycrystalline transparent full dense alumina was measured using sharp initial cracks. It was found that PCA Alumina is rate sensitive, in terms of initiation toughness. As part of this ongoing research, additional statistics will be added to the results, and a fractographic study will be carried out, aimed at elucidating the discrepancies between static and dynamic fracture toughness values.

References:

7. ASTM C1621-99, "Standard Test for Determination of Fracture Toughness of Advanced Ceramics at Ambient Temperature"
EFFECT OF THE CHEMICAL COMPOSITION ON THE MECHANICAL BEHAVIOR OF BULK METALLIC GLASSES USED AS MATRIX IN BULK METALLIC GLASSES - W COMPOSITES

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Abstract: The fabrication of metallic glass (MG)-W composites and the study of new metallic glass alloys as matrix for the composites are reported. The composite is prepared by mixing MG and W powders and application of powder metallurgy techniques of sintering assisted uniaxial compaction. Sintering of the MG is preliminary reported in details, emphasizing detrimental evolution of the amorphous phase during the milling process. MG deformation is controlled by shear band initiation and propagation. An attempt is made to adjust the local flow rate in shear band by variation in composition of the alloys. Chemical variations were applied to a Zr-based bulk MG by addition of W, Ta, Sn. The new alloys were investigated using nanoindentation at room temperature. A clear effect of each element on the MG properties is not straightforward. However it was noticed a linear correlation with a negative slope between the apparent activation volume and Young modulus.

1. INTRODUCTION

Metallic glasses (MG) are intensively studied for exhibiting unusual combination of properties. They are macroscopically homogenous but featured by local atomic (or as suggested recently, atomic cluster) complex disordered structure. Due to the metallic character of atomic bonds, MG have elastic modulus similar to those of main metals and metallic alloys. However, absence of structural ordering leads to plastic deformation by atomic displacement localized in thin shear bands. For a Zr based BMG the low Young modulus (80 GPa), the viscous flow induced by the stress relaxation which leads to high strength (1.7 GPa) and strong localization of the deformation result in large elastic deformation (2%) and absence of macroscopic ductility. MG are also featured by thermal properties similar to those of glass polymers and oxides; above a glass transition temperature $T_g$, they exhibit macroscopic homogenous deformation under high viscous flow rate. Afterward, MG alloys undergo crystallization at $T_c$ few tenth of K above $T_g$ which make them sufficiently stable to allow in particular easy shaping. These properties are efficiently used to produce MG-W composites by infiltration of the MG above its liquid temperature, followed by cooling in a porous W sintered pre-form [1,2] or W wires [3].

MG-W composites are among the most intensively studied materials including MG for they mechanical behavior. Among other applications, MG-W composites are potential candidate for armor-piercing projectiles in replacement for depleted uranium. Under dynamic loading conditions, MG exhibit localized shear band deformation mechanism. Filled with W the materials should be appropriate with a good balance between mechanical behavior under dynamic loading and volume weight, compared to regular W compounds whose thermo-mechanical behavior is inappropriate. It is clear now that the mechanical behavior of MG in quasistatic and dynamic loading is controlled by shear bands initiation, propagation, and interactions [4-6]. Now, improvement or changing in properties of MG need to understand the shear band initiation and its control through the chemical composition.

Our objective is to fabricate a composite architecture where W particles are uniformly dispersed inside a percolated amorphous phase. Different properties are then expected compared to those of the isotropic composite fabricated by infiltration of the glassy phase inside a percolated W sponge structure and where mechanical behavior of W is dominant [1, 2]. In our approach, a strong effect of the mechanical properties of the amorphous phase is expected. Indeed, the properties of the MG-W interfaces and of the W deformation under heavily localized shear stresses should be most likely involved in the overall behavior of the composite. Effect of shear bandings on the composite properties and possible chemical effects on shear band flow, both under quasi-static or dynamic loading have incited our current interest in the synthesis of
new compositions including elements with various properties. For example, heavy metals with strong localized atomic bonds like W should have strong effects on the local flow in the shear bands.

In this article, preliminary studies of the fabrication of a MG reinforced W composite are first reported. The synthesis of new Zr-based amorphous phases is then detailed. It follows the characterization of their mechanical behaviors using nano-indentation and the potential effect of the composition on the elementary deformation mechanism. The new compositions were investigated through the analysis of activation volume characterizing the elementary thermally activated event in the deformation process.

2. APPROACH TOWARD THE FABRICATION OF MG-W COMPOSITES

Dispersion of the W phase inside a MG matrix was approached by powder metallurgy technique. Initially, the BMG Zr_{57.5}Cu_{20}Al_{15}Ni_{10}Ti_{5} obtained as large size specimen was milled into powder with particle size of about 20 μm by mechanical milling. The composite was prepared by mixing in a 50% vol. fraction, this powder with a W powder having a particle size of 150 μm (provided by Neyco). Uniaxial pressure assisted sintering was studied using a mechanical testing machine MTS/20. For this, a WC die-punch tool was conceived and the machine was equipped with a three heating zones oven. Calibration was achieved to know the temperature inside the tool as a function of the external temperature regulated by the oven. In a first step, pressure assisted sintering of the MG powder only was studied to evaluate the level of pressure necessary and the temperature range for the densification and the consolidation. The relative density (or densification parameter) defined as the ratio of the volume weight of the compacted powder to that of the theoretical fully dense material: $d = \rho_{mg}/\rho_{\text{theoretical}}$ was recorded during compaction from the machine cross head displacement as a function of the applied pressure (Figure I (a)). These experiments were carried out at various temperatures and with various subsequent annealing times under constant load.

From experimental densification curves of metallic or alloy powders, it was postulated, that the variation in the porosity level with pressure is proportional to the residual porosity. This is formulated following:

$$\partial(1-d)/\partial P = -k_d (1-d)$$

which by integrating leads to the Konopicky-Shapiro equation of state [7]:

$$Ln\left(1 - \frac{1}{1-d}\right) = k_d P + \alpha_d$$

$P$ is the applied compaction pressure and $k_d$ and $\alpha_d$ are constants. Ductile materials show two linear domains in the Konopicky-Shapiro plot corresponding to two distinct densification mechanisms. At low pressure, densification is achieved by particles rearrangement, controlled by surface friction. It was shown that this re-packing is related to the elastic properties of the alloy; it was also shown that the slope of this first domain is linked to the yield stress of the material, $\sigma_y = 1/3k_d$. In the second domain, at higher pressure, densification occurs by plastic flow of the particles and the slope is associated to the Meyer work hardening index.

The curves in the figure 1(a) shows that similar densification are achieved whatever the conditions, from annealing temperature of 500°C to 540°C and annealing time from 1h to 2h45 mins under constant loading. The MG powders reach a densification of 87% at 800 MPa. The Konopicky-Shapiro plot in the figure 1(b) shows a single domain indicating that during the compression and the sintering process, the MG powder undergoes densification by particle rearrangement only with the absence of plastic flow. This is observed in the figure 2(a) exhibiting a fracture surface of a sintered specimen. Besides, the slope from the figure 1(b) gives a yield strength $\sigma_y = 1/3k_d \approx 260$ MPa, which is consistent with the strength measured on the BMG in a compression test at around the glass transition temperature [8].
Figure 1. (a) Dynamic densification curves of MG powders at various temperatures followed by annealing time at the maximum compaction load (500°C-1h, 510°C-1h, 540°C-1h, 540°C-2h45mins). Densifications are nearly similar. Curves irregularities are intermediate relaxations applied by interruption of the cross head displacement, to improve particles packing (b) One of the densification data re-plotted in the Konopicky-Shapiro coordinates.

Figure 2. (a) SEM micrograph of the fracture surface of the sintered metallic glass powder at 540°C followed by annealing during 2h45 mins. Particles flow does not occur during the sintering process. (b) Characterization of the glass powders consolidation state for the various compression and sintering conditions (from bottom to top: 500°C-1h, 510°C-1h, 540°C-1h, 540°C-2h45 mins).

Consolidation of the powders (local particles welding) was evaluated by mechanical testing of the sintered parts. The stress-strain curves in the figure 2(b) reveal the effect of the temperature but also the dominant effect of the annealing time under constant loading. Precisely, an increase in strength from 600 MPa to 800 MPa was recorded for sample annealed at 540°C for respectively 1h and 2h45 mins. It is emphasized that some ductility happens in the sintered powders due to strain hardening and attributed most likely to a residual porosity in the material [9,10]. The densification conditions were used to fabricate a MG-W composite. Homogenous dispersion of the W phase is obtained as shown in the figure 3(a), though the mechanical performance are still poor and make necessary to optimize the process by use of a spark plasma sintering technique [11].
Additional characterizations were carried out to explain the absence of plastic flow during compaction of the MG powder at 540°C well above the glass transition temperature $T_g = 387°C$ and the crystallization temperature $T_x = 446°C$. Transmission electron microscopy observations reveal the presence of crystalline particulates related to pollution during mechanical milling with WC jars and balls. Main part of the materials is still amorphous as confirmed by the electron diffraction in the inset of the figure 3(b).

![Figure 3](image)

**Figure 3.** (a) SEM micrograph of the fracture surface of a sintered MG-W composite at 540°C and annealed for 1h. (b) TEM image of the sintered MG powder at 540°C followed by annealing for 2h45mins. Presence of crystalline phase due to pollution is observed, though main part of alloy is amorphous as shown by the selected area diffraction in the inset.

![Figure 4](image)

**Figure 4.** In situ X-ray diffraction analysis of the crystalline variations with temperature for (a) the bulk MG and (b) the mechanically milled MG.

The crystalline variations with temperature were investigated using in situ X-ray diffraction. As reference, the crystallization temperature of the BMG of 450°C (Figure 4(a)) is consistent with that measure by differential scanning calorimetry. The diffractogram of the MG powder is more complex (Figure 4(b)) and shows the presence of pollution due to the milling process. Part of the powder is also already partially crystallized which may be ascribed to milling as well. Most likely crystallization is induced by severe deformation and mainly surface crystallization after MG fracture under shear banding process and associated heat release. Large scale crystallization with the formation of the same phase as in the BMG is observed at 600°C well above $T_x$. At the temperature of sintering (540°C), no variation is observed indicating that the MG is stable though above $T_g$ and $T_x$. It was concluded that the milling process induced structural relaxation in the MG changing the thermal properties with increase of $T_g$ and $T_x$ and most likely
an inversion with $T_g > T_x$. This behavior is of course detrimental for the fabrication of a MG-W composite where both the absence of crystallization and particle flow are expected.

### 3. EFFECT OF THE COMPOSITION ON THE MECHANICAL BEHAVIOUR OF MG

This study consisted in varying the composition of the Zr$_{55}$Cu$_{35}$Al$_{10}$Ni$_5$Ti$_2$ BMG by addition of W, Ta or Sn. Alloys were prepared by pre-melting using r.f. induction in copper cold crucible, followed by quenching using planar flow casting technique. The results were also compared to the Vitreloy EMG. Various models at atomic scale were proposed to approach the shear band initiation in MG. The widely used are monatomic free volume model derived from liquid behavior [12] and the displacement of group of atoms proposed by Argon [13]. These models are described by the same initial analytical relation. But Argon suggested that stress relaxation should occur on a representative group of atoms where free volume formation would lead to shear displacement initiation. Atoms displacement involved in the rate controlling process is thermally activated and can be approached by measurement of an apparent activation volume ($V_{app}$). It is called apparent since measured from macroscopic shear rate and stress different than the local ones. As $V_{app}$ characterized the relation between shear band initiation and the atoms involved, it should be a sensitive parameter to variation in local chemistry of the alloy.

The apparent activation volumes were measured by nano-indentation constant load tests at room temperature. MG are characterised by absence of plastic deformation in macroscopic tests below glass transition (tension, compression, bending) which makes investigations of the localised plastic flow extremely difficult. The confined character of the nano-indentation technique gives access to some plasticity and then allows investigating the deformation mechanism. The various states of the material, whatever it is, under the indent (plastic, elastic strains and rigid part) and the associated hydrostatic pressure component, have indeed an influence on the result compared to other techniques (jump test, stress relaxation). For MG where deformation occurs by formation and propagation of localized shear bands, the effect of the type of mechanical testing used is even more pronounced. First, for a macroscopic applied strain rate, the volume fraction of shear bands should vary from one type of experiment to the other, with direct consequence on the local strain rate in shear bands. Indeed, with low fraction of the strained regions, the strain rate in the shear band is most likely several orders higher than the macroscopic strain rate. Second, it is accepted that MG are pressure sensitive and the high confined pressure in the vicinity of the indent, as well as the non uniform distribution of loading pressure in the deformed region, should be dominant in the assessment of the activation volume [6]. In the present work, the nano-indentation technique was used to measure data which can be compared to draw trend in the relation between the behaviour and the chemical composition. Indeed, the nano-indentation allows performing mechanical testing on a thin ribbon which is the most convenient shape for obtaining and studying synthesis of metallic glass. It was verified previously that measurements on a 50 μm thick ribbon were identical as those on the same metallic glass in the bulk form.

The experiments were carried out with a Hysitron triboscope nano-indenter equipped with a Berkovitch tip. The load was increased up to 8000 μN at a rate of 80 mN/s and maintained 5 s before unloading. Initially the strain rate sensitivity $m$, was derived from a log-log plot in the dependence between the stress and the deformation rate:

$$\sigma = \alpha \left( \frac{h}{h_0} \right)^m$$

(3)

$\alpha$ is a constant depending on temperature. The depth variation with time, $\dot{h} = dh/dt$, is derived from the fit of the depth-time curve (figure 5) by a logarithmic function. The stress is calculated using the following relation:

$$\sigma = \frac{P}{A_c \times \Psi} = \frac{P}{24.5h^2 \times 3}$$

(4)
\( \Psi \) is the plastic constraint factor estimated as 3.0, from the ratio of the nanohardness by the macroscopic yield stress [14]. \( P \) is the applied load and \( A_c \) is the projected area of the Berkovitch tip approximated by 24.5\( h^2 \).

**Figure 5.** Variation of the indent depth as a function of time at constant load during a nano-indentation experiment on a metallic glass.

The apparent activation volumes are then calculated by:

\[
V_{\text{app}}^n = \frac{\sqrt{3} \times kT}{m\sigma}
\]

(5)

\( k \) is the Boltzmann constant and \( \sqrt{3} \) is the Taylor factor such that the shear stress is \( \sigma/\sqrt{3} \). To improve accuracy in the calculation of \( V_{\text{app}}^n \), nanoindentations were repeated for each sample and a statistical data processing developed by S. Nowak was used [15]. The activation volume calculated from the fit of the depth-time curve (figure 5) can vary by a factor of 2-2.5 in multiple measurements on the same sample. These variations may be attributed to various factors such as temperature drift effect, short time measurement increasing scattering during data recording, alloy heterogeneities and surface imperfections. A linear correlation was observed between the apparent activation volume calculated and the correlation factor in the log fit of the depth-time curve. Average and comparable \( V_{\text{app}}^n \) values were then estimated for a 100% correlation factor by extrapolation.

From the loading-unloading curves, the Young modulus \( E \), the hardness \( H \) and then the strength, \( \sigma_s \), were also deduced from:

\[
E = \frac{dP}{dh} \times \frac{1}{1.167 \times \sqrt{A_{c_{\max}}}}, \quad H = \frac{P}{A_{c_{\max}}} \quad \text{and} \quad \sigma_s = \frac{H}{3}
\]

(6)

\( dP/dh \) is measured at the onset of the unloading curve, \( A_{c_{\max}} \) is the maximum projected area, 1.167 is a geometric parameter characterizing the Berkovitch tip.

The data are reported in the table 1. along with structural characteristics of the MG. It is emphasized that over the overall composition, the Young modulus was increased by 30%, the hardness by 20%, the strength by about 10%. The apparent activation volume was decreases by about a factor of 4.
Table 1. Young modulus \((E)\), nano-hardness \((H)\), strength \((\sigma_y)\) and apparent activation volume. 
Alloys were sorted off to emphasize the gradual variations.

<table>
<thead>
<tr>
<th>Name</th>
<th>MG composition</th>
<th>Nature of phases identified</th>
<th>(E) (GPa)</th>
<th>(H) (GPa)</th>
<th>(\sigma_y) (GPa)</th>
<th>(V_{app}^\text{app}) ((\Lambda^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z301</td>
<td>Zr_{0.5}Cu_{0.5}</td>
<td>Amorphous (RX)</td>
<td>94.5</td>
<td>6.2</td>
<td>1.5</td>
<td>225</td>
</tr>
<tr>
<td>ZW102</td>
<td>Zr_{0.5}Cu_{0.5}Al_{0.5}Ni_{0.5}Ti_{0.5}W_{0.5}</td>
<td>ZrW_{2} crystallites (RX)</td>
<td>99.7</td>
<td>6.3</td>
<td>1.5</td>
<td>214</td>
</tr>
<tr>
<td>Z101</td>
<td>Zr_{0.5}Cu_{0.5}Al_{0.5}Ni_{0.5}Ti_{0.5}</td>
<td>Amorphous (RX+TEM)</td>
<td>99.8</td>
<td>6.4</td>
<td>1.6</td>
<td>204</td>
</tr>
<tr>
<td>ZT203</td>
<td>Zr_{0.5}Cu_{0.5}Al_{0.5}Ni_{0.5}Sn_{0.5}Ta_{0.5}</td>
<td>Ta crystallites (RX)</td>
<td>104.5</td>
<td>6.9</td>
<td>1.7</td>
<td>196</td>
</tr>
<tr>
<td>ZW402</td>
<td>Zr_{0.5}Cu_{0.5}Al_{0.5}W_{0.5}</td>
<td>ZrW_{2} crystallites (RX)</td>
<td>98.5</td>
<td>7.2</td>
<td>1.7</td>
<td>145</td>
</tr>
<tr>
<td>Z401</td>
<td>Zr_{0.5}Cu_{0.5}Al_{0.5}</td>
<td>Amorphous (RX)</td>
<td>105.5</td>
<td>7.4</td>
<td>1.8</td>
<td>149</td>
</tr>
<tr>
<td>ZW205</td>
<td>Zr_{0.5}Cu_{0.5}Al_{0.5}Ni_{0.5}Sn_{0.5}Sn_{0.5}W_{0.5}</td>
<td>ZrW_{2} crystallites (RX+TEM)</td>
<td>111.3</td>
<td>7.1</td>
<td>1.8</td>
<td>147</td>
</tr>
<tr>
<td>ZT202</td>
<td>Zr_{0.5}Cu_{0.5}Al_{0.5}Ni_{0.5}Sn_{0.5}Ta_{0.5}</td>
<td>Ta crystallites (RX)</td>
<td>115.0</td>
<td>7.3</td>
<td>1.9</td>
<td>148</td>
</tr>
<tr>
<td>ZW403</td>
<td>Zr_{0.5}Cu_{0.5}Al_{0.5}W_{0.5}</td>
<td>ZrW_{2} crystallites (RX)</td>
<td>116.0</td>
<td>7.3</td>
<td>1.9</td>
<td>136</td>
</tr>
<tr>
<td>ZW404</td>
<td>Zr_{0.5}Cu_{0.5}Al_{0.5}Sn_{0.5}W_{0.5}</td>
<td>ZrW_{2} crystallites (RX)</td>
<td>116.0</td>
<td>7.6</td>
<td>2.3</td>
<td>137</td>
</tr>
<tr>
<td>ZW302</td>
<td>Zr_{0.5}Cu_{0.5}W_{0.5}</td>
<td>ZrW_{2} crystallites (RX)</td>
<td>109.1</td>
<td>6.5</td>
<td>1.6</td>
<td>109</td>
</tr>
<tr>
<td>ZW204</td>
<td>Zr_{0.5}Cu_{0.5}Al_{0.5}Ni_{0.5}Sn_{0.5}Sn_{0.5}W_{0.5}</td>
<td>ZrW_{2} crystallites (RX)</td>
<td>113.3</td>
<td>7.2</td>
<td>1.8</td>
<td>62</td>
</tr>
<tr>
<td>Vitreloy</td>
<td>Zr_{0.5}Cu_{0.5}Ti_{0.5}Ni_{0.5}Be_{0.5}</td>
<td>Nanocrystallites</td>
<td>123.5</td>
<td>7.6</td>
<td>1.7</td>
<td>60</td>
</tr>
</tbody>
</table>

Correlations between the physical properties and the variations in compositions are not straightforward before the complexity in composition of these MG. In addition, some of the materials contain various types of nanocrystallites which may influence the properties and change the local composition of the surrounding amorphous phase. Nevertheless, the Young modulus related to bonding energy gives rise to an average characteristic of the complex system. It was found that the plot of the activation volume as a function of the Young modulus exhibits a near linear correlation (Figure 6). An attempt is made to evaluate the influence of the chemical additions of the various alloys on the Young modulus and then draw tendency on the effect of the chemistry in the apparent activation volume.

![Figure 6. Activation volume as a function of the Young modulus for various Zr-based MG showing a linear correlation.](image-url)
These results give a first insight of the possibilities for controlling shear band initiation by the chemistry. Further understanding needs to perform systematic studies on series of relevant and gradually changed compositions to identify the role of specific atomic element. Furthermore, the impact of nanocrystallites on the apparent activation volume should be necessarily clarified.

4. CONCLUSION

The fabrication of metallic glass (MG)-W composites and the study of new metallic glass alloys as matrix for the composites are reported. In our approach the composite is prepared by mixing MG and W powders and application of powder metallurgy techniques of sintering assisted uniaxial compaction. Sintering of the MG is preliminary reported in details, emphasizing detrimental evolution of the amorphous phase during the milling process. A shift towards higher temperature for the MG powder $T_g$ and $T_x$, compared to bulk MG is observed. This makes the domain of homogenous viscous flow deformation for the MG powder inaccessible.

MG deformation is controlled by shear band initiation and propagation. An attempt is made to adjust the local flow rate in shear band by variation in composition of the alloys. Chemical variations were applied to a Zr-based bulk MG by addition of W, Ta, Sn. The new alloys were investigated using nanoindentation at room temperature. A clear effect of each element on the MG properties is not straightforward. However it was noticed a linear correlation with a negative slope between the apparent activation volume and Young modulus.

Acknowledgments

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References

DEFORMATION AND FAILURE OF METALLIC GLASSES

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Abstract. We discuss the development of shear bands in bulk metallic glasses under both static and dynamic loads. Kolsky bar and microcompression experiments have been used to identify the deformation and failure modes.

1. SUMMARY

In a number of pure single crystal face-centered cubic (fcc) metals, strength is found to be highly dependent on the specimen size in the micrometer range perhaps because the size of the specimen is smaller than the characteristic length scale of dislocation multiplication. In contrast, plastic deformation in metallic glasses is not controlled by dislocation dynamics. One result of this is that yield strengths of bulk metallic glass specimens approach theoretical limits. A second logical consequence would be that metallic glasses should not show a significant effect of specimen size on strength. We present quasi-static, room temperature compression data for Pd_{40}Ni_{40}P_{20} metallic glasses for both bulk and micro-scale specimens.

At all sizes, plastic flow is localized in shear bands which are accompanied by sudden strain bursts in the micro-scale tests. We have found a modest increase of ~9% in the compressive strengths of micrometer-sized specimens when compared to the bulk counterparts. Given that there is a population of flaws and defects in millimeter-sized specimens, we suggest that the decrease in the defect population in micrometer-sized specimens results in some enhanced strength. Presumably, this behavior could be modeled using Weibull statistics, but we do not have a sufficient number of specimens to provide a complete analysis. We find the average strengths of specimens that are ~2 μm and ~10 μm in diameter are roughly equivalent. Comparing the peak strengths for each nominal specimen size, there is some indication of enhanced strength in the smallest specimens, though the magnitude of the increase is comparable to the scatter in the data.

Acknowledgments

The author gratefully acknowledges the support of the Army Research Laboratory for work in this area.

References

DEFORMATION BEHAVIOR OF ZR-BASED BULK METALLIC GLASSES – TEMPERATURE AND STRAIN RATE INFLUENCES ON SHEAR BANDING

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Abstract. At low temperatures metallic glasses exhibit localized flow in form of shear bands. This is associated with flow instabilities, which reflect serrated flow curves, where single stress drops of the order of few MPa up to several tens of MPa occur within time spans of milliseconds. The width of the shear bands and the time-dependent heat conduction is suggested to be not fully adiabatic at low strain rates, although high temperatures occur leading to viscous-flow features on shear planes. Evaluation of the deformation kinetics at cryogenic temperatures, where non-serrated flow prevails, suggests an increase in viscosity within the shear band, although temperatures are still sufficiently high to cause localized melting at fracture. This macroscopic change in the flow behavior as a function of strain rate and temperature is directly related to a change in the strain rate sensitivity from negative to positive values, suggesting a clear change in deformation behavior. Here we present an alternative shear dilatation model to describe our experimental findings.

1. INTRODUCTION

Bulk metallic glasses (BMGs) are known for their extraordinary rheological properties: at high temperatures close to the glass transition temperature \( T_g \) they behave like a Newtonian liquid and thus can be used for net shape forming processes, which allow to make structures difficult to machine by abrasive methods. If cooled down to room temperature (RT) such net-shape formed parts exhibit ultra-high strength and a high elastic strain limit (~2% strain), which is, i.e. ideal for spring applications. Their high corrosion resistance and isotropic microstructure down to the nanometer scale further allows for applications in harsh environments and/or where a miniaturization of parts is requested [1, 2, 3, 4].

Recently we observed that the deformation behavior bears not only at room temperature interesting mechanical properties, but also at sub-ambient temperatures [5, 6]. This behavior is different from their crystalline counterparts. Crystalline materials are generally known to show a reduction in ductility when temperatures are decreased. This is related to the restricted mobility of dislocations to cross-slip or to surpass obstacles by thermally activated mechanisms. Due to their disordered nature metallic glasses on the other hand do not possess dislocations as carriers of plastic flow. They rather are described by shear transformation zones (STZ), which structurally are not detectable as inhomogeneities in the same way as defects are in a crystal, but describe rather as a transient state, where a cluster of atoms is sheared cooperatively over a certain distance (Ref. [7] and Refs. therein) resulting in macroscopic shear bands.

Shear banding in crystalline coarse-grained ‘hard-to-deform’ metals typically occurs under dynamic loading, where micrometer-wide shear bands result [8]. However, reducing grain size in metals which in their coarse-grained state are regarded as being ‘soft’ also generates a gradual shift in their affinity to deform via shear banding. For example, nanocrystalline Ni exhibits shear bands, while its coarse-grained counterpart does not when tested at room temperature and at strain rates of \( 10^3 \) s\(^{-1} \) [9, 10]. The resulting increase in strength due to grain size reduction actually causes a reduction in strain and strain hardening ability, which is a favourable condition for the initiation of shear localisation, i.e. shear banding even at lower strain rates [11]. This is why the fracture angle of many fractured ultra-fine-grained or nanocrystalline samples tested in tension measures ~45° [12]. In metallic glasses, on the other hand, shear localisation is even more pronounced than in nanocrystalline metals. Only at temperatures close to their glass transition temperature, shear localisation can be avoided. In the temperature range where shear banding is present, the deformation kinetics are not yet clearly understood. Shear bands are significantly thinner than in crystalline metals, on the order of tens of nanometers [13, 14, 15, 16, 17]. Preferential etching of shear bands indicates their difference in structure [18]. Positron annihilation spectroscopy indicates that the free volume in metallic glasses (in analogy to the defect concentration in crystalline metals) is increased for BMGs which have been heavily deformed via cold rolling [19, 20]. These results and also recent transmission electron micros-
copy observations of shear bands suggest that the operation of STZs, i.e. shear bands alters its medium-range ordered atomic configuration [21]. This structural information has however not be accounted for in models describing the deformation kinetics of BMGs. In addition, it is not clear to date if this process is adiabatic or not under quasistatic conditions. And third, it is still arguable as to what the exact deformation mechanisms in BMGs are (Ref. [7] and references therein). Apart from the temperature increase during localised shearing, the shear dilatation models (the shear transformation zone (STZ) model [22] and the free volume or diffusive-jump-like model [23, 24]) have found wide acceptance in explaining the drop in viscosity as also recently reviewed by Schuh et al. [7]. On the other hand, however, none of the constitutive equations for inhomogeneous plastic flow ascribed by these models addresses the serrated flow as a kinetic phenomenon sufficiently well, this partially due to the lack of experimental evidence. Towards this end we recently have shown by mechanical tests at various strain rates and temperatures that the deformation kinetics and thus the final structure of a shear band is very much dependent on its strain, strain rate and temperature history. Here, we summarize recent results deduced from different Zr-based BMGs, where compression experiments were performed.

2. EXPERIMENTAL PROCEDURE

Cu_{65}Zr_{35}, Zr_{67.5}Cu_{25}Fe_{8}Al_{12}Pd_{0.1} and Zr_{53.5}Ti_{3}Cu_{17.5}Ni_{14}Al_{10} (Vit105) prealloys were prepared by arc-melting the pure elements (purity > 99.995%) in a Zr-gettered argon atmosphere from which cylindrical rods were suction-cast into a copper mold with a length of ~30 mm and diameters of 3 and 2 mm, respectively. Compression test specimens with a length-to-diameter ratio of 1.7 were cut from these rods and subsequently polished. The amorphous structure of the specimens was confirmed by means of X-ray diffraction (XRD) using a PANalytical X'pert diffractometer with Cu-Kα radiation, and by differential scanning calorimetry (DSC) using a Setaram Labsys DSC. The deformed specimens were examined with a LEO 1530 scanning electron microscope (SEM) equipped with a field emission gun. Constant cross-head displacement tests and strain rate jump tests in compression were performed on a 4-column Schenck-Trebel machine equipped with a 100 kN load cell. Tests were performed at various crosshead velocities ranging from 1.0 to 0.1 mm/min, resulting in initial strain rates of $3 \times 10^{-3}$ to $3 \times 10^{-4}$ s$^{-1}$. The strain was measured from the crosshead displacement and a strain gauge positioned on the pistons above and below the specimen. Acquisition rates of 20 to 1200 Hz were used to provide information on the shear band velocity.

3. RESULTS AND DISCUSSION

Figure 1 shows a stress-strain curve of a Cu_{65}Zr_{35} specimen tested at room temperature and with an initial strain rate of $1.0 \times 10^{-3}$ s$^{-1}$. The inset shows the magnitude of stress drops in the course of deformation. A clear increase in the stress drops from ~5 MPa at the beginning of deformation to values close to 30 MPa towards the end of deformation was recorded. A lower limit of 5 MPa was used to clearly differentiate the serration amplitude from the noise in the range of 2-3 MPa. In this context it should be noted that these stress drops are understood as the lower limit of the effective stress drops occurring in the sample. It was shown by Kimura and Masumoto [25] that the damping effects of the machine assembly, typically with load cells which are far from the specimens, substantially lower the ability to capture the dynamic stress response occurring during a serration event. Applying their evaluation method to the effective stress drops to the machine assembly used in this study yields a stress drop per shear event 2 to 3 times larger than that measured and shown in Figure 1. Therefore, effective stress drops close to 100 MPa have to be envisioned and supported by the material in order to prevent fracture.

Figure 2 shows two regions, designated as rectangles in the stress-strain curve of Fig. 1, plotted as a function of strain and time. The curve was recorded with an acquisition rate of 150 Hz, yielding a data-point (open squares) every 6.67 ms. In the lower strain range after ~30 seconds small stress drops are measured, which in some cases show several data points on the downward branches of the serrations. The drop times measured lie between 10 and 100 ms. In the larger strain range, after ~40 seconds significantly larger stress drops are captured which are recorded between a few data points only, resulting in stress drop times of approximately 10 ms. Our results thus provide evidence that not only the amplitude increases with increasing
strain, but that also the speed of the stress drops (that is, the speed of a shear band event) increases with increasing deformation. In addition, we observed, within the same strain range for the various samples analysed, a decrease in the stress drop magnitude with increasing strain rate: from \(-15\pm10\) MPa at strain rates of \(-10^4\) s\(^{-1}\) to \(-8\pm5\) MPa at \(-10^3\) s\(^{-1}\). The same trend, but with somewhat larger stress amplitudes, was also observed in Vit105 [31]. In addition, a decrease in the time needed for a stress drop or shear event to initiate, propagate and become arrested was observed with increasing strain rate. Whether this is due to the smaller drops at higher strain rate or whether the shear events are faster is, however, not clear.

Fracture surfaces of BMGs typically show a vein or river pattern indicative of very high temperature bursts at the moment of fracture, which instigates to a significant drop in viscosity and thus a formation of a viscous-like layer or the fracture surface. However, before fracture shear surfaces have not been analyzed sufficiently so far. Here in Figure 3 an SEM image of a sample (Zr\(_{52.5}\)Cu\(_{37.5}\)Fe\(_{10}\)Al\(_{12}\)Pd\(_9\)) deformed without fracture which exhibits a shallow viscous-like layer underneath a more brittle structure. This information suggests that even before fracture, sufficiently high temperatures can be reached which yield to viscous flow features. Thickness estimates from this and similar SEM images together with cross-sectional views made by transmission electron microscopy (TEM) suggest that the heat-affected width is restricted to one to two hundred nanometers maximum, and often less. Note that at the moment of fracture, stresses are relieved which are approximately 3 orders of magnitude higher than during shear banding before fracture [26]. Thus at the moment of fracture the viscous layer is a few micrometers thick [26].

Under adiabatic conditions the following expression must be fulfilled

\[
x = \sqrt{\Delta t \alpha},
\]

where \(x\) is the width of the heat-affected zone (here taken as the width of a shear band), \(\alpha\) is the thermal diffusivity, and \(\Delta t\) is the time needed for this process to occur. Table I shows that using equation (1) with a diffusivity of \(3.2 \times 10^{-6}\) m\(^2\)/s at \(T_g\) [27], duration times in the sub-nanosecond range arise for a shear band of 10 nm width, while for a shear band of 100 nm width a few nanoseconds would be required. A width of 5 microns would on the other hand require a few microseconds to heat up this area. There are several approaches to estimating the duration time. All, however, assume that the duration time for the heat burst is the same time span required for the activation of a local shear event (independent of the size of such an event).

During spatially inhomogeneous flow deformation can also occur in a temporal inhomogeneous manner. This is the case at room temperature and is reflected by a jerky flow or serrated flow curve. Below a critical temperature smooth yielding occurs (temporally homogeneous, but spatially inhomogeneous). Figure 4 shows two compressive flow curves at room temperature, 195K and liquid nitrogen temperature, where the crosshead velocity is changed by one order of magnitude, i.e. where a change in the strain rate between \(10^3\) and \(10^4\) s\(^{-1}\) is applied. The duration time of such stress drops at room temperature as measured from Figure 2 reveals time scales on the order of a few tens of milliseconds (irrespective of the acquisition speed). Assuming this to be the duration time \(\Delta t\) the thickness of the heat-affected width would be far too large before fracture if one assumes adiabatic conditions; however, at fracture agreement with the thickness of the viscous-like layer of the fracture surface results. Thus it is assumed here that adiabatic heating is not entirely fulfilled during shear banding in BMGs. In addition, if equations evaluating the temperature increase within a shear band [26] are taken into account, a discrepancy between values at fracture and before fracture results. In agreement with current literature [28, 29, 30] this suggests that shear localisation is the cause of a temperature increase due to frictional sliding, and not vice versa.

In the following the deformation kinetics of Zr-based BMGs is addressed. The three stress-strain curves produced from the same sample batch shown in Fig. 4 were measured at 77 K, 195 and at 300 K indicate a different response of the flow stress upon a change in the strain rate \(\dot{\varepsilon}\) by one order of magnitude from \(10^3\) s\(^{-1}\) to \(10^5\) s\(^{-1}\). Figure 5 shows the strain rate sensitivity (SRS) which is defined as

\[
m = \left(\frac{\partial \ln \sigma}{\partial \ln \dot{\varepsilon}}\right)_T,
\]

For a number of strain rates as a function of temperature. In agreement with our other current observations (see also Refs. [31, 32, 33]) it shows a decrease in the steady-state strain rate sensitivity (SRS) with decreasing temperature from values of 0.004 at 77 K to values of approximately -0.002 at 300 K. This change
in the deformation kinetics strongly suggests a fundamental change in the deformation mechanism. We recently compared the phenomenological similarities of serrated flow behaviour in metallic glasses [31, 32, 33] with that of crystalline alloys which show the so-called dynamic strain aging (DSA) effect [34], more commonly known as the Portevin - LeChâtelier phenomenon. In the alloys studied here, we observe a transition, similar to the DSA effect, from negative to positive SRS with decreasing temperature, which accompanies a change from serrated to smooth yielding (Fig. 4). Our results show that shear bands in metallic glasses exhibit a memory of their strain history, which is reflected by the increase in $\Delta \sigma$ and shear displacement with strain (Fig. 3) and the decrease of the SRS at room temperature [32]. In DSA-deforming crystalline alloys such behaviour has been explained by considering the stress relaxation in the vicinity of a shear band [35].

Our micromechanical view of the shear process in BMGs is based on the fact that a shear band represents an energetically-unfavourable structural state, which if time and temperature permit will structurally relax spontaneously towards a lower energy state [33]. Based on this, we introduced a state variable $(1g)$ into the rate equation, which accounts for this dynamical structural change within a shear band, i.e. the shear strain rate is

$$\dot{\gamma} = \dot{\gamma}_0 \exp \left( \frac{-\Delta G}{k_B T} \right) = \gamma_0 \exp \left( \frac{-\left(\Delta G_0 + \Delta g(T, \dot{\gamma}, \gamma) - V_{ap} \sigma_{eff} \right)}{k_B T} \right),$$

where $\dot{\gamma}_0$ is typically taken as the characteristic strain rate that depends on an attempt frequency and $k_B$ and $T$ are the Boltzmann constant and temperature, respectively. Note that due to the high applied stress, backward fluctuations are unlikely to occur. The Gibbs free energy $\Delta G$ required for the process to take place is equal to the difference between the total energy required (total energy barrier, $\Delta G_0$), the energy state variable $\Delta g$ and the work performed by the effective stress $\sigma_{eff}$ on a volume $V_{ap}$. The latter, defined as the apparent activation volume, is

$$V_{ap} = k_B T \left( \frac{\Delta \ln \dot{\gamma}}{\Delta \tau} \right)$$

and can be experimentally measured by strain rate jump or relaxation tests [10]. This quantity can be further related to the volume of a shear transformation zone (STZ) by $V_{ap} = \Omega_0 \gamma_0$, where $\gamma_0$ is the critical strain of a STZ, which is on the order of 0.1 and $\Omega_0$ is the size of a STZ [22]. For Vit 105 (Zr52.1Ti17.5Cu14.5Ni4.6Al10) $V_{ap}$ increases with increasing strain rate from 0.15 to 0.23 nm$^3$ at 77 K, which for a characteristic shear strain $\gamma_0 \sim 0.1$ [22] yields $\Omega_0 \sim 70 - 120$ atoms [26, 36]. The values deduced here are of the same order of magnitude and accord very well with recent theoretical models and molecular dynamic simulations, where the volume of a STZ has been identified to be in the range of 100-140 atoms [37, 38, 39]. In addition to the increase in $V_{ap}$ with increasing strain rate, we also measured an increase of $V_{ap}$ with increasing temperature from 0.15 nm$^3$ at 77K to 3.6 nm$^3$ at 195 K [36]. The variable $\Delta g$, which depends on temperature, strain and strain rate, introduces the temporal evolution of the atomic structure (dilatation and structural relaxation) within shear bands after a shear event has taken place (i.e. in the absence of effective stress).

4. CONCLUSIONS

This work summarises recent results obtained for various Zr-based bulk metallic glasses. Detailed analysis of compression curves at various strain rates and temperature reveals a low-temperature regime where deformation is spatially inhomogeneous but temporarily homogeneous, producing non-serrated flow curves and positive strain rate sensitivities. Above a critical strain rate and temperature deformation is spatially and temporarily inhomogeneous and generates a serrated flow curve. An alternative model for deformation kinetics is proposed in which a state variable $(11g)$ accounts for the structural variation in a shear band, which at sufficiently high temperatures and slow strain rates is prone to structurally relax to a more favourable configuration. Based on mechanical testing and on microstructural information deduced by SEM observations of shear planes before fracture, we suggest that deformation does not occur under adiabatic conditions, but that the heat generated is a cause of flow localisation and frictional effects.
Table 1. Values for the width of the heat-affected zone and the time duration calculated according to Eq. (1).

<table>
<thead>
<tr>
<th>Width of heat-affected zone, x [nm]</th>
<th>Time Δt [ns]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.03</td>
</tr>
<tr>
<td>100</td>
<td>3.1</td>
</tr>
<tr>
<td>200</td>
<td>12.5</td>
</tr>
<tr>
<td>1000</td>
<td>312.5</td>
</tr>
<tr>
<td>5000</td>
<td>7812.5</td>
</tr>
</tbody>
</table>

Figure 1. Stress-strain curve recorded with an initial strain rate of $1.0 \times 10^{-3} \text{ s}^{-1}$ at a data-acquisition rate 150Hz on Cu$_{39}$Zr$_{50}$. The inset shows the increase in stress drop magnitude with increasing strain.
Figure 2. Detail taken from the curve measured at room temperature (Fig. 1), showing the magnitude of stress drops, indicating the temporal resolution of stress drops ($\Delta t$) and the associated strain ($\Delta e$). Neighboring data points are 6.67 ms apart from each other.

Figure 3. Viscous flow features on a shear plane of an unfractured compression test sample of Zr$_{37.5}$Cu$_{22.5}$Fe$_9$Al$_{13}$Pd$_{0.5}$. 

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Figure 4. Stress-strain curve at varying strain rates for Zr$_{30}$Cu$_{70}$ measured at room temperature, 195K and liquid nitrogen temperature.

Figure 5. Strain rate sensitivity as a function of temperature for different mean strain rates measured for Zr$_{30}$Cu$_{70}$. 
5. REFERENCES

SHEAR BANDING AND FRACTURE BEHAVIORS OF BULK METALLIC GLASSES UNDER DYNAMIC LOADING

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Abstract: Choosing a typical tough Zr_{41.2}Ti_{12}Cu_{28}Ni_{12.5}Be_{22.5} (Vit I) bulk metallic glass (BMG) as a model material, dynamic shear and high-velocity plate impact tests were performed with split Hopkinson pressure bar (SHPB) and one-stage light gas gun, respectively. It was found that the dynamic strain rate facilitates the shear banding instability, producing more shear bands before fracture. A clear fractographic evolution from vein pattern, dimple structure and then to periodic corrugation structure, followed by crack microbranching pattern, was observed on dynamic fracture surface of this tough Vit I. Shear instability analysis is made and the dominant mechanism governing the formation of shear bands in BMGs is revealed. By taking into account the competition between the two elementary processes, namely shear transformation zone (STZ) and tension transformation zone (TTZ) underlying local softening and quasi-cleavage ahead of the crack tip, respectively, an energy dissipation mechanism of fracture in BMGs is proposed to unify the above-mentioned fracture patterns. Finally, a model based on fracture surface energy dissipation and void growth is constructed to characterize this dynamic microbranching instability.

1. INTRODUCTION

Bulk metallic glass (BMG), with characteristic sizes in excess of 1mm, is produced by cooling an alloy melt under conditions that prevent crystallization. The close to dense random packing of atoms in BMGs dictates their interesting and promising suite of mechanical properties, including extraordinary strengths (~1-3GPa), high hardness (~2-12GPa), and large elastic deflections (~2% elastic strain) [1-6]. These excellences make them candidates for potential structural applications, attracting significant interests [7-9]. However, their Achilles heel is the deformation-induced shear bands that render these materials mechanically unstable at high stress. At ambient temperature, BMGs usually suffer a strong tendency for shear localization into a few very thin shear bands with characteristic thickness of ~10nm [10-11], immediately following macroscopically brittle fracture [12-14]. Hence, shear banding and resultant fracture behaviour are the central issues for the utilization of BMGs. Substantial progress has been made in understanding these two aspects over the past decades, yet many key questions remain unclear to date. The first is the physical origin of shear banding instability [15-18]. For example, during a real process of loading a BMG, there always occurs the creation of free volume within the material due to an application of shear stresses [15]. Meanwhile, significant rising in temperature can be achieved because of very high strain rate [13]. Furthermore, the free volume concentration often varies with the temperature rising [19-20]. Therefore, the two physical processes are naturally coupled during the shear banding formation in BMGs undergoing dynamic loading. A question naturally arise: during dynamic loading process, is the shear banding still triggered by the free volume creation? The second is whether fracture of metallic glasses is essentially brittle or plastic. As macroscopically brittle materials, BMGs’ dynamic crack processes exhibit much more intricate fracture patterns; (i) microscale cell or river like vein patterns [12-13, 21-22], (ii) new-found nanoscale dimples and periodic corrugations observed very recently on regions corresponding to featureless mirror zones of silicate glasses or PMMA [23-24], and (iii) even featureless mirror zones at atomic scale [25]. This diversity in patterns indicates that the mechanisms that underpin the fracture properties of metallic glasses are of particularity as compared with crystalline alloys.

Our purpose in this article is to highlight the mechanisms of shear banding and fracture energy dissipation of BMGs based on the recent works in our group. We choose Zr_{41.2}Ti_{12}Cu_{28}Ni_{12.5}Be_{22.5} (Vit I) BMG as a model material. Experiments of split Hopkinson pressure bar (SHPB) dynamic shear, and high-velocity plate impact were conducted. As compare to the quasi-static case, we found that shear banding instability is more probable at dynamic stain rates. On the plat-impact fracture surfaces of a tough Vit I, a clear fractographic evolution from vein pattern, dimple structure and then to periodic corrugation structure, followed by microbranching pattern along the crack propagation direction, was observed. An energy dissipation mechanism taking in account the competition between the two elementary processes, namely shear transformation zone (STZ) and tension transformation zone (TTZ), underlying local softening and...
quasi-cleavage ahead of the crack tip, respectively, was proposed to unify the fracture patterns mentioned above [14].

2. EXPERIMENTAL PROCEDURE

2.1. Material preparation

Zr$_{41.3}$Ti$_{13.8}$Cu$_{19.6}$Ni$_{10.2}$Be$_{25.5}$ BMGs were produced by arc-melting elemental Zr, Ti, Cu, Ni and Be with a purity of 99.9% or better together under a Ti-gettered Ar atmosphere to obtain master ingots. To ensure homogeneity, the master alloy ingots were re-melted several times, and were subsequently suction cast into copper molds with different dimensions, i.e. 8mm in diameter and 100mm in length for the samples used for high-velocity plate impact tests, and 100mm×20mm×2mm for SHPB dynamic shear specimens. The amorphous structure of the obtained samples was confirmed by conventional X-Ray diffraction (XRD) in a Philip PW 1050 diffractometer using Co K$_\alpha$ radiation. As shown in Fig. 1, the two kinds of samples for mechanical tests show only broad diffraction maxima and no peaks of crystalline phases can be seen, revealing the glassy structure.

![XRD patterns of Vit 1 BMGs for (a) high-velocity impact; (b) SHPB dynamic shear.](image)

2.2. Dynamic mechanical tests

The specimens for shear tests were obtained by wire electrical discharge machining the as-cast amorphous plates to a special “plate-shear” shape. Dynamic shear tests were performed on a SHPB at room temperature. The detailed process can refer to references 13 and 14, and the average strain rate was fixed at 1.4×10$^5$ s$^{-1}$ by controlling impact velocity. By contrast, a quasi-static (1.5×10$^{-3}$ s$^{-1}$) plate shear was also performed using a Microtest-2000 (GATAN) instrument.

Plate impact experiments were performed on the one-stage light gas gun. The Vit.1 BMG samples used in the present study were machined into the disks with 8 mm in diameter and 0.3mm in thickness, which were sandwiched between the front and the base steel plates being of higher wave impedance than Vit.1. The launched aluminum flyer plate at the speed of 500 m/s was impacted onto the front steel plate. At the moment of impact, the generated planar compressive shock wave in the front steel plate passes through the Vit.1 samples and induces a circumferential tensile stress on the free edge of the sample. This circumferential tensile stress exceeds the tensile strength of Vit.1 and thus leads to cracks at the edge propagating along the radial direction which finally separates the sample into several small pieces.

After testing, an FEI Sirion high resolution scanning electron microscope (HRSEM) with spatial resolution of 1.5 nm was used to characterize the fracture surfaces of all specimens.

3. RESULTS AND DISCUSSION
3.1. Shear-banding behavior

The formed patterns of shear bands at two different strain rates \(1.5 \times 10^{-3} \text{s}^{-1}\) and \(1.4 \times 10^{2} \text{s}^{-1}\) are presented in Fig. 2. It can be readily seen from the figure that the number of shear bands at dynamic strain rate is greater than that at quasi-static strain rate [13]. This rate-dependency was also observed by Liu et al in their quasi-static and dynamic shear-punch tests [26]. It is also worth pointing out that numerous liquid droplets and melted belts can be clearly observed on the fracture surface at dynamic strain rates [13]. This implies that adiabatic heating may exert certain influence on the shear banding evolution in BMGs. In order to elucidate the physical origin of shear instability, we consider a bulk metallic glass under one-dimensional dynamic simple shearing, e.g., deformation can only occur in the direction of x-axis but there may have a gradient along y-axis [27]. Then, the governing equations for such a simple shear deformation involving both free volume softening and thermal softening are given by [16-17]

\[
\tau = f(\gamma, \dot{\gamma}, \theta, \xi) \tag{1}
\]

\[
\frac{\partial^2 \tau}{\partial y^2} = \rho \frac{\partial^2 \gamma}{\partial t^2} \tag{2}
\]

\[
\frac{\partial \theta}{\partial t} = k \frac{\partial^2 \theta}{\partial y^2} + \rho C_v \frac{\partial \gamma}{\partial t} \tag{3}
\]

\[
\frac{\partial \xi}{\partial t} = D \frac{\partial^2 \xi}{\partial y^2} + G(\tau, \theta, \xi) \tag{4}
\]

where Eqs. (1), (2), (3), and (4) are the constitutive equation, the momentum equation, the energy equation, and the diffusion-production equation of the free volume concentration, respectively. Noticeably, the addition of Eq. (4) to the system of equations implies the consent to the shear-induced dilatation in BMGs, for which, actually, further validation is still needed. In these equations, \(\tau\) is the shear stress, \(\gamma\) the shear strain, \(\dot{\gamma}\) the shear strain rate, \(\rho\) density, \(\theta\) the temperature, \(C_v\) the specific heat, \(k = \lambda / \rho C_v\) the thermal diffusion coefficient, \(\lambda\) the thermal conductivity, \(K \approx 0.9\) the Taylor-Quinney coefficient, \(\xi\) the free volume concentration [28], and \(D\) the diffusion coefficient of the free volume concentration. While \(G\) in equation (4) is the net generation rate function of the free volume concentration [15, 29].

Shear banding, a physically unstable event, can be regarded as the appearance of mathematical instability in the differential equations governing the inhomogeneous deformation. Thus, by performing a linear perturbation on the system of governing equations (1)-(4), we find that an easy way to shear instability is [16-17]

\[
G_{\xi} > Dk^2 \tag{5}
\]

where \(G_{\xi} = \partial G / \partial \xi\) is the free volume compound creation rate and \(Dk^2\) is the free volume diffusion rate. Obviously, the competition between these two microscopic rate-dependent processes controls the stability. If the free volume compound creation rate is faster than the diffusion rate, perturbation will grow exponentially and deformation becomes unstable, whereas for the opposite case, perturbation will die out.
and deformation remains stable. Further analysis demonstrates that the coupled shear instability is more like
the free volume-induced instability while the thermal softening also favors the onset of the instability [30].
Furthermore, through examining the dominant mode in stability, we obtain the characteristic time due to
coupled instability [16-17]:
\[ t_c \sim \frac{2R_b}{\sqrt{A_{3}P_b - Q_b + G_b^2 R_b}} \left( \sqrt{A_{3}P_b - Q_b - G_b^2 R_b} + 4A_{3}G_b F_g R_b \right) \]
According to the relative importance of the free volume softening and thermal softening, the coupled
instability growth time can be converted into the internal time due to free volume instability and the thermal
softening time, respectively [16]. Numerical analysis has showed that the shorter the characteristic time the
higher the strain rate [30]. This means that shear banding instability in BMGs is more probable at high
strain rates, which is consistent with the available experimental observations.

Since most experimental observations are post mortem patterns of shear bands, to get some theoretical
estimation on the mature shear band width and to make comparison to the observations are helpful. Based on the basic equations (1)-(4), the late-stage steady equations and band-like solutions for the
thermal softening and free volume softening can be obtained. Their respective expression of the shear band
width can be written as [17, 31-32]
\[ \delta_r \approx \frac{\sqrt{\kappa \gamma^* \delta^*}}{\gamma^*} \quad \delta_r \approx \frac{\sqrt{D \xi^*}}{G^*} \]
where * denotes tie values within the band. Again, take Zr_{41.5}Ti_{13.8}Cu_{12.6}Ni_{10}Be_{21.5} bulk metallic glass as a
model material [28]. Roughly, we take the following approximate estimations for the relevant parameters
for \( \gamma^* \sim 10^{-4} s^{-1} \) case: \( \kappa \sim 10^{-6} \) ms\(^2\), \( D \sim 10^{-6} \) ms\(^2\), \( \gamma^* \sim 10^5 \), \( \gamma^* \sim 10^5 \) s\(^{-1}\), \( \xi^* \sim 10^{-2} \), and \( G^* \sim 10^1 \) s\(^{-1}\).
Accordingly, we have \( \delta_r \sim 10 \) \( \mu m \) and \( \delta_r \sim 1 \) nm, respectively. It is noted that the theoretical estimation of
the width of shear bands for free volume softening is consistent with the available experimental
observations in BMGs, where the band width ranges from several to tens nanometers [10-11]. More
complete theoretical and numerical investigations are needed to clarify the whole process of shear band
evolution.

3.2. Dynamic fracture behavior

Examining the fracture surfaces of the loaded samples with a HRSEM, a clear nanoscale structures and
their transition process are observed as shown in Fig. 3. Figure 3b, corresponding to the rectangle mark in
Fig. 3a, displays a fractographic transition from vein pattern to dimple structure to periodic corrugation
pattern, followed by crack microbranching zone along the crack propagation direction in the dynamic
fracture. Four zones as shown in Fig. 3b from A to D, as the arrow illustrated, are divided and their enlarged
images are clearly shown in Figure 3c-f. Their characteristic length scales along the crack propagation
direction are measured and plotted in Fig. 4.

The energy dissipation underlying these fracture patterns mentioned above must be sought at the atomic
level. In BMGs, their elements, having negative enthalpies of mixing, tend to form characteristic local
atomic cluster [34]. These local atomic clusters correspond to sites of high free volume [15,35], through
which the crack would progress more easily. Consequently, we can reasonably assume that the crack tip
moves by preferentially breaking local atomic clusters in stead of atoms in crystalline solids. Usually, a
local cluster of atoms undergoes an inelastic shear distortion to dissipate energy, leading to local softening
ahead of the crack tip. This shear-dominant flow event is commonly referred to as [35-36] a “shear
transformation zone” (STZ) (see figure 5a). There is general consensus that the fundamental unit process
underlying plastic softening must be a STZ that can accommodate shear strain [6]. It is beyond argument
that vein patterns (figure 3c) and dimple structures (figure 3d) form through the continue operations of
STZs ahead of the crack tip. Parallel to this consideration, a local atomic cluster that is directly broken by a
tensile stress can be envisioned, and similarly defined as [14] a “tension transformation zone” (TTZ) (see
figure 5b). Through TTZs, stored energy is dissipated mainly by forming new surface, finally resulting in
local quasi-cleavage. The occurrence of a TTZ must satisfy the following two conditions:

1. High levels of tensile stress at the crack tip, due to the stress singularity arose from the curvature radius
   \( R \) of crack tip remarkably decreasing, approaches the ideal normal fracture stress \( \sigma_n \) of materia.
The time scale of crack propagation must be very short, and less than that of structural relaxation or plastic flow stemming from intrinsic dilatation effect [10, 37-38] in metallic glasses. Thus, the time scale of less than 100 s is expected [14], during which the visco-inelastic medium, behaving as a solid, has no enough time to fully flow [20]. STZs therefore are restrained.

It is well known that the BMG usually fractures in a shear mode, during which STZs are dominant. In the dynamic quasi-cleavage crack process, TTZs are regarded as a transient activation from STZs satisfied the above conditions. As compared with a STZ that is the elementary process of ductile crack, a TTZ can be considered as the basic of quasi-cleavage, during which tension stress concentrated in the small process zone ahead of the crack tip is fast mitigated by new surface formation. It is reasonable to believe that STZs and/or TTZs operations on nanoscale in metallic glasses should be responsible for fracture patterning including conventional vein patterns and new-found nanoscale dimples or periodic corrugations. If the curvature radius of the crack tip or fluid meniscus $R$ is larger than the critical wave length of instability $\lambda_c$, i.e. $R > \lambda_c$, the meniscus instability as a result of continue STZs ahead of the crack tip fully develops. Once $R < \lambda_c$, TTZs control the formation of fracture pattern, during which some brittle-fracture phenomena similar to those of e.g. silicate glasses emerge on the crack surfaces. It is clear that alternatively activation of TTZs and STZs ahead of the crack tip leads to the arrest and propagation of a mode I crack, which gives rise to formation of periodic corrugations (figure 4c). However, the characteristic spacing of periodic corrugation is determined by the local quasi-cleavage cracking, and can be approximately estimated by [14]:

$$L = b \left( \frac{\sigma_{th}}{\sigma_y} \right)^2$$

(11)

where $b$ is the TTZs spacing of ~10nm. Besides, we reasonably choose that $\left( \frac{\sigma_{th}}{\sigma_y} \right)^2 \approx 10$, then the calculated $L$ is (or smaller than) about 100nm. This value is in a good agreement with the actually measured values of spacing of the periodic corrugations [14, 23-24].

Figure 3. The fracture features of Vit 1’s fracture surface [33]. (a) The macro morphology of one separated piece; (b) The macro morphologies evolution in the fracture surface; (c) Vein patterns; (d) Dimples structures; (e) Periodic corrugations; (f) Microbranching (inset showing the whole feature).
Figure 4. Characteristic width ($W$) of the micro structures and the ratio of crack propagating velocity to Rayleigh wave speed ($v/V_R$) along the crack propagate process in the fracture surface [33]. Regions I, II, III and IV correspond to the vein patterns, dimple structures, periodic corrugations, and micro-branching zone, respectively.

Figure 5 Two-dimensional schematics of collective atomic motion in metallic glasses, including (a) a classical shear transformation zone (STZ) [35], and (b) an envisioned tension transformation zone (TTZ) [14].

To characterize the crack microbranching phenomenon, we consider that this dynamic crack is a single edge crack accompanied with continuous void growth process in a semi-infinite body. The crack propagation velocity can be written as [39] $v = V_a[1 - \Gamma(v)E/K_r(v)]$, where $K_r(v)$ is the dynamic stress intensity, and $\Gamma(v)$ is the fracture surface energy of the material. The dynamic stress intensity factor $K_r(v)$ can be characterized by $K_r(v) = k(v)K_r'$, where the crack velocity coefficient $k(v) = (1 - v/V_R)$ and $K_r'$ is the static stress intensity factor which is given by $K_r' = 1.12\sigma\sqrt{\pi l}$, where $l$ is the crack propagation distance from the sample edge. The fracture surface energy can be estimated by [33, 40] $\Gamma(v) = r(v)\mu/2\Omega$, where $r(v)$ is taken as the half of the characteristic width of the fracture surface patterns, $\mu$ is the free volume energy chemical potential about 10-18J, and $\Omega$ is the average atomic volume. Then we have the equation
\( \nu/V_r = 1 - [(\nu(\mu E)/(2.51\Omega^2 \pi^{1/3}))^{1/3} \). After calculating, we get the evolution of \( \nu/V_r \) along the crack propagation direction [33], which is shown in figure 4. We find that on the stages of dimple and periodic corrugation, \( \nu/V_r \) increase sharply from 0.01 to 0.52, and when \( \nu/V_r \geq 0.52 \) the nanoscale periodic corrugation pattern become unstable and microbranching, presenting the fracture dynamic instability, occurs. Examining more kinds of amorphous materials shows that there is a linear correlation between the critical crack velocity and the intrinsic strength of materials [33]. This means that this microbranching instability might be universal behavior in amorphous materials.

4. CONCLUSION

In this article, we reviewed our recent advances in understanding the shear-banding instability and the energy dissipation underpinning dynamic fracture in BMGs under dynamic loadings. A typical tough BMG, \( \text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{10}\text{Ni}_{12.5}\text{Be}_{22.5} \) (Vit 1), is chosen as the model material. Dynamic shear and high-velocity plate impact tests were conducted with SHPB and one stage light gas gun, respectively. Experimental results have demonstrated that shear banding forms easier at dynamic strain rates than at quasi-static cases. Linear perturbation analysis indicates that the shear banding instability is of free volume creation origen, even under dynamic loadings. The dynamic mode I crack plane of this tough Vit 1 can display a fractographic transition from vein pattern to dimple structure, then further to periodic corrugation pattern, followed by microbranching zone along the crack propagation direction. Energy dissipation of metallic glasses is determined by two competing element processes, viz. STZ or TTZ ahead of the crack tip. Finally, a model based on fracture surface energy dissipation and void growth in fracture surface is developed to rationalize this microbranching instability phenomenon. The results indicate that once the crack velocity reaches a critical one, the crack instability occurs and then microbranching appears.

Acknowledgments

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ON THE ELASTIC PROPERTIES OF BULK METALLIC GLASSES

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Abstract: The relationships between the elastic moduli, glass forming ability and response to deformation of bulk metallic glasses are investigated. Five bulk metallic glasses are prepared from high purity elements via suction casting. The results confirm that there exists a correlation between energy absorbed to failure during compression testing and the bulk to shear modulus ratio. This finding is developed such that it corresponds only to the elastic component of energy absorption, and that the bulk modulus dominates this. Plastic deformation appears to be favoured by a reduced shear modulus, although it shows greater dependence on structural features that are frozen in during the glass transition, and so may well be dependent on the liquid fragility.

I. INTRODUCTION

Amorphous alloys represent a novel and exciting group of materials with many favourable properties as compared to their crystalline counterparts. The high cooling rates required to produce these materials limits the maximum dimension obtainable, preventing not only their favourable properties from being exploited in many ideal applications, but also limiting the extent of feasible research activities. Over the last couple of decades, however, the critical cooling rate to completely amorphise a metallic alloy has been reduced, partly due to greater understanding of which specific alloying characteristics retard crystallisation. This has opened up a wide range of bulk metallic glasses, leading to an increase in research activities regarding this exciting class of engineering material. Much of this has concentrated on two central issues which represent the most limiting aspects for their widespread usage: increasing the limiting dimension across which an alloy is amorphous and extending the amount of plastic flow displayed by a system.

Recent work has established relationships between elastic moduli and thermal and physical properties of bulk metallic glasses (BMG) [1]. These relationships go beyond simple chance results and, instead, their basis lies within the amorphous nature of BMGs. Perhaps the most striking of these relationships is that the observed toughness during compressive loading increases with the shear divided by bulk modulus value. This is a very exciting discovery as it opens up the possibility of developing BMGs based on their elastic moduli.

It is the aim of this study to analyse this correlation between toughness and shear and bulk moduli on some bulk metallic glasses. The importance of elastic moduli to the plasticity of crystalline metals has been established; it was found that high values of the shear modulus, \( \mu \), divided by the bulk modulus, \( B \), favoured brittleness, with the converse being true for plasticity [2]. A critical value, \( (\mu/B)_{\text{crit}} \), was established for FCC, HCP and BCC structures for the transition from ductile to brittle behaviour. From this it was concluded that a strong relationship exists; metallic glasses with \( \mu/B < 0.4-0.43 \) can absorb more energy prior to failure than ones with a higher ratio [3].

The data reported in [3] has made it possible to create samples which can absorb more energy before failing. Indeed, Liu et al. [4] cited this theory as being key in their production of a superplastic metallic glass. However, this relationship does not differentiate the energy that is accommodated by elastic deformation from that absorbed in by plastic deformation. Elastic moduli are therefore clearly useful in creating a tough glass, although not necessarily a ductile one. Additionally, the importance of \( \mu \) on the melting temperature has been isolated [5]. It can therefore be seen that elastic moduli influence not only...
the properties of amorphous metals, but also their formation. Wang [6] showed that an elastic modulus, $M$, of an amorphous alloy calculated using

$$M^{-1} = \sum_{i=1}^{n} f_i M_i^{-1}$$  \hspace{1cm} (1)

where $M_i$ and $f_i$ are the corresponding elastic modulus and atomic concentration of (the implicitly crystalline) element $i$, were in good agreement with elastic moduli determined via longitudinal and transverse sound velocities.

2. EXPERIMENTAL PROCEDURE

Bulk metallic glass compositions Cu$_{40}$Zr$_{40}$Al$_{15}$, Zr$_{40}$Al$_{10}$Ni$_{10}$Cu$_{15}$, Cu$_{77}$Ti$_{13}$Zr$_{11}$Ni$_{8}$, Cu$_{60}$Zr$_{32}$Ti$_{5}$ and Pd$_{77}$Si$_{16}$Cu$_{5}$ were prepared from high purity elements (>99%) by arc melting in a purified argon atmosphere. A Ti button was employed as an oxygen "getter" due to its high solubility of oxygen, ensuring a low oxygen concentration within the chamber. Each sample was melted, allowed to solidify and then turned over and remelted several times to encourage formation of a chemically homogeneous ingot. Then, the alloy ingots were cast into a water-cooled copper mould using an in-situ suction-casting facility. The resulting cylindrical BMG rods have dimensions of 3 mm in diameter and 50 mm in length. The presence of impurities during melting is particularly undesirable when producing metallic glasses as they can create nucleation sites, which promote crystallisation. Sample purity and cleanliness were therefore maintained throughout and melting was conducted under vacuum conditions in an argon filled chamber. The glassy structure of the rod samples was analysed by X-Ray diffraction (XRD) with Co $\text{K}\alpha$, using Philips PW 1730/10.

Uniaxial compression testing was performed at room temperature on rods with an aspect ratio of 1.5:1; the samples were carefully prepared in order to ensure parallelism with the ends of the test jig. Compression testing was performed using a Hounsfield testing machine at a constant strain rate of $10^{-4}$ s$^{-1}$. Before these mechanical tests, both ends of each specimen were examined by XRD to make sure that the rod samples were fully amorphous and that no crystallisation had occurred due to unexpected factors. The compliance was then subtracted from the apparent extension, giving the actual extension experienced by the sample and an origin correction was made so as to remove initial deformation being accommodated within the test equipment.

Densities of the bulk glassy samples were measured using Archimedes' principle by measuring the weight of the samples in air ($w_1$), suspended from string ($w_2$) and suspended from string in deionised water ($w_3$). The density of the samples ($\rho_{\text{BMG}}$) was then determined using

$$\rho_{\text{BMG}} = \frac{w_1}{w_2-w_3} \times \rho_{\text{H}_2\text{O}}$$  \hspace{1cm} (2)

where $\rho_{\text{H}_2\text{O}}$ is the density of water obtained by measuring the temperature of the water and correlating this to a density from tabulated values.

Young's modulus of each sample was determined via measurement of the longitudinal sound wave velocities using a Wave Runner LT432 to measure the time-of-flight for sound waves to propagate through the material. Then, from knowing the length of the sample i.e. the distance the waves have travelled, the longitudinal wave speed, $v_l$, was calculated and hence Young's modulus was derived using

$$E = v_l^2 \rho_{\text{BMG}}$$  \hspace{1cm} (3)

3. THEORETICAL CALCULATION OF ELASTIC MODULI

Two approaches were used to calculate theoretically the elastic moduli. In the first approach

$$B = \frac{1}{3} (C_{11} + 2C_{12})$$  \hspace{1cm} (4)
\[ \mu = \frac{3C_{44}(C_{11} - C_{12})}{4C_{44} + C_{11} - C_{12}} \]  

where \( C_{ij} \) is the elastic stiffness on the \( i \)-plane in the \( j \)-direction, were used to calculate the theoretical bulk and shear moduli for the individual elements. The elastic constants were sourced from [7]. Young’s modulus was then calculated using

\[ E = \frac{9B\mu}{3B + \mu} \]

and then the elemental moduli obtained from equations (3), (4) and (5) were used in equation (1) to determine the elastic moduli for the alloy systems. As noted above, Wang [6] has shown that the weighted moduli of the (crystalline) elements can be used to calculate the moduli of BMGs.

In the second approach, the volume per atom, \( V_i \), and the BMG molar volume \( V_{BMG} \), were calculated using

\[ V_i = \frac{m_i}{\rho_i N_A} \]

\[ V_{BMG} = \frac{m_{BMG}}{\rho_{BMG} N_A} \]

where \( N_A \) is Avagadro’s number, \( \rho_i \) is the density of the element \( i \), \( m_i \) and \( m_{BMG} \) are the molar masses of element \( i \) and the BMG respectively. Upper bounds, \( M_{upper} \), for the elastic moduli were then calculated using

\[ M_{upper} = \sum_{i=1}^{n} \frac{M_i f_i V_i}{V_{BMG}} \]

and lower bounds, \( M_{lower} \), were calculated using

\[ M_{lower} = \left( \sum_{i=1}^{n} M_i V_i \right)^{-1} \]

Equations (9) and (10) are based on models of composites assuming, respectively, equal strain or equal stress on each phase in the composite [8].

4. RESULTS AND DISCUSSION

True stress versus true strain graphs for four of the samples investigated are shown in figure 1, which have been processed to account for the compliance of the test equipment. Toughness has been determined as the area under the true stress versus true strain curves and these values are given in table 1.

### Table 1: Full results for the tests shown in figure 1 (\( \sigma_{UCS} \) – ultimate compressive strength; \( \sigma_y \) – yield strength, \( \varepsilon_{elastic}, \varepsilon_{plastic}, \varepsilon_{total} \) – elastic, plastic and total strain; \( T_{elastic}, T_{plastic}, T_{total} \) – elastic, plastic and total toughness).

<table>
<thead>
<tr>
<th>BMG</th>
<th>( \sigma_{UCS} ) (GPa)</th>
<th>( \sigma_y ) (GPa)</th>
<th>( \varepsilon_{elastic} ) (%)</th>
<th>( \varepsilon_{plastic} ) (%)</th>
<th>( \varepsilon_{total} ) (%)</th>
<th>( T_{elastic} ) MJ/m²</th>
<th>( T_{plastic} ) MJ/m³</th>
<th>( T_{total} ) MJ/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₅₀Zr₄₅Al₁₅</td>
<td>1.7</td>
<td>1.5</td>
<td>3.8</td>
<td>0.9</td>
<td>4.7</td>
<td>51.0</td>
<td>10.0</td>
<td>61.0</td>
</tr>
<tr>
<td>Cu₆₀Zr₂₃Ti₁₇₅</td>
<td>2.2</td>
<td>4.2</td>
<td>4.2</td>
<td>4.2</td>
<td>8.4</td>
<td>65.0</td>
<td>0</td>
<td>65.0</td>
</tr>
<tr>
<td>Cu₇₂Ti₃₂Zr₁₁Ni₈</td>
<td>1.8</td>
<td>1.6</td>
<td>3.1</td>
<td>0.2</td>
<td>3.3</td>
<td>25.2</td>
<td>3.6</td>
<td>28.8</td>
</tr>
<tr>
<td>Pd₇₇.₅Si₁₅.₅Cu₆</td>
<td>2.1</td>
<td>1.4</td>
<td>4.1</td>
<td>10.4</td>
<td>14.5</td>
<td>58.6</td>
<td>191.2</td>
<td>249.8</td>
</tr>
<tr>
<td>Zr₆₅Al₁₀Ni₁₀Cu₁₅</td>
<td>1.6</td>
<td>1.6</td>
<td>3.0</td>
<td>0.12</td>
<td>3.12</td>
<td>23.7</td>
<td>2.0</td>
<td>25.7</td>
</tr>
</tbody>
</table>
Figure 1: True stress versus true strain graph for the BMGs studied; curves for different alloys have been displaced along the x axis for clarity.

Table 2: Experimentally determined densities, longitudinal sound velocities and Young’s moduli, along with theoretical molar masses ($m_{\text{BMG}}$) and molar volumes $V_{\text{BMG}} = m_{\text{BMG}}/\rho_{\text{BMG}}$.

<table>
<thead>
<tr>
<th>BMG</th>
<th>$\rho_{\text{BMG}}$ (kg m$^{-3}$)</th>
<th>$\nu_l$ (m s$^{-1}$)</th>
<th>$E_{\text{exp}}$ (GPa)</th>
<th>$M_{\text{BMG}}$ (kg mol$^{-1}$)</th>
<th>$V_{\text{BMG}}$ (m$^3$ mol$^{-1}$ x 10$^{-4}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{50}$Zr$</em>{45}$Al$_5$</td>
<td>7510</td>
<td>4718</td>
<td>84</td>
<td>7.42</td>
<td>9.90</td>
</tr>
<tr>
<td>Cu$<em>{60}$Zr$</em>{32.5}$Ti$_{7.5}$</td>
<td>8040</td>
<td>4743</td>
<td>90</td>
<td>7.14</td>
<td>8.88</td>
</tr>
<tr>
<td>Cu$<em>{70}$Ti$</em>{30}$Zr$_{10}$Ni$_8$</td>
<td>7007</td>
<td>4991</td>
<td>87</td>
<td>6.10</td>
<td>8.70</td>
</tr>
<tr>
<td>Pd$<em>{77.5}$Si$</em>{16.5}$Cu$_6$</td>
<td>9972</td>
<td>4455</td>
<td>100</td>
<td>9.10</td>
<td>9.18</td>
</tr>
<tr>
<td>Zr$<em>{65}$Al$</em>{15}$Ni$<em>{10}$Cu$</em>{10}$</td>
<td>7070</td>
<td>4686</td>
<td>78</td>
<td>7.74</td>
<td>10.94</td>
</tr>
</tbody>
</table>

Table 3: Upper and lower bounds for the shear and bulk moduli calculated using equations (9) and (10), respectively. $\mu_2$ and $B_2$ are the corresponding average values; $E_2$ was calculated from these values using equation (5).

<table>
<thead>
<tr>
<th>BMG</th>
<th>$V_{\text{BMG}}$ (m$^3$) x 10$^{-27}$</th>
<th>$\mu_{\text{upper}}$ (GPa)</th>
<th>$\mu_{\text{lower}}$ (GPa)</th>
<th>$\mu_2$ (GPa)</th>
<th>$B_{\text{upper}}$ (GPa)</th>
<th>$B_{\text{lower}}$ (GPa)</th>
<th>$B_2$ (GPa)</th>
<th>$E_2$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{50}$Zr$</em>{45}$Al$_5$</td>
<td>1.640</td>
<td>45.1</td>
<td>19.6</td>
<td>32.4</td>
<td>149</td>
<td>063</td>
<td>106</td>
<td>88</td>
</tr>
<tr>
<td>Cu$<em>{60}$Zr$</em>{32.5}$Ti$_{7.5}$</td>
<td>1.474</td>
<td>35.4</td>
<td>30.1</td>
<td>32.8</td>
<td>125</td>
<td>104</td>
<td>115</td>
<td>90</td>
</tr>
<tr>
<td>Cu$<em>{70}$Ti$</em>{30}$Zr$_{10}$Ni$_8$</td>
<td>1.442</td>
<td>37.3</td>
<td>33.6</td>
<td>35.5</td>
<td>129</td>
<td>117</td>
<td>123</td>
<td>97</td>
</tr>
<tr>
<td>Pd$<em>{77.5}$Si$</em>{16.5}$Cu$_6$</td>
<td>1.514</td>
<td>38.5</td>
<td>35.1</td>
<td>36.8</td>
<td>173</td>
<td>155</td>
<td>164</td>
<td>102</td>
</tr>
<tr>
<td>Zr$<em>{65}$Al$</em>{15}$Ni$<em>{10}$Cu$</em>{10}$</td>
<td>1.817</td>
<td>37.2</td>
<td>31.0</td>
<td>34.1</td>
<td>111</td>
<td>92</td>
<td>102</td>
<td>92</td>
</tr>
</tbody>
</table>
Figure 2: Energy absorbed (T) during compression testing versus μ/B for the BMGs tested.

Table 4: Shear, bulk and elastic moduli calculated using equation 1 (subscript 1) and equations 9 and 10 (subscript 2) and experimentally measured Young’s moduli for the five compositions studied.

<table>
<thead>
<tr>
<th>Composition</th>
<th>μ_1 (GPa)</th>
<th>μ_2 (GPa)</th>
<th>B_1 (GPa)</th>
<th>B_2 (GPa)</th>
<th>E_1 (GPa)</th>
<th>E_2 (GPa)</th>
<th>E_{exp} (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu_{52}Zr_{48}Al_3</td>
<td>31</td>
<td>32.4</td>
<td>111</td>
<td>106</td>
<td>85</td>
<td>88</td>
<td>84</td>
</tr>
<tr>
<td>Cu_{60}Zr_{32.5}Ti_{7.5}</td>
<td>27</td>
<td>32.8</td>
<td>119</td>
<td>115</td>
<td>88</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Cu_{67}Ti_{32}Zr_{1}Ni_{8}</td>
<td>34</td>
<td>35.5</td>
<td>126</td>
<td>123</td>
<td>95</td>
<td>97</td>
<td>87</td>
</tr>
<tr>
<td>Pd_{77.5}Si_{16.5}Cu_{6}</td>
<td>35</td>
<td>36.8</td>
<td>163</td>
<td>164</td>
<td>98</td>
<td>102</td>
<td>100</td>
</tr>
<tr>
<td>Zr_{68}Al_{10}Ni_{10}Cu_{12}</td>
<td>34</td>
<td>34.1</td>
<td>103</td>
<td>102</td>
<td>92</td>
<td>92</td>
<td>78</td>
</tr>
</tbody>
</table>

The experimentally determined densities and Young’s moduli are given in Table 2, along with theoretical molar masses of the BMGs and the molar volumes determined from the molar masses and the measured densities. The results for the upper and lower bounds of the bulk and shear moduli, calculated using equations (9) and (10), are given in Table 3 along with average values calculated from the upper and lower bounds. Table 4 then compares the elastic moduli calculated using the two different methods, as well as the experimentally measured Young’s moduli for four compositions. It can be seen that both methods of calculating theoretical elastic moduli yield similar values and that these values are similar to the measured Young’s moduli. This indicates not only that these equations can accurately predict moduli, but also that the actual compositions of the samples prepared in this study are close to those targeted. Indeed, sample composition will account for some difference between theoretical and measured value as will experimental error in determining the time-of-flight. Equation (1) has a slightly higher accuracy, indicating that it should be favoured over equations (9) and (10) for predicting moduli. An additional important benefit of using equation 1 is that it is a quicker and simpler approach that only requires knowledge of elemental moduli and composition, whereas equations (9) and (10) require densities which will not be accurately known until the glass has been produced. Hence equation (1) is not only potentially more accurate than equations (9) and (10) but is simpler and easier to use in a predictive fashion. Therefore, equation (1) is recommended for use in future studies.

Figure 2 shows the total energy absorbed and the elastic energy absorbed in order to create two surfaces for each of the five alloys tested versus μ/B. It can be seen that the results here confirm those presented in [3], where more energy is absorbed with a decreasing μ/B value. However, the trend is arguably over-emphasised by the significant amount of plastic deformation exhibited by Pd_{77.5}Si_{16.5}Cu_{6} which dominates the total energy absorbed by this alloy. Figures 1 and 2, along with table 3, show that the other 4 alloys studied here exhibit little or no plastic deformation in compression and, in fact, significant amounts of plastic deformation are not common in bulk metallic glasses, justifying the use of other techniques to improve this important property e.g. the use of composites. It should be noted, however, that ribbons of, for example, Cu_{60}Zr_{32.5}Ti_{7.5}, can display very significant bend ductility, which was confirmed in the present study, although the same ribbons exhibit only slight plasticity, on the shear plane itself, in pure.
tension. It is also notable that the degree of elastic behaviour exhibited by Pd<sub>77</sub>Si<sub>16</sub>Cu<sub>6</sub> is similar to that seen in the other alloys studied and examination of just the elastic energy component suggests that the elastic energy absorbed does indeed increase with decreasing $\mu/B$ in an approximately linear fashion.

The bulk modulus is the second differential of free energy which characterises the ability of a material to resist a volume contraction under an applied force. We suggest that the amount of energy absorbed during compression testing is more strongly dependent on the bulk modulus than on shear modulus, with a high bulk modulus resulting in the absorption of the most energy. The fact that the amount of stored energy increases with bulk modulus is to be expected; the harder it is to compress a material then the more energy will be required to do so. However, another important parameter in determining the amount of stored elastic energy is the degree of elastic strain the structure can accommodate before plastic flow is activated. The bulk modulus tells us nothing about this. Indeed, the crucial answer to this question could lie in how easy it is to activate plastic flow and the associated formation of shear bands. If the formation of shear bands is very difficult in a sample then elastic deformation may be favoured over plastic strain. If, on the other hand, plastic flow occurs more easily, then limited elastic flow may take place; the results for Pd<sub>77</sub>Si<sub>16</sub>Cu<sub>6</sub> appear to confirm this as it is the only sample that shows more plastic than elastic strain, while displaying a similarly low yield point to the other samples (see Table I), indicating that plastic flow in compression is more readily activated than in other systems.

Plastic deformation occurs via the activation of shear bands. These nucleate at shear transformation zones which are regions where the localised atomic structure is capable of some rearrangement. The extent of plasticity is therefore determined by the number of shear bands that are activated and by their ability to accommodate strain. Recent molecular dynamic simulations of shear band propagation phenomena [9] have reported that the temperature within a sample increases around the crack tip, up to temperatures above $T_g$ in the shear band, and that the shear stress increases in the vicinity of a crack tip, reducing to a minimum within the shear band due to the high temperatures. Because temperatures within the shear band are above $T_g$ viscous flow is activated and the viscosity is reduced. Shear bands therefore represent regions that have been able to overcome the activation energy for viscous flow, which is proportional to the instantaneous shear modulus multiplied by a volume. The ideas of the shoving model [10] are therefore applicable here - that shear bands are created in a metallic glass when a localised region is capable of shearing with respect to another region, under the applied driving force of stress, causing a temperature to rise within a material. This subsequently causes further heating if a shear band is nucleated and permitted to propagate. It would therefore appear that a low shear modulus would favour plasticity. Pd<sub>77</sub>Si<sub>16</sub>Cu<sub>6</sub>, which showed extensive plasticity, displays a shear modulus higher than any of the other samples tested, however. It is therefore reasonable to ask why this sample should display the most plasticity if the generation of multiple shear bands is favoured by a low shear modulus. It can be proven that multiple shear bands were activated in this system by studying figure 1. Here, it can be seen that once plastic deformation has started the sample undergoes serrated flow, corresponding to the start/stop motion of shear bands. The fact that they cannot continue to move throughout the whole sample (proved by the presence of serrations) indicates that something must retard their global migration and emergence at a free surface, favouring the activation of new shear systems. It would therefore appear that a structural parameter is important in aiding the activation of shear bands and that this dominates over the influence of the shear modulus. Shear transformation zones are regions capable of undergoing atomic rearrangement, and so it is reasonable to suggest that a less homogeneously packed disordered structure favours more shear transformation zones, due to the presence of local variations in density. This can be linked back to positron annihilation studies that proved the existence of such cavities within metallic glasses [11]. It is possible that the size of these determines the ease with which a shear transformation zone can be created.

It is useful to analyse the conditions for plastic flow and the apparent dependency of plasticity on structural features rather than elastic moduli by considering the superplastic BMG [4]. The shear and bulk modulus of this system were measured to be 29 GPa and 109 GPa respectively, from sound wave velocities, giving a $\mu/B$ value of 0.266. This shear modulus is relatively low compared to other metallic glasses and so would appear to confirm the idea that a low shear modulus is beneficial in activating shear bands. However, a low shear modulus is clearly not the only factor in deciding the extent of plasticity, and it is fair to say that it is not the dominating factor. This can be shown by the fact that the $\mu/B$ for the
superplastic BMG would not predict the extent of energy absorbed during compression testing as compared to other compositions with a lower \(\mu/B\) values (see figure 2). For example, the \(\mu/B\) value of 0.215 for the Pd\(_{73}\)Si\(_{16.5}\)Cu\(_6\) composition studied here suggests that it should absorb more energy than the superplastic composition, but it can only be strained to 14.5% compared to 160% shown by the superplastic composition. This therefore suggests that the correlation between toughness and \(\mu/B\) is not, in fact, able to predict the amount of energy absorbed plastically by a system. Also, the ability of this material to show superplastic behaviour appears to be down to two factors: that multiple shear bands could be activated and that there were regions present within the amorphous structure to prevent them from moving, leading to some work hardening, which is not usually shown by metallic glasses. This confirms that there is a strong structural element to the extent of plasticity displayed by a system and while a low shear modulus may contribute to reducing the activation energy for a shear band to be created, this factor is not dominant, as proved here by the palladium alloy sample with a high shear modulus showing large amounts of plastic flow. It is well known in glass science that the structure of a glassy material is dependent on the slowing down of relaxation kinetics on cooling through the glass transition. The fragility of a system therefore plays a crucial role in determining the final solid structure i.e. the rate of change of viscosity with decreasing temperature close to \(T_g\) will vary the atomic structure of different systems. It may therefore be the case that it is the final atomic topology that decides the extent of plastic flow that is possible in a metallic glass, and it is the solidification kinetics around \(T_g\) that determine the structure.

It has been identified here that shear modulus theoretically plays a role in determining the activation energy for plastic flow to start, and so a low shear modulus should favour plasticity. However, some structural parameter appears to dominate the ability of a metallic glass to show plastic flow. This parameter could relate to the topology of the glassy structure with many open cavities creating shear transformation zone nucleation sites. This suggestion requires further investigation. Although there is a correlation between the ratio of shear to bulk moduli and toughness during compression testing it does not offer a simple way of predicting the energy absorbed if significant plasticity is present; this is proven by its inability to predict the behaviour of the superplastic BMG. The requirements for elastic and plastic energy absorption are not the same and so cannot both be characterised by a single \(\mu/B\) ratio despite implied claims in the literature.

5. CONCLUSIONS

- The amount of energy absorbed by a bulk metallic glass increases as the ratio of shear to bulk modulus decreases. Most metallic glasses undergo essentially zero plasticity in compression, shown by the fact that only one out of five systems tested displayed appreciable plastic flow, does not offer a simple way of predicting the energy absorbed if significant plasticity is present; this is proven by the inability of it to predict the large amount of energy absorbed by a superplastic bulk metallic glass.
- We suggest that the elastic behaviour of a metallic glass during compressive loading is dominated by the bulk modulus.
- Theory would suggest that the shear modulus should determine the ease of activation of shear bands, as plasticity can be considered to be a viscous flow event, such as occurs during the glass transition. A low shear modulus does not appear to predict plastic behaviour though, and, instead, specific atomic structural features, which are frozen in during the glass transition, may account for plastic behaviour. The fragility of a sample is likely to have a strong influence over specific structural features.
- Different criteria favour elastic and plastic energy absorption. It is therefore not necessarily useful to characterise the overall deformation response of a metallic glass by a single shear modulus divided by bulk modulus value as suggested in [3]. Instead the elastic and plastic components should be considered separately, presenting the possibility of optimise one of these specifically. This represents a new direction of thought that is not currently present in the literature.
- It should be borne in mind also that as-quenched thin ribbon samples (typically ~50 \(\mu\)m thick) of the glassy alloys exhibit good ductility in bending, though these will be in a different state of quench and thus may have a slightly different short-range atomic configuration from the corresponding bulk glassy samples.
References

CERAMIC POLYCRYSTALS THAT ARE TRANSPARENT IN THE VISIBLE RANGE

G. Bernard-Granger

_Saint Gobain CREE, Cavaillon, France_

Abstract.

We firstly present low cost manufacturing process for polycrystalline ceramics, which are transparent in the visible to mid infrared ranges (cubic and non-cubic structure).

In a second time, we will focus on polycrystalline alumina (optical, mechanical and thermomechanical properties).
IDENTIFICATION AND MODELLING OF THE STRAIN RATE SENSITIVITY OF AN ORGANOCLAY NANO COMPOSITE

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Abstract. Strain rate effects on quasistatic-to-dynamic response of PMMA organoclay nanocomposite is studied in this paper. Quasistatic tensile, dynamic compression tests and dynamic flexural mechanical analysis for a wide range of strain rates until rupture were performed. Not only the rheological and the mechanical properties were identified from the stress-strain response but also the effect of the volume fraction of nanofillers. The effects of the exfoliation and the intercalation of the nano particles inside the PMMA matrix were also experimentally determined. A first approach to model the strain rate sensitivity of the mechanical properties is proposed. This modelling is developed using a micromechanical approach. Preliminary results of our simulations and comparison to the experimental results are presented and discussed.

1. INTRODUCTION

Polymers have been widely used all over the world. Moreover, various applications of polymer composites have been studied actively and this trend has led to an increase in the research on polymers. Nowadays, one of the latest challenges in polymer technology is the polymer-filled with nanoparticles. The nanocomposites offer attractive potential for diversification and application of traditional polymeric materials [1-6]. The melt-intercalation approach is considered as an attractive method for preparing polymer nanocomposites [7]. It consists of inserting the thermoplastic polymer melt into the interlayer space of the mineral layers to process ordered nanocomposites. Interestingly, these nanostructured materials can be prepared using conventional melt-processing techniques such as extrusion [8-9].

With the increasing use of nanoparticles, the synthesis, morphology and structure of nanocomposites have been well reviewed by [3], [10], [11], [12] and [13]. It has been highlighted that modulus of elasticity increases with the nanoclay weight. By contrast, the yield strength varies a little and the fracture strength decreases with the increasing clay content. Moreover, it has been observed that, as compared to bulk materials without clay, the low strain-rate tensile strengths of the nanocomposites decrease due to the existence of clay. Thus, differing conclusions on mechanical improvement of nanoclay fillers in the composites exists in the open literature.

The nanocomposites have been used in the applications subjected to dynamic loadings. But the high strain rate mechanical behaviour is very little studied. Most of the research concerns the DMA experimental tests to obtain the viscoelastic modulus. The aim of this work is to identify the strain rate sensitivity of the nanocomposite materials. Experimental tests were performed for a wide range of strain rates varying from quasistatic to dynamic loadings. Experimental tests have also been carried out for different temperatures. Experimental results have pointed out not only strain rate effect but also the effect of the nanoparticles and the process to introduce the nanoparticles in comparison with polymeric matrix. The obtained experimental results are used to validate a first micromechanically-based model to describe the yield stress evolution in function of strain rate and temperature.

2. MATERIALS

Poly(methylmethacrylate) (PMMA) based nanocomposites were synthesized by melt intercalation technique using organoclays (Cloisite 30B and Cloisite 20A) as fillers, in a mixer (Haake Rheomix 600) machine and an extruder (BUSS). The nanoparticles were dried prior at 80°C and 70°C respectively for 12 hours. The PMMA and the different clay contents were mixed at 180°C for 10 minutes with a rotating speed of 50rpm. Specimens for experimental analysis were obtained by injection molding [10]. Two
morphologies; an intercalated structure in the case of PMMA/C20 and an exfoliated structure for the PMMA/C30B were processed in order to better understand the effect of each process. And finally, the effect of filler content was studied by means of samples with filler contents varying from 1 to 5wt%.

3. EXPERIMENTAL CHARACTERIZATION

Thermomechanical tests including tensile test and dynamic mechanical analysis (DMA) were used to evaluate the Young's modulus. The tensile tests until rupture were carried out with an Instron tensile testing machine (model 4204, USA), at temperatures from 40 to 100°C and at constant strain rates from 10^{-4} to 10^{-3} s^{-1}. For tests conducted at elevated temperatures, the test samples were held at those temperatures for 40min to ensure equilibration of the samples. Not all the experimental data is presented in this paper. The yield stress in our work was defined in the traditional sense for polymers as the first stress maximum on the material. Dynamic mechanical properties were measured on a Netzsch DMA242C. Specimen dimensions were 50mm length, 10 mm width and 4 mm thickness. The temperatures were ranging from -50°C to 150°C with a heating rate of 1°C / min. The specimen were submitted to a three point bending mode at an oscillation frequency of 1Hz.

Dynamic uniaxial compression loading was applied using a Split High Pressure Bar (SHPB). The SHPB tests were carried out at room temperature. The test fixture was composed of 22 mm diameter and 3 m length steel bars. The specimen was blocked between the incident bar and the transmitter bar, as described in figure 1. The striker, also 22 mm diameter but 1m length in steel, was launched with a gun against the incident bar to generate the pressure pulse (the incident wave). Tests were performed for several samples for each strain rate condition. The thickness of the samples was 3 mm and the diameter was 16 mm according to [14].

![Figure 1. Experimental setup used in dynamic compression test](image)

4. RESULTS AND DISCUSSION

The stress-strain response, under tensile loading, of the nanocomposites reinforced with the Cloisites 30B and 20A at room temperature is presented in Figures 2a and 2b respectively. For both nanocomposites, the increase of the nanoparticle content leads to an increase in the stiffness and a decrease in the strain to failure.

![Figure 2. Stress-strain curves at 25°C and 10-4 s^{-1} for pure PMMA and PMMA organoclay nanocomposites: (a) PMMA/C30B, (b) PMMA/C20A, at different clay contents](image)
Figure 3 presents the variation of the Young's modulus as function of the clay content, for both nanocomposites. Both materials show an important increase in the Young modulus. The improvement in Young's modulus is attributed to the good dispersion of nanosize clay particles and good interfacial interaction between the clays and the PMMA matrix.

Figure 4. Flexural storage modulus versus temperature of the nanocomposites: (a) PMMA/C30B, (b) PMMA/C20A, with different clays contents.

On figure 4, results obtained for DMA show an increase in the flexural storage modulus with the clay content up to 3%, and then decreases very little, but remains higher than the pristine PMMA flexural storage modulus (see figures 4a, 4b). As the temperature increases, all the nanocomposites show a drop in storage modulus. The addition of cloisites 20A and 30B have a significant effect on the $T_g$. For both nanocomposites PMMA/C20A and PMMA/C30B, an offset glass transition temperature to higher values can be seen.
Figure 5. Stress-strain curves obtained in dynamic compression test of the nanocomposites: (a) strain rate effects on PMMA/C20A for 3 and 5% of clay contents (b) comparison between PMMA/C20A and PMMA/C30A.

On figure 5a, both materials exhibit similar behaviour in the dynamic range. The different dynamic responses of the materials show continuing rate dependence. An important point is that similar effects are observed under dynamic compression behaviour. As the filler content increases, the stiffness increases too. Moreover, as can be seen on figure 5b, the exfoliation improves the dynamic behaviour in comparison with the intercalated filled specimen. But preliminary results need additional analysis for a better understanding.

4. MODELLING

Due to the strong sensitivity of polymeric materials to the strain rate and temperature, it is obvious that good modelling needs to take into account the internal morphology and micromechanism which have been affected by this strain rate and the temperature. Thus, the yield behavior of the nanocomposite polymers identified previously is modeled using a new micromechanically based formulation of the cooperative model proposed by [15] [16]. This new modelling is based on a strain rate and temperature superposition principle. This modelling results of the cooperative model provides evidence of the secondary transition by linking the yield behavior to the energy associated to the \( \beta \) mechanical loss peak. The cooperative model, given by Equation (1), has been adapted to predict the PMMA/C30B and PMMA/C20A based nano-biocomposites yield stress dependence versus strain rate and temperature.

\[
\frac{\sigma_y}{T} = \frac{\sigma_y(0)}{T} - m \cdot T + \frac{2k}{V_{\text{eff}}} \sinh^{-1} \left( \frac{\dot{\varepsilon}}{\dot{\varepsilon}_0 \exp \left( -\frac{\Delta H_{\text{eff}}}{kT} \right)} \right)^{\frac{1}{m}} \tag{1}
\]

Where \( \sigma_y(0) \) is the athermal internal yield stress, \( m \) is a material parameter roughly equal to \( \sigma_y(0)/T_y \) in the case of amorphous polymers in agreement with [17-18].

\( V_{\text{eff}} \) and \( \Delta H_{\text{eff}} \) is the effective activation volume and energy respectively. In fact, in the open literature [18-20], it is found that the yield behavior of both amorphous and semi-crystalline polymers could not be represented by a single molecular process, but rather at least two activated processes acting in parallel. Thus \( V_{\text{eff}} \) and \( \Delta H_{\text{eff}} \) is described with two activation volumes \( (V_1 \text{ and } V_2) \) and two activation energies \( (\Delta H_1 \text{ and } \Delta H_2) \). These expressions are given by:

\[
\frac{1}{V_{\text{eff}}} = \frac{1}{V_1} + \frac{1}{V_2} \tag{2}
\]

\[
\Delta H_{\text{eff}} = \frac{V_1 \Delta H_1 + V_2 \Delta H_2}{V_1 + V_2} \tag{3}
\]

\( k \) is the Boltzmann's constant, \( \dot{\varepsilon}_0 \) is a constant pre-exponential factor.
The strain rate versus stress/temperature is depicted on Figures 4 and 5. Tensile yield stress/temperature evolution with strain rate obtained for the organoclay nanocomposite PMMA/C20A 5wt% is reported in Figure 6. It can be seen from these results that the cooperative model is in fair agreement with the yield properties of PMMA and its organoclay nanocomposites.

![Graph showing strain rate versus stress/temperature](image)

**Figure 6.** Tensile yield stress/temperature evolution with strain rate obtained for the organoclay nanocomposite PMMA/C20A 5wt%.

5. CONCLUSION

Strain rate effects of unfilled and nanofilled composite based PMMA has been studied in this paper. Experimental methods are used in order to correlate them and give good conclusions of the different results. The nanocomposite displayed a ductile-brittle transition with increasing strain rate. The loss in ductility was due to changes in the morphology. This change was observed by the evolution in the shape of the stress-strain curves. The volume fraction of the nanofillers on the quasistatic and on the dynamic mechanical properties of nanocomposite based PMMA have also been investigated. Similar effects have been observed in the quasistatic tests and in the dynamic tests. A first modelling of yield stress has also been performed and a good correlation has been obtained.

References


CARBON NANOTUBE FIBERS WITH VERY HIGH ENERGY TO FAILURE

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Abstract. We report on the fabrication, treatments and mechanical properties of wet spun composite fibers made of single wall carbon nanotubes and polyvinyl alcohol (PVA). These fibers exhibit a nanocomposite structure along with a high fraction of nanotubes. Their properties are characterized by tensile measurements and dynamical analysis. Without treatment, the fibers exhibit a very large strain-to-failure, and the energy needed to break the fibers exceeds that of any other known materials. However, untreated composite nanotube fibers absorb a very small amount of energy at low strain; which is a limitation for certain applications. We use hot-drawing treatments to improve the rigidity of the fibers. Such treatments yield structural modifications of the fibers which affect their mechanical and thermo-mechanical properties. Another way of increasing the Young’s modulus of the fibers consists in applying chemical treatments to the polymer in order to create covalent or hydrogen bonds. These nanotube/PVA fibers hold great potential for a number of applications such as bullet-proof vests, protective textiles, helmets, and so forth.

1. INTRODUCTION

Absorption of mechanical energy requires materials that combine rigidity and deformability. Both properties are not simultaneously met in classical synthetic materials. However this combination is common in biomaterials that have a hierarchical and nanocomposite structure such as bone, nacre, spider silk, etc. They are made of rigid nanoparticles (mineral or organic) at high volume fraction in a deformable matrix (proteins, collagen, chitin, etc). Because of their particular structure, biomaterials exhibit unique properties in terms of toughness and energy to failure. Carbon nanotubes (CNTs) are extremely rigid nanoparticles [1] which could be used for making novel synthetic nanocomposites that exhibit a large absorption of mechanical energy. In analogy with biomaterials, synthetic nanocomposites have to be properly organized and sufficiently loaded with nanoparticles to achieve a large energy to failure. Making such structures is still particularly challenging.

Fibers and yarns are among the most promising forms for assembling CNTs on a macroscopic scale [2-9]. They allow CNTs to be preferentially oriented along the main axis of the fibers which can then be easily manipulated and woven into textile structures or used as cables.

By using a process already described in previous publication [3], we confirmed the great potential of CNT fibers for creating high performance materials. This process indeed allows the fabrication of fibers that contain a large fraction of oriented CNTs. Their energy to failure can reach 870J/g and a large strain to failure of 430% for the best fibers investigated [10]. This energy to failure is one order of magnitude larger than that of polyaramide fibers such as Kevlar® or Twaron®.

However, for some applications such as bullet-proof vests, high strain remains a major limitation. Absorption of energy is required at small strain. Another main limitation of classical high toughness CNT fibers is their swelling due to the water soluble polymer matrix [11]. New treatments are developed in order to modify the structure of the fibers [10] and overcome these limitations. Hot drawing treatments yield improvements of crystallinity and orientation of the CNTs and of the polymer chains. Chemical treatments are performed in order to create three-dimensional cross-linked networks of the polymer and to improve the links between the CNTs and the polymer matrix. The structure and properties of the fibers are characterized by X-ray diffraction, scanning electron microscopy, mechanical tensile tests and dynamical mechanical analysis. Correlation between the structure, treatments and properties of the fibers are discussed in this article.
2. EXPERIMENTAL PART

2.1 Fiber preparation

We use Elicarb single wall carbon nanotubes from Thomas Swan (UK). CNTs (0.3 wt%) are dispersed in water using sodium dodecyl sulphate (SDS) as dispersant (1 wt%). The dispersion is homogenized by a sonication treatment. The spinning process consists of injecting the nanotube dispersion in the co-flowing stream of an aqueous solution of polyvinyl alcohol (PVA) (5wt%, MW 195K). This can be achieved by injection in a rotating bath or in a co-axial geometry. Coagulation of the nanotubes can be effectively achieved by the adsorption of PVA chains onto the nanotubes. The spinning rate is about 6m/min. A 10m long fiber collected onto a small winder is shown in Fig.1. The obtained fibers have a composite structure with large fraction of oriented CNTs bound by the polymer. The CNT fraction in as-spun fibers is about 15 wt%. Their diameter can be varied typically from 10μm to 100μm depending on the preparation conditions. PVA was chosen because it exhibits strong interactions with CNTs.

![Figure 1. 10m long nanotube fiber collected on a small winder.](image)

2.2 Characterizations

The structure of the fibers is characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The degree of alignment of the polymer chains and nanotubes is directly deduced from the Gaussian fits of the angular distribution of the scattered intensity at well defined wave vectors as described in details in ref 12 and 13. The mechanical properties of the fibers are characterized under tensile load using a Zwick Z2.5/TN1S instrument. Thermo mechanical experiments have been carried out in an oven coupled with the Zwick instrument. Dynamic mechanical analysis is done using a RSA II (rheometries system Analyser) with the following experimental conditions: slope of temperature raise of 2°C/min from -10°C to 200°C, solicitation frequency of 1Hz and strain if 2%.

3. RESULTS AND DISCUSSION

3.1 “Super tough” CNT composite fibers

![Figure 2. Stress vs strain curve of a super tough SWNT fiber.](image)
After performing several tests, we found reproducible results within a 30% margin of reproducibility. Untreated CNT fibers exhibit a strain to failure above 250% on a reproducible basis. These high levels of deformation yield very high energy to failure, up to 870 J/g for the best samples.

As shown in Figure 2, the strain-to-failure reaches 430%, which is more than 4 times the highest strain-to-failure found previously for similar nanotube fibers [9].

3.2 Structural modifications by thermal treatment

Even though untreated fibers exhibit very promising properties, they remain unsuitable for several applications. They swell in water and lose their mechanical properties. In addition, for some specific applications such as bullet-proof vest, energy absorption at low strain has to be enhanced.

To overcome these limitations, the fibers are dried and then drawn to 850% in a flow of hot air at 180°C, a temperature well above the PVA glass transition (80°C). This treatment improves the nanotube and PVA alignment and increases the PVA crystallinity. The latter has been shown to be critical for enhancing stress transfer between nanotubes and PVA in composite materials [14]. So called “hot-stretched” fibers exhibit a mechanical behaviour markedly different from that of any nanotube fibers reported previously, including thermally untreated super-tough fibers.

XRD characterizations, shown in Figure 3, confirm the strong effect of hot drawing. The characteristic data for two types of fibers are shown: a super-tough type fiber and a hot-stretched fiber. Assuming a Gaussian distribution for the chain orientation, the alignment of the PVA chains for an untreated super-tough fiber is about ±27° (±HWHM: half width at half maximum of the Gaussian distribution). As observed in previous nanotube fibers, it matches the alignment of the nanotubes [11-15]. Hot-stretched fibers exhibit a significant structural improvement. As shown in Figure 3, the alignment is significantly more pronounced. A fit with a Gaussian distribution yields an orientation of the PVA chain of ±4.3°. However, the nanotube alignment is slightly lower than that of the PVA chains. It is about ±9° for the CNT. The structural differences between untreated and hot-stretched fibers are coupled directly to distinct mechanical behaviour.

![Figure 3](image)

Figure 3. Angular scattered intensity at Q=1.4 Å⁻¹ (wave vector corresponding to the diffraction from the PVA chains). (a) For a super-tough CNT fiber. (b) For a CNT hot-stretched fiber.

3.3 Impact on mechanical properties

After thermal treatment, the Young’s modulus and tensile strength of the fibers are highly improved with respective values of 45 GPa and 1.8 GPa.

The strain versus stress curves shown in Figure 4 demonstrates that hot-stretched fibers exhibit a higher strength and, more importantly, a significantly greater energy absorption at lower strain. The fiber
exhibits a strain-to-failure of about 11% and a toughness of about 55 J/g, which is greater than the value of Kevlar® [9]. We believe that the improvements of the strength and Young's modulus are primarily due to the best alignment of the nanotubes and to the crystallinity of the PVA which enhances stress transfer between the polymer and the nanotubes [14].

![Figure 4](image1.png)

**Figure 4.** Stress vs strain curves of a super-tough CNT fiber without any treatment (black line) and for a hot-stretched fiber (red line). Inset: zoom on the data at low strain.

### 3.4 Dynamic mechanical thermal analysis

CNTs substantially alter the thermomechanical properties of the composite fibers in several ways. First, and as shown in figure 5, they act as reinforcements characterized by an increase of one order of magnitude of the storage modulus. Then, they enhance the stabilization of crystalline domains. This can contribute to the storage and locking of mechanical constraints. However, the most distinctive feature arises from the alteration of the relaxations of the polymer. Neat PVA can exhibit several thermomechanical relaxations, depending on its degree of cross-linking and humidity. The glass transition (Tg) of the material presently used is about 80°C in its dry state. The relaxation at Tg is characterized by a large decrease of the storage modulus. The main relaxation in the vicinity of Tg is not seen in the presence of CNTs. Moreover, the storage modulus is much less temperature-dependent and reflects a broadening of the glass transition.

![Figure 5](image2.png)

**Figure 5.** Storage modulus $E'$ as a function of temperature
3.5 Structural modifications by chemical treatment

Another way of increasing the energy absorption at low strain consists in improving the links between the CNTs and the polymer matrix, or in creating covalent bonds of the polymer chains. This will allow a better stress transfer during the mechanical solicitation of the fiber. This can be done by generating three dimensional cross-linked networks of the PVA. In a first approach, a cross-linking agent, glutaraldehyde is directly added to the CNTs dispersion after sonication. Then the fibers are made using the set-up described in section 2.1. The fibers were observed by scanning electron microscopy (SEM) as shown in figure 6. It can be noted that the addition of cross-linking agents improves the homogeneity of the fibers. Their cylindrical shape is more uniform and less rough.

Moreover, the coagulation during the spinning of the fiber is improved making the fiber spinning process easier and more robust. This can be explained by the increase of the viscosity of the CNTs dispersion when glutaraldehyde is added. The viscosities of the CNT dispersion and of the coagulating liquid play indeed a major role in the spinning process through the width and stabilization of the jets. The exact influences of these factors are currently under study.

Another approach is used to attempt to create covalent bonds of the PVA chains. It consists in immersing the wet raw fiber in a bath composed of glutaraldehyde and water. According to the time the fibers stay in this bath and to the concentration of cross linking agent, this chemical treatment leads to an increase of the fiber diameter and linear density, as shown in figure 7.

3.3 Impact on mechanical properties

The fibers treated by the first approach are characterized under tensile load. Young's modulus of chemically treated fibers is lightly improved but not as much as with thermomechanical treatments. The fibers may not be sufficiently cross-linked as they still swell when they are immersed in water. The absence of cross-linking can be due to the very low mobility of the polymer chains in their dry state. It is also possible that the cross-linking agent quickly diffuse from the CNT dispersion to the coagulation bath during spinning. That decreases the concentration of cross-linking agents in the final fibers: preventing thereby the formation of a 3D network during the drying of the fiber.

Fibers obtained in the second approach clearly exhibit a signature of effective cross-linking through the increase of their diameter. This is also confirmed by the absence of swelling when the fibers are immersed in water. However the mechanical properties of the fibers are not affected by such treatments.
Figure 7. Linear density vs concentration of glutaraldehyde in the cross-linking bath, as obtained in the second approach described in the text.

4. CONCLUSION

Carbon nanotube fibers are promising materials for energy absorption applications. Nevertheless their mechanical properties have still to be optimized to fulfill requirements of specific needs. It was shown that thermomechanical treatments and chemical treatments can affect the structure and properties of the fibers. Their control and exact influence are still under study. We hope that these efforts will in the future lead to materials with novel dynamical mechanical behaviour and applications in various fields such as ballistic applications to composites, smart and strong textiles and aeronautics.

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References
STUDY OF THE STRAIN RATE SENSITIVITY OF AN ULTRA FINE GRAIN COPPER

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Abstract. In order to increase the performance of material for warhead (KE and CE projectile), nano-cristalline materials are investigated. In this context, the aim of this work is to determine the strain rate sensitivity of the mechanical response of an Ultra Fine Grain (UFG) copper. This material is produced by Equal Channel Angular processing, which leads to a grain size of about 300 nm. This special feature involves a very high elastic yield stress related to a specific plastic behaviour at room temperature. Several mechanical tests (in tension and compression) are carried out at different strain rates \(10^{-3} \text{s}^{-1} < \dot{\varepsilon} < 5 \times 10^{-3} \text{s}^{-1}\) and at different temperatures. Microcristalline pure copper specimens are also tested as a reference. From this results it appears that the strain rate sensitivity (viscous behaviour) of the UFG copper is of the same order of magnitude than the microcristalline copper one. Nevertheless transmission electron microscopy shows that the deformation mode in UFG copper is controlled by the grain boundaries dislocation moving, instead of the transgranular deformation mode of the microcristalline copper.

1. INTRODUCTION

Afin d’accroître les performances des têtes militaires (projectiles cinétiques et charges formées), le CTA s’intéresse depuis quelques années au comportement mécanique des nanomatiériaux. Ils se caractérisent par leur taille de grain extrêmement faible qui leur confère des propriétés mécaniques spécifiques, en particulier une très forte résistance et pour certaines céramiques un comportement ductile [1,2]. De nombreuses hypothèses [1] ont été évoquées pour expliquer ces comportements, plus particulièrement sur le rôle des joints de grain lors d’une déformation plastique. Il existe un grand nombre de modes de préparation de ces nouveaux matériaux. Cependant, une des seules méthodes pour obtenir des échantillons massifs exempts de porosité est la méthode des déformations plastiques sévères (Super Plastic Deformation SPD). Les matériaux possèdent alors une taille de grain de quelques centaines de nanomètres et sont appelés UFG (Ultra Fine Grain).

Cet article présente les caractéristiques mécaniques d’un cuivre UFG ayant une taille de grain de 300 nm. Les échantillons sont testés en compression et en traction à des vitesses comprises entre \(10^{-3}\) et \(5 \times 10^{-3} \text{s}^{-1}\). Pour appréhender plus précisément les contraintes internes liées à la microstructure de ces matériaux, des essais de sauts de vitesses de déformation ont été effectués dans le domaine des fortes vitesses de sollicitation lors d’essais aux barres d’Hopkinson.

2. PRESENTATION DU MATERIAU

Le cuivre UFG est élaboré par la méthode des déformations plastiques sévères. Cette méthode consiste à extruder un certain nombre de fois, un barreau de métal de section carrée ou ronde au travers d’une filière coudée dans des conditions de pression isostatique. L’évolution de la microstructure lors des différents passages a été étudiée par Lowe et Valiev [3]. Dès le premier passage dans la filière, des bandes de cisaillement apparaissent ; leur microstructure se caractérise par la présence de sous grains présentant des joints de faible désorientation. Lors de la succession des passages, les bandes deviennent de plus en plus denses, et la désorientation entre les sous-grains s’accentue. Lorsque les grains deviennent équiaux, un mécanisme de recristallisation dynamique est invoqué ; cependant, un grand nombre de joints n’atteint pas l’équilibre thermodynamique. Le cuivre UFG de notre étude, a été élaboré en Russie dans le laboratoire du Professeur Valiev de "l’Ufa state Aviation Technical University". Deux lots ont été étudiés. La taille moyenne des grains du premier lot est égale à 300 nm et la morphologie des grains, visible sur la Figure
1, est équiaxe. Cependant on peut observer au niveau des joints de grain une accumulation importante de défauts [4]. Le lot 2 se caractérise par une taille de grain inférieure, égale à 100 nm. Les analyses chimiques de ces deux lots permettent de conclure que ces cuivres correspondent à la catégorie OFHC (oxygen free high conductivity) et peuvent être classés sous la désignation Cu-c (leur teneur en cuivre étant supérieure à 99.95%).

Figure 1. Microstructure d'un cuivre UFG (G = 300 nm) à l'état initial.

Figure 2. Variations de la limite d'élasticité (déterminée en traction statique, \( \dot{\varepsilon} = 10^{-3} \text{ s}^{-1} \)) en fonction de la taille de grain.

L'évolution de la limite d'élasticité du cuivre en fonction de sa taille de grain est reportée sur la Figure 2. Le passage d'une structure microcristalline à une structure submicronique (quelques centaines de nanomètres) conduit à une hausse de la limite d'élasticité de plus de 300%.

3. PROCEDURE EXPERIMENTALE

Trois types d'essais ont été menés sur ce matériau. Des essais de traction statique qui ont permis d'étudier la ductilité, des essais de compression sur une large plage de vitesse de sollicitation afin d'estimer la
composante visqueuse de la contrainte. Enfin, des essais de saut dynamique-dynamique permettent de soumettre le matériau à une brusque variation de vitesse de déformation pour évaluer les deux composantes de la résistance du matériau, à savoir la contrainte interne ou contrainte athermique liée aux obstacles à longue distance et la contrainte efficace liée aux obstacles à courte distance pouvant être vaincu par activation thermique. Ces deux composantes peuvent alors être déterminées pour un état microstructural dynamique donné. Le déchargement est obtenu grâce à l'utilisation d'un projectile étage (Figure 3) développé par Leroy [5] sur un montage de barres d'Hopkinson en compression.

Figure 3. Schéma de principe de l'essai de saut dynamique-dynamique

4. RESULTATS

4.1. Essais de traction quasistatique

Des essais de traction quasistatique ont été réalisés pour deux Cu UFG et un cuivre microcristallin. Les résultats de ces essais (courbes conventionnelles) sont présentés sur la Figure 4. Outre, l'évolution de la limite d'élasticité discutée précédemment, la variation de la taille de grain a une forte influence sur la ductilité de ce matériau. En effet, le cuivre microcristallin présente une ductilité de plus de 50% avec une plage de déformation homogène occupant la plus grande partie de la courbe. En revanche, les cuivres UFG présentent une ductilité inférieure à 20% qui se caractérisent par l'apparition du maximum de contrainte pour une déformation très proche de la limite d'élasticité et un domaine de striction important occupant la majorité du domaine plastique.
Figure 4. Courbes de traction quasistatique ($\dot{\varepsilon} = 10^3 \text{s}^{-1}$) conventionnelle (résistance – élongation), pour des cuivres 20 µm, 300 nm et 100 nm.

4.2. Essais à différentes vitesses de déformation

Des essais de compression ont été réalisés sur des cylindres de 8 mm de diamètre et de 8 mm de hauteur. Pour les fortes vitesses de sollicitation, les essais sont faits sur barres d'Hopkinson. A titre de comparaison, l'évolution de la limite d'élasticité d'un cuivre microcristallin obtenu lors des essais de traction est aussi reportée sur la Figure 5. Pour le cuivre microcristallin, l'évolution de la limite d'élasticité en fonction de la vitesse de sollicitation a été étudiée par de nombreux auteurs [6, 7, 8].

Figure 5. Variation de la limite d'écoulement à 0.2 % en fonction de la vitesse de sollicitation

La première partie de la courbe présente un palier où la contrainte d'écoulement croît très légèrement avec la vitesse de sollicitation. Dans cette partie, il est couramment admis que le mouvement des dislocations...
qui sont supposées se déplacer à l'intérieur des grains, est contrôlé par un mécanisme activé thermiquement (interaction des dislocations avec des obstacles à courtes-distances) [6]. Puis à forte vitesse de sollicitation, les phénomènes d'amortissement visqueux deviennent prépondérants et la résistance du matériau croît très fortement avec la vitesse de déformation [6]. La frontière entre ces deux domaines est difficile à établir. En effet, les matériaux ne peuvent être testés avec les mêmes moyens d'essai (machine hydraulique, barres de Hopkinson) sur toute la gamme de vitesses de déformation. De plus pour les essais dynamiques, la géométrie des éprouvettes semble avoir une influence sur la mesure de la limite d’élasticité [9]. La courbe décrivant le comportement du cuivre UFG présente une évolution similaire à celle du cuivre microcristallin. Les pentes correspondant au domaine activé thermiquement sont équivalentes. Dans le domaine des fortes vitesses de déformation, l'évolution de la limite d'élasticité du Cuivre UFG avec la vitesse de sollicitation est plus faible que celle du cuivre microcristallin. Toutefois, compte tenu du faible nombre d'essais, il est difficile de conclure. Aussi pour compléter cette étude des essais de déchargement dynamique ont été réalisés.

4.3. Déchargement dynamique

Les essais sont réalisés sur les deux types de cuivre, avec la procédure expérimentale décrite ci-dessus. Les vitesses de sollicitation imposées aux éprouvettes sont représentées sur les Figures 6a et 6b. Le saut a lieu lorsque l’éprouvette a subi entre 0,1 et 0,2 de déformation plastique. Les variations $\Delta \varepsilon$, mesurées sur les courbes 6c et 6d dépendent de la contrainte efficace induite a priori par les obstacles agissant sur les dislocations. Les oscillations ne permettent pas de quantifier précisément les sauts de contrainte, cependant l'ordre de grandeur est conservé. Ainsi, il n'est pas possible de mettre en évidence une différence de comportement de ces deux matériaux.

Figure 6. Essais de saut dynamique-dynamique

- a- cuivre microcristallin (20 µm), histoire de la vitesse de déformation
- b- cuivre nanocristallin (300nm), histoire de la vitesse de déformation
- c- cuivre microcristallin (20 µm), courbe contrainte/déformation
- d- cuivre nanocristallin (300nm), courbe contrainte/déformation
5. CONCLUSION

Le cuivre UFG obtenu par déformation sévère se caractérise lors d'une sollicitation quasistatique par une limite d'élasticité 3 fois plus élevée qu'un cuivre microcristallin et une ductilité beaucoup plus faible. En revanche, l'évolution de sa résistance en fonction de la vitesse de sollicitation est proche de celle observée pour du cuivre microcristallin. Ces deux matériaux apparaissent peu sensibles à la vitesse de déformation. Dans le cas du cuivre microcristallin, les mécanismes de déformation ont été largement étudiés et permettent de comprendre ce comportement. Dans le cas des nanomatériaux, les mécanismes de déformation ne sont pas encore clairement établis, en particulier, le rôle des joints de grain en tant qu'obstacles aux dislocations transgranulaires [10] ou deuxième phase participant pour une grande part à la déformation.

Références
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A MODEL OF ENERGY ABSORPTION USING MULTI-LAYERS FABRICS TO IMPROVE BALLISTIC IMPACT FRACTURE

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Abstract. Composite made with fiber reinforcements are mainly used in ballistic applications due to their drape ability and lightweight. High performance yarns combined inside a 3D woven fabric help to design new textile material. A model of energy absorption has been designed to cope with the different phenomenon occurring during a ballistic impact. The obtained results of the fired target highlight the expected behavior of the different plies of the 3D fabric.

1. INTRODUCTION

Some studies demonstrate that 3D composites have high ballistic impact damage resistance and low velocity impact tolerance [1][2][3]. A higher performance of 3-D structural composites compared to 2-D laminates has been also revealed [4]. Taking into account the impact studies achieved on 3D woven composites [5][6][7][8], high performance has been revealed due to their resistance to delamination [9][10]. Low velocity impact properties of 3D woven composites are important for their various applications. This type of loading can occur when tools are dropped on the surface of a composite or when the material is impacted by debris, fragments, or projectiles. In a recent study, two types of 3D woven Basalt/Aramid hybrid composites with similar fibre volume fraction and dimension have been recently tested. Post-mortem photographic analysis indicated that inter-ply hybrid failed in a layer-by-layer mode, leading to much larger energy absorption, while intra-ply composite showed a brittle mode, resulting in significantly lower energy absorption [11]. It can be also noticed that 3-D textile structural composites are much tougher between layers because many reinforcing yarns exist in the through-thickness direction.

2. DELAMINATION PROCESS IN BALLISTIC IMPACT

3D textile structures are commonly considered to enhance the through-the-thickness properties, such as inter-laminar shear and normal strength, damage tolerance and fracture toughness [12]. Particularly relevant in the structural design process is to enhance the delamination resistance. First, a brief description of the different phenomenon occurring during the fabric deformation is given.

2.1. Macroscopic deformation process of a fabric

Different deformation mechanisms have already been clustered according to the length scale over which they occur [13]. For the single layer of fabric, two types of deformation mode can be noticed; the intra ply shear as in figure 1 and the intra ply extension as shown in figure 2.

Figure 1. Intra ply shear of a single layer fabric.
For the multi layer fabric, slip between adjacent layers can be considered into two modes; the inter ply slip as described in figure 3 and the inter ply rotation as shown in figure 4.

Different kind of propagation modes I, II and III of the delamination rupture can be represented in the figure 5 [14]. The mode I corresponds to inter ply gauge, the mode II can be assumed as an inter ply slip and mode III tends to be an inter ply rotation of two layers of the fabric.

During tests impact at speeds in excess of 300 m/s, at the beginning of the penetration, a rigid behaviour of the structure is observed, causing a fracture of transverse shear fibre followed by a flexural behaviour, creating multiple delamination and breaks in tension fibres [15][16][17][18].
The ballistic performance of a flat structure increases at the same time with the speed of the bending waves and the rupture time of plies [19]. The simultaneous increase of these two parameters allows the material to absorb more energy from damage and deformation before the complete rupture of the flat structure. This implies the need to initiate and encourage very early, during the impact, the spread of delamination in the plate by a careful choice of materials. They can, for example, use a low resistance inter-laminar shear containing thick plies formed by resistant or ductile fibres. Mechanisms of delamination have been the subject of many studies in the problems of impact [20][21][22]. Most authors agree that delamination is with the fibre breaks the main mechanisms for absorbing energy and they promote the perforation resistance.

In order to improve the perforation resistance, it is necessary to increase the thickness of the target, in other words, mass per unit area of these [23][24]. Materials made of ductile fibres (aramid, polyethylene) absorb more energy by deformation and are more perforating resistant than materials reinforced with glass fibres [25][26][27]. It can be assumed that there is a joint action between the bending rigidity of plies and properties of fibres break into it, which governs the propagation of delamination and therefore energy absorption of the plate.

In addition to the components' mechanical properties, the structure and the thickness of fabrics can influence the perforation resistance of a composite plate. In the case of a plate-reinforced by aramid fabric, the speed limit increases with perforation of the thickness. It therefore appears that the bending rigidity of plies and especially the thickness of the latter are crucial to the overall ballistic performance of a plate.

The main absorption mechanisms of energy involved in such interaction have been identified. They are:

- Broken fibre transverse shear (section A),
- Broken fibres tension (section B)
- Delamination (section C)

There is a challenge between the rupture mechanisms of fibres and delamination spread, which depends both on projectile shapes, the characteristics of fracture components and bending rigidity of plies. Thus, to optimize the impact resistance, we must encourage the spread of delamination, in the sense that the plate has to absorb more energy from damage and deformation of the fibres before the complete failure of the material. Therefore it is necessary to decrease the inter-laminar shear resistance of the material and increase joint stiffness bending plies resistance to deformation or fibres rupture.
2.3. Interest of using 3D textile structure for a ballistic impact

3D orthogonal interlock fabrics utilize through-thickness (z axis) reinforcement in order to enhance the inter-laminar fracture toughness of the composite [28]. In a recent study, the inter-laminar fracture toughness of carbon/epoxy composites has been experimentally determined by the use of a Tabbed Double Cantilever Specimen for Mode I analysis [29] and an End Notch Specimen for Mode II analysis [30]. Through-thickness yarns reduced the in-plane Young’s modulus and ultimate strength. The mode I strain energy release rate of orthogonal interlock composites is more than ten times higher than that 2D laminates, whereas the Mode II strain energy release rate shows an increase of 2-3 times.

The failure mode of orthogonal interlock fabric composite has been examined [29]. The through-the-thickness yarns tend to increase the energy required to propagate an inter-laminar crack in the following ways:

- the fracture and pull-out of the z axis fibres,
- Crack branching and deviating in the vicinity of z axis fibres as well as in-plane fibres.

Taking into account all these data, the textile solution corresponding to our requirements is oriented to a thick warp interlock fabric made of high modulus polyethylene fibres.

3. EXPERIMENTAL RESULTS

Three targets have been tested with 12.7mm armour piercing ammunitions of 43g weight which correspond to a total energy of 8000J. Considering the MIL-PRF-46103-E Norm, only one bullet is fired at the middle of each target with a speed of 610m/s. None of them have failed and it can be measured a height of 25mm of the created shape-of-cone hole for one of these target. After this first impact, most of the ceramic tiles are still “glued” on the backing which may lead to a good propagation of a kinetic energy part to the textile backing.

A transverse cut of the composite material may lead to understand the delamination process occurred during the ballistic impact.

In figure 7, the first two plies of the warp interlock structure have been used to absorb the impact energy from the 12.7 mm ammunition and spread it transversely inside the 3D fabric. The last ply partially damaged by the impact plays the role of stopping the bullet. The delamination area of this ply is quite large with respect to the size of ballistic impact section.

![Figure 7. Delamination of the warp angle interlock fabric](image)

4. CONCLUSION

Focused on the ballistic impact with armour piercing ammunition, the energy absorption of a special 3D warp interlock fabric has been demonstrated. The new architecture and fibres arrangement inside the warp interlock fabric helps to increase the inter ply slip between the multiple layers. According to the technical performance, it can be noticed that the 3D woven solution is lightweight.

However, more investigations are needed to estimate the incidence phenomenon of each layer on the others. Thanks to this new knowledge, the design of a new structure will be done to integrate a chain reaction phenomenon of the delamination process which helps to improve the energy absorption during a ballistic impact.
References


ANALYTICAL AND NUMERICAL SIMULATIONS OF THE SPARK PLASMA SINTERING OF NANOMATERIALS

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Extended abstract.

The Spark Plasma Sintering (SPS) process consists in the consolidation of material powder embedded in graphite dies by means of a high electrical current. Because a high current is applied, a fast heating is generated minimizing the growth of powders. With such characteristics, these processes are promising for the sintering of advanced materials such as bulk ultrafins and nanostructured materials and has been applied to nickel, see companion paper on the mechanical properties of nickel in these proceedings. Because the SPS process involves components with variable electrical conductivities, non-homogeneous current intensities are generated implying different local heating rates. Such properties have motivated numerical simulations of the SPS process [1-3].

Numerical simulations of SPS processing of alumina and nickel have been conducted with the finite element numerical code ABAQUS (166 Valley Street, Providence RI 02909, USA). The thermal-electrical module of ABAQUS has been validated through an analytical study using Fourier series to solve the heat equation [3]. The numerical model is composed of a die, Inconel spacers, a specimen and pistons incorporating quadrilateral elements 0.5 mm in size, see Figure 1. The temperature was calculated by solving the heat equation. The loss of heat by radiation was taken in account with an emissive coefficient of 0.8 and with an exterior temperature of 26°C. The SPS cycle was simulated by imposing the experimental current and an estimate of the temperature boundary conditions. These temperature conditions were deduced from a specific set of experiments, to be reported, providing temperature data at several locations along the SPS setup.

![Figure 1. Comparison between numerical and experimental temperatures during an SPS cycle of a nickel specimen.](image)

References

MECHANICAL BEHAVIOUR OF AMORPHOUS SOFTMAGNETIC FE AND CO BASE WIRES PROCESSED BY INROLISP

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Abstract. Fe- and Co-based amorphous wires of diameters ranging from 50 to 120 \( \mu \text{m} \) were produced by rapid solidification technique using in-rotating-liquid spinning (INROLISP). The process parameters, such as the velocity of the melt jet, stable free flight length, nozzle geometry, and cooling rate, were optimised to achieve high quality wires. These were characterised by scanning electron microscopy (SEM), Vickers hardness measurements, and tensile testing. The tensile strengths and the Young's moduli are \( \sigma = 3000 \text{ MPa} \) and \( E = 150 \text{ GPa} \) for the Fe\(_71\)B\(_{20}\)Si\(_{15}\)Nb\(_2\)Cu\(_x\) wires and \( \sigma = 2630 \text{ MPa} \), \( E = 135 \text{ GPa} \) for the Co\(_{70}\)Si\(_{12}\)B\(_{15}\)Nb\(_2\) wires. The strain to fracture of both materials is about \( \varepsilon_f = 1.8 \% \) and no microscopic uniform plastic strain was observed. The fracture surface of a Co-based wire deformed in tension exhibits a vein-like pattern on the shear plane tilted about 48° towards the wire axis and some shear bands are present at the circumference of the fracture zone. Also bending tests indicate the formation of microscopic shear bands. The shear band density is related to the applied bending radius. The elastic strain energies for tension and shearing as well as the critical shear stress for the shear band formation were calculated based on the tensile tests results and fracture surface analysis in correlation with the glass transition temperature \( T_G \).

1. INTRODUCTION

Rapidly solidified materials exhibit extraordinary physical and mechanical properties which may differ considerably from the values in the usual as-cast condition. Origin of these modified properties is the change in the microstructure. Depending on the alloy composition and cooling rate the material will exhibit an amorphous or nanocrystalline state. The processing of amorphous wires of FeSiB and CoSiB alloys are potentially rewarding because of their soft magnetic properties which are the basis for the construction of very sensitive and straightforward magnetic field sensors based on the Procopiu effect [1]. The magnetic properties of the sensor core are determined by the alloy composition, the microstructure, and the wire diameter. The microstructural features strongly relate to the process parameters of the in-rotating-liquid-spinning technique (INROLISP) which provides cooling rates up to \( 10^5 \text{ K/s} \). A computer controlled casting facility was designed for continuous casting of thin metallic wires of 50 to 120 \( \mu \text{m} \) in diameter. Besides the unique softmagnetic properties, these wires require high mechanical strength for its use in magnetic devices as a sensor core due to induced magnetic fields. Another potential application of the high strength wires is the reinforcement of plastics.

In the present investigations as-cast wires of the compositions (at\%) Fe\(_{71}\)B\(_{20}\)Si\(_{15}\)Nb\(_2\)Cu\(_x\) and Co\(_{70}\)Si\(_{12}\)B\(_{15}\)Nb\(_2\) were tested in uniaxial tensile tests and the fracture surfaces were examined in the scanning electron microscope (SEM). The results of the tensile tests and microindentations are presented and compared with data from literature. Bending tests in a scanning electron microscope were performed in order to observe the initiation and growth of localized shear bands.

2. EXPERIMENTAL PROCEDURE

The In-Rotating-Liquid-Spinning process (INROLISP) enables the processing of thin wires in a single step by injecting a molten metal jet into a rotating liquid coolant of laminar flow behaviour. The melt jet solidifies rapidly which causes grain refinement. The alloy was molten in a glass crucible by an induction coil and ejected from a nozzle at the base of the crucible by applying an argon pressure as shown in figure 1a. The horizontal arrangement of the drum provides a smooth surface of the cooling liquid and an easy process handling.

The physical parameters of the melt, such as density \( \rho \), surface tension \( \sigma \), and viscosity \( \eta \), as well as the injection pressure influence the jet velocity \( v_j \). These parameters together with the nozzle diameter affect the stability of the melt jet as calculated by Liebermann et.al [2]. To avoid jet disintegrations, such as dropping or atomisation in small droplets, the jet should exhibit a laminar flow dynamic yielding to a varicose breakup. Hence, the distance between the nozzle tip and coolant surface should be kept in the range of the stable jet.
An optimum and reproducible wire quality requires physical properties of the melt and casting parameters to be well balanced. The influences of the process parameters on the quality and the stability of the jet have been determined in detail for different alloys in preceding publications [3].

A high speed camera was used to display the casting process quantitatively. The injection angle and the cooling section, as well as the cavitations and perturbations of the metal jet in the coolant were examined and presented in figure 2. The ratio of the tangential melt jet velocity and coolant velocity $v_t/v_c$ will affect the roundness, surface appearance, and continuous length of the processed wires. A high ratio results in wavy wires whereas a low one shortens their length. A velocity ratio in the range of $0.75 \leq v_t/v_c \leq 0.95$ results in an optimum performance, thus, the tangential velocity component of the coolant moves slightly faster than the melt jet.

The substantial aspect of rapid solidification is the fast heat transfer through the metal – substrate interface. This is strongly influenced by the surface to volume ratio and the heat transfer coefficient of the surrounding coolant.

The jet enters into the coolant with an approximate temperature of 1300°C, which leads to a formation of a steam layer around the jet due to the Leidenfrost-effect, which inhibits the direct contact with the coolant. The heat flow balance of a FeSiB base thin melt jet of 100 μm in diameter and the injecting temperature of 1250 °C with an estimated heat transfer coefficient of about $\alpha = 10^4$ W/m²K for the nucleate boiling of water [4] yields to a cooling rate of $\dot{T} = 6 \times 10^6$ K/s.

In order to achieve a good castability, the viscosity and the surface tension of the melt should be quite low; hence the ejection through the very small nozzle diameter is possible. The selected alloys in this study are based on the (Fe, Co)-Si-B-system with additional transition metals, such as Nb and Cu. The optimum
contents of silicon and boron provide a high glass forming ability and a sufficient surface tension for stabilizing the free flying jet after leaving the nozzle [5].

The amorphous state has been investigated by optical microscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD) as well as differential scanning calorimetry (DSC) measurements. Uniaxial tensile tests were performed using the as cast wires of 80 to 100 μm in diameters and 70 mm in gauge length. The tests were carried out at different strain rates ranging from $10^{-2}$ to $10^{-5}$ s$^{-1}$. The tensile strength $\sigma_t$ were determined in uniaxial tensile tests, and the Young’s modulus $E$ were derived from the slope of the recorded stress-strain curves. Vickers’ hardness was measured with a load of 300 g. The characteristics of the fractured fragments and the bended samples were studied by using SEM.

3. RESULTS AND DISCUSSION

Upon heating the Fe$_{71}$B$_{15}$Si$_{10}$Nb$_3$Cu$_1$ wire reveals a glass transition, followed by a small supercooled liquid region and a crystallization in three steps as shown in figure 3. A transition temperature of $T_G \approx 545°C$, and the crystallization temperatures of $T_{x1} = 554°C$, $T_{x2} = 627°C$, $T_{x3} = 701°C$ and the liquidus temperature of $T_L = 1172°C$ were determined. The supercooled liquid region $\Delta T_{x} = T_x - T_G$ of 9°C and the coefficient of the glass forming ability $\gamma = T_G/(T_0+T_L)$ of 0.323 are quite low and predict a moderate glass forming ability of this material.

The DSC plot of the Co$_{70.3}$Si$_{12.5}$B$_{15}$Nb$_{2.2}$ wire exhibits a two-step crystallization of $T_{x1} = 581°C$, $T_{x2} = 685°C$ and reveals a liquidus temperature of $T_L = 1081°C$. A glass transition peak was not observed, which indicates no supercooled region possessing low viscosity.

![Figure 3. DSC plot shows the heat flow vs. temperature of continuously cast and rapidly solidified thin Fe$_{71}$B$_{15}$Si$_{10}$Nb$_3$Cu$_1$ and Co$_{70.3}$Si$_{12.5}$B$_{15}$Nb$_{2.2}$ wires determined at a heating rate of $\dot{R} \sim 20$ K/min](image-url)
The stress-strain curves of the wires tested in tension are shown in figure 4. The Fe-based wires exhibit tensile stresses of $2678 \text{ MPa} < \sigma_t < 3062 \text{ MPa}$ and fracture strains of $1.78 \% < \varepsilon_f < 1.93 \%$. The Young’s modulus was extracted from the slope of the stress-strain curves to $E \approx 150 \text{ GPa}$.

The Co-based wires exhibit fracture stresses of $2079 \text{ MPa} < \sigma_t < 2449 \text{ MPa}$ and fracture strains ranging from $1.51 \% < \varepsilon_f < 1.84 \%$. A Young’s modulus of $E \approx 135 \text{ GPa}$ was determined from the linear elastic region.

![Stress-strain curves](image)

**Figure 4.** a) Stress-strain curves of Co- and Fe-based amorphous alloys tested at strain rates ranging from $10^{-2}$ to $10^{-5} \text{ s}^{-1}$, b) The fracture section of the Co-based thin wire, showing a vein pattern on the fracture surface was tested with $\varepsilon = 10^{-4} \text{ s}^{-1}$.

Vickers’ microhardness of 932 HV$_{0.3}$ for the Fe-based alloy and an average hardness value of 884 HV$_{0.3}$ for the Co-based wires were recorded.

Table 1 summarises the constitutional and mechanical data and compares them to data of similar alloy compositions reported in the literature.

Inoue et al. [8] tested bulk metallic glass samples in compression and supposed that cracks in the material are initiated simultaneously because of the high stress level. The shock wave caused by the initiation of one crack induces the generation of additional cracks at different sites. Audoly and Neukirch [9] described a similar behaviour occurring in bending tests with “spaghetti”, which leads to a fracture in more than two pieces and a similar fracture surface observed on the Fe-based wire, as shown in figure 5a. The first fracture occurs when the critical stress exceeds the theoretical cohesive strength, then a flexural wave travels along the fragments, increases the local stress and new fracture segments occur. In the bending test the Fe-based alloy reveal a brittle fracture with a typical vein like pattern on the fracture surface section in the initial stage of the fracture.

**Table 1.** Thermoanalytical data and mechanical properties of the investigated iron- and cobalt-based alloys in comparison with some similar selected compositions from the literature

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$T_G$ (°C)</th>
<th>$T_x$ (°C)</th>
<th>$\sigma_t$ (MPa)</th>
<th>$\varepsilon_t$ (%)</th>
<th>$E$ (GPa)</th>
<th>HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{71}$B$</em>{28}$Si$_{10}$Nb$_3$Cu$_1$</td>
<td>545</td>
<td>554</td>
<td>3062</td>
<td>1.93</td>
<td>150</td>
<td>932</td>
</tr>
<tr>
<td>Fe$<em>{56}$Co$</em>{7.2}$Ni$<em>{7.2}$B$</em>{15}$Si$_{11}$Nb$_3$</td>
<td>560</td>
<td>589</td>
<td>1272</td>
<td>0.6</td>
<td>184</td>
<td></td>
</tr>
<tr>
<td>Fe$<em>{57}$Co$</em>{3}$Nb$<em>{5.2}$B$</em>{18}$Si$_{14}$Nb$_3$ [6]</td>
<td>527</td>
<td>582</td>
<td>4160</td>
<td>0.4</td>
<td>210</td>
<td>1210</td>
</tr>
<tr>
<td>(Fe$<em>{50.3}$B$</em>{30.1}$Si$_{19.8}$)$_2$Nb$_4$ [7]</td>
<td>652</td>
<td>607</td>
<td>3400</td>
<td>2.2</td>
<td>180</td>
<td>1070</td>
</tr>
<tr>
<td>Co$<em>{68}$Si$</em>{12}$B$<em>{20}$Nb$</em>{12}$</td>
<td>none</td>
<td>581</td>
<td>2449</td>
<td>1.84</td>
<td>135</td>
<td>884</td>
</tr>
<tr>
<td>Co$<em>{42.5}$Fe$</em>{20}$Ta$<em>{5.5}$B$</em>{31.5}$ [6]</td>
<td>637</td>
<td>709</td>
<td>5185</td>
<td>0.03</td>
<td>268</td>
<td>1455</td>
</tr>
</tbody>
</table>

Glass transition temperature $T_G$ (°C), crystallisation temperature $T_x$ (°C), tensile stress $\sigma_t$ (MPa), strain $\varepsilon_t$ (%), Young’s modulus $E$ (GPa) and Vickers hardness HV$_{0.3}$
Figure 5. SEM images recording a) a Fe-based wire after bending test, exhibits a brittle fracture surface. b) The plastically deformed Co-based wire (90° bend angle) with localized and accumulated shear bands show the vein like pattern.

On the contrary, the Co-based alloy reveals plastic deformation due to severe shear band formation during bending up to 90°. The shear planes, exhibits the typical vein-like pattern, as shown in figure 5b. Figure 6 exhibits SEM images of an additional bending experiment, conditioned by the bending radius reveal the generation of the shear planes as well as its growth with increasing bending diameter until fracture at bending radius of 1.25 mm occurs.

Figure 6. SEM images of bended Co-based wire samples of 80 µm in diameter. The bending radii were 2.5 mm, 1.75 mm, 1.4 mm, and 1.25 mm from the left to the right.

The strength values result in a specific elastic energy $w_{el}$ of 30 MJm$^{-3}$ by taking the Poisson's number $v$ of 0.36 into account. The Poisson's number was extracted from the literature [10]. A shear modulus $G$ of 55.15 GPa for Fe$_{71}$B$_{15}$Si$_{10}$Nb$_{3}$Cu and of 49.6 GPa for Co$_{70.3}$Si$_{12.3}$B$_{15}$Nb$_{2.2}$ was calculated. A shear strain of $\gamma = 0.0216$ was determined from the fracture surface of the Co-based wire according to the length of the sheared elliptic surface, shown in figure 4b. This results in a critical shear stress $\tau_{band}$ for the formation of shear bands of 1071 MPa and an elastic deformation energy for generating the shear bands of 11,5 MJm$^{-3}$ was determined. According to the Tresca criterion the maximal shear stress is $\tau_{max} = 1500$ MPa which is somewhat higher than the shear stress for shear band formation $\tau_{band}$. The ratio $G / \tau_{band}$ is 46.3 and the $G / \tau_{max}$ is 33 are in good agreement with the theoretical shear strength of defect free metallic whiskers of f.c.c metals [11] and of metallic glasses [12]. The ratio $E/\sigma_t$ attains values of 50 and 55.5 respectively for Fe and Co-based wires. A number of amorphous alloys reported [13] show a $E/\sigma_t$ ratio about 50 and the present investigation follow the same trend.

These two tested materials indicate that the fracture of metallic glasses occur either in a maximum shear mode or in a maximum stress mode, depending on the constituent elements and the defect structure, such as accumulated free volumes or localized alloying atom clusters, which may differ from one region to the other due to the cooling condition in the casting process.

4. CONCLUSION
Rapidly solidified thin wires produced by the INROLISP process experience a cooling rate of about $10^5$ K/s resulting in a nonequilibrium solidification. The produced amorphous wires of the composition:
Fe$_7$B$_{15}$Si$_{10}$Nb$_3$Cu$_6$ and Co$_{70.3}$Si$_{12.5}$B$_{13}$Nb$_{2.2}$ exhibit high strength at room temperature, but no macroscopic plasticity was observed in the recorded stress-strain curves. In bending tests a plastic deformation was observed for the Co-based alloy whereas the Fe-based material exhibits a fracture caused by the high normal stress. SEM investigations reveal shear bands in the Co$_{70.3}$Si$_{12.5}$B$_{13}$Nb$_{2.2}$ wire.

References

MECHANICAL BEHAVIOR OF BULK METALLIC GLASS ZR_{57}CU_{20}AL_{10}Ni_{8}Ti_{5} UNDER QUASISTATIC AND DYNAMIC LOADING.

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Extended abstract.

Metallic glasses (MG) alloys are macroscopically homogenous but featured by local atomic (or as suggested recently, atomic cluster) complex disordered structure. Due to the metallic character of atomic bonds, MG have elastic modulus similar to those of main metals and metallic alloys. However, absence of structural ordering leads to plastic deformation by atomic displacement localized in thin shear bands. For a Zr based BMG the low Young modulus (80 GPa), the viscous flow induced by the stress relaxation which leads to high strength (1.7 GPa) and strong localization of the deformation result in large elastic deformation (2%) and absence of macroscopic ductility.

MGs are intensively studied for their mechanical behavior. Among applications, MG-W composites are potential candidate for armor-piercing projectiles in replacement for depleted uranium. Under dynamic loading conditions, MG exhibit localized shear band deformation mechanism. Filled with W, the materials should be appropriate with a good balance between mechanical behavior under dynamic loading and volume weight, compared to regular W compounds whose thermo-mechanical behavior is inappropriate. It is clear now that the mechanical behavior of MG in quasistatic and dynamic loading is controlled by shear bands initiation, propagation, and interactions. Now, improvement and changing in properties of MG need to understand the shear band initiation and propagation.

In this poster, preliminary results are reported on the mechanical behavior of a bulk metallic glass (BMG) in quasistatic and dynamic loading conditions in compression tests. Zr_{57}Cu_{20}Al_{10}Ni_{8}Ti_{5} BMG cylinders with 40 mm length and 8 mm diameter and bars with 30x20x5 mm³ are prepared by r.f. induction levitation melting and casting in water chilled copper mold. Sample with square shape section were cut from the bars with dimensions 4x4.1x6.6 mm³ and 1x1.2x2.2 mm³ for investigations in quasistatic conditions. The large specimens exhibit a usual pure elastic deformation before fracture with 2% deformation at strength of 1.7 GPa. Small specimens exhibit some ductility up to 3% and scattering in strength value over 14 different tests. A statistical Weibull analysis of strength gives a Weibull modulus of 18.1, consistent with fragile materials. Application of the Weibull law emphasizes that the statistical analysis is not relevant when specimen size increases with discrepancy on the estimation of strength at various probability. Nevertheless, the results would mean that the size effect on strength and ductility is most likely related to macro-defects in the BMG produced during the casting process. For all specimens fracture at about 45° is observed consistent with a Mohr-Coulomb plasticity criterion.
Cylinder with height 3.3 mm and diameter 6 mm were used for dynamic loading. The same specimen was initially tested in quasistatic conditions where, consistently, strength of 1.7 GPa was obtained. Ductility up to 45% was observed related to the ratio of the height by the length lower than 1, for which shear bands at 45°, are not able to cross the all section of the specimen. Dynamic compression was carried out at room temperature at at a strain rate of 9000 s⁻¹, using a Hopkinson bar device. In contrast to main literature data, high strength of about 3.5 GPa was measured with 5% ductility before failure. These results need to be confirmed by further investigations.

Deformation curves in quasistatic and dynamic loading conditions and the sample after dynamic deformation at 9000 s⁻¹.
MECHANICAL BEHAVIOUR OF VITRELOY 6 METALLIC GLASS UNDER QUASISTATIC AND DYNAMIC LOADING AT ROOM TEMPERATURE

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Abstract. Effects of quasistatic and dynamic loading on deformation modes were investigated directly observing fracture appearance for the Zr57Cu15.4Ni12.6Al10Nb5 bulk metallic glass (Vitrela) at room temperature. On the fracture surface two vein-like patterns are observed, and solidified droplets. Deformation and fracture are associated with viscous flow; the vein shapes and directions depend on disturbances in fluidized layers, especially in case of strong variations of viscosity.

1. INTRODUCTION

Metallic glasses are by definition non crystalline amorphous and disordered metallic alloys the atomic lattice of which does not present a long range periodicity.

The first amorphous materials used were glass oxides 6000 years ago, but it is only in 1960 that Klement et al. [1] synthesized the first metallic glass by rapid quenching. The elaboration of this kind of materials needs high cooling rates to avoid crystallization phenomenon and until the 90s only ribbons up to ten micrometers thick were synthesized. They are still merely used but new alloy compositions are produced in the bulk form with relatively low cooling rates. Studies carried out on the mechanical properties of bulk glasses in the last years have confirmed that they possess high strength associated with spectacular deformation capacity. Nevertheless, the mechanisms of deformation and fracture are not understood yet, as well as the mechanisms of warm deformation, beyond their glass transition temperature [2].

Because of their superior bulk mechanical properties, metallic glasses are in many cases the most promising candidates in a large range of applications such as sport equipments (golf clubs, ski and tennis rackets), electronics and tools. They could be useful in the fields of medical instruments, aerospace and military industries where the ability of armor piercing have been already tested [3].

Recently new metallic glasses with promising mechanical properties (high strength, high elastic strain limit in tensile loading, good fatigue resistance, etc.) have been developed [4]. Among the new compositions, the Zr-Cu-Ni based system called Vitreloy [4] is one of the best discovered until now. This is the first one providing glasses with a sufficient low cooling rate thus increasing the production. We have studied the Vitreloy 6 (Vit 6) and compared the effect of quasistatic and dynamic loading on the fracture mode at room temperature.

2. METALLIC GLASSES

2.1. Glass and crystal

Metallic glasses are non crystalline amorphous and disordered metallic alloys in which the atomic lattice does not present a long range periodicity. Moreover the elaboration is based on a hyperquenching to suppress nucleation and growth of crystalline phases.

According to the diagram showing specific volume (or enthalpy) vs. temperature, if a liquid is cooled below a specific temperature T1, the steady state corresponds to the crystalline phase [3] (figure 1). But if the cooling rate is fast enough during the elaboration, the nucleus crystallization is not possible and the liquid crystal transition does not happen. This metastable state is called undermelting liquid. Below the glass transition temperature Tg, the system leaves the metastable state. This temperature depends on the cooling rate.
2.2 Mechanical behaviour

Metallic glasses possess unusual mechanical properties compared to other materials. They show higher yield stress and strength (800 to 4000MPa), hardness and Young's modulus (40 to 180MPa) than their polycrystalline counterparts. They also display good toughness compared to ceramics and plastic deformation ability [2].

2.2.1. Deformation modes

The glass transition temperature is not only a thermodynamical parameter but also strongly influences the strain mechanisms and strain rate of metallic glasses. The deformation modes can be divided into 3 groups [6-9]:
- at room temperature and high strain rate:
  In glasses, deformation and fracture occur from shear bands which are characteristics of a localized plasticity. Their macroscopic behaviour is fragile while plasticity occurrence usually appears on the fracture surface. As long as the fraction of crystalline phases is weak, these observations are not modified. But for higher amounts of crystals, the materials tend to be more fragile.
- at moderate temperature (T< Tg) and intermediate strain rates:
  Glasses present a high ductility with a non constant viscous flow (non-Newtonian flow mode).
- at high temperature (T>0.8Tg) and low strain rates:
  The viscous flow becomes Newtonian and the yield stress reaches a steady state over the elasticity limit. No shear bands are formed and the whole specimen contributes to the deformation.

The first mode (shear localization) is an inhomogeneous flow mode, while the other two (non Newtonian and Newtoninan) are usually considered as homogeneous flow modes.

2.2.2. Fracture

Heterogenous deformation

The differences in mechanical properties between crystalline materials and metallic glasses are a direct consequence of deformation and fracture mechanisms.

The the plastic deformation of glasses tends to be localized in the shear bands and leads to a macroscopic fracture. The fracture surface exhibits a “vein like” pattern usually considered as a localized plasticity phenomenon. These vein patterns are different according to the test type, tensile or compressive (figure 2). However some kinds of glasses (especially Mg based) are overall and locally fragile: no veins are visible and the fracture leads to a bursting of the specimen to pieces.
The type of loading, compression or tensile, influences the fracture, as suggested by fracture appearance and angle between test direction and fracture surface. Usually the fracture angle is smaller after compression test than after tensile test [12, 13].

Homogeneous deformation

In homogeneous deformation 2 regimes exist:

- stationary regime:
  When the strain rate is sufficiently low, viscosity is independent from the strain rate (Newtonian regime); when the strain rate is higher, viscosity decreases with it (non Newtonian regime) [14-16].
  During heat treatment, the Newtonian viscosity of the glass decreases progressively. When temperature is sufficiently high, a transition towards a homogeneous mechanism type occurs: the deformation is no more localized in the shear bands, but within the whole specimen, allowing large deformation. The stationary regime is reached when the viscosity regime depends on the deformation. Thus, viscosity depends only on strain rate and temperature, provided that the material does not suffer any structural changes.

- transitional regime:
  Bulk metallic glasses can be characterized by an overshoot during compression tests at constant strain rate, before decrease, to a steady state corresponding to a stationary regime. These overshoots are favoured by a decrease in the temperature or by an increase in the strain rate (figure 3). Moreover the overshoot intensity can be affected by the thermo-mechanical history of the material [17]. For instance a previous deformation with an inferior strain rate tends to decrease the overshoot.
3. EXPERIMENTAL PROCEDURE

Vitreloy 6 composition is Zr57Cu15.4Ni12.6Al10Nb5. Dynamic compression tests at strain-rates ranging from $9 \times 10^2$ s$^{-1}$ to $3 \times 10^3$ s$^{-1}$ were carried out at ambient temperature using a split-Hopkinson-pressure-bar (SHPB) [19 - 21]. Specimens (3 mm in diameter and 3 mm long) were cut from the Vit 6 rods using an electro-discharge machine. The specimens were lubricated with ball bearing grease prior to testing. For comparison quasistatic compression tests were performed on universal testing machine at a strain-rate of about $5 \times 10^3$ s$^{-1}$. The fracture surface appearance was observed with a scanning electron microscope (SEM) ZEISS DSM 982 GEMINI.

4. RESULTS AND DISCUSSION

4.1. Mechanical behaviour

Figure 4 displays the evolution of true stress vs. true strain for different strain rates. From the quasistatic compression test, Vit 6 is characterized by a yield stress around 1760MPa, a stress strength of 1854MPa and a Young's modulus close to 65MPa. The yield stress is in accordance with the data found in the literature for Vitreloys. For instance, for Vit 1, which is the most studied Vitreloy system glass, the value of yield stress is around 1900MPa [13, 22, 23]. In our study, no particular evolution of the mechanical properties vs. strain rate can be observed. More tests at intermediate rates (from $5 \times 10^3$ to $10^4$ s$^{-1}$) seem necessary in order to draw a conclusion regarding the influence of strain rate.

Figure 4. True stress-strain curves for quasistatic and dynamic compression tests with Vit 6 (room temperature, strain rate from $5 \times 10^3$ to $3 \times 10^3$ s$^{-1}$).
4.2. Microstructure

4.2.1. Quasistatic test

The quasistatic test carried out at room temperature on the Vit 6 has shown a fragile microscopic behavior (figure 5a). The fracture takes place in the immediate vicinity of the deformation zone. The SEM images highlight that the fracture occurs in shear mode by deformation and propagation of a main shear band. The fracture surface appears as relatively smooth and flat. The average fracture angle lies between 41 and 42°, which is the same range as those observed usually in the literature for metallic glasses [12]. This angle is lightly smaller than 45°, which indicates that deformation and fracture formed along the maximal shear stress but also that they do not follow Von Mises criterion.

At microscopic level, 2 veins types are observed (figures 5c-d) on the nearly totality of specimen fracture, which characterize a ductile behavior. The first vein type displays a uniform direction corresponding to the shear band propagation; this also reveals uniform arrangement characterizing a fracture with a pure shear mode along the direction indicated by the red arrow (figure 5c).

Figure 5. SEM images of the fracture surface after quasistatic loading showing the 2 types of vein patterns and solidified droplets.
The second type of veins (figures 5d, 5f) is most commonly observed during tensile tests. Zhang et al. [12] propose a mechanism based on the radial vein formation from nucleus. Thus, the fracture surface of specimens after tensile test shows usually 2 zones: a smooth one, corresponding to the initial deformation band, and a veined one resulting in a sharp viscosity drop. In the second vein pattern type, the fracture does not come from a pure shear mode, while when the first vein type predominates, the fracture is mainly controlled by the shear stress. Solidified droplets (figure 5b) are also observed on the fracture surface and are related, as well as the veins, to localized meltings:

- during the final fracture, which demonstrates a strong increase in temperature.
- through adiabatic warming in the shear bands during plastic deformation.

**Figure 6.** SEM images of fracture surface after dynamic loading showing the 2 types of vein networks and solidified droplets.

During the deformation, this warming is mainly at the origin of a fine fluid layer with low viscosity in the shear area [41]. The stress applied to the material can be divided into 2 parts:

- A shear stress within the flow plane which is responsible for the sliding between the two halves.
- A stress normal to the flow plane which favors the separation of the two halves. This stress could be considered as the rupture stress of the liquid layer. Thus the vein network shape and direction depend on disturbances (free volume, viscosity variation) appearing in the layer before the specimen fails.

4.2.2. Dynamic tests

From the dynamic compression tests carried out on Vit 6 at room temperature, the fracture did not occur along a particular angle, which indicates that fracture and deformation have not developed along a particular shear stress plane (figure 6a). For all strain rates studied, the fracture surface shows vein patterns indicating a significant viscosity drop. As previously observed in quasistatic conditions, 2 types of patterns appeared, but in this case the second type predominates with random vein orientation (figure 6c). Solidified particles ten micrometers large are observed on the fracture appearance; they could come from the fluid layer and microscale areas with viscous flow characteristics (figure 6d-f). From these observations we suppose that under dynamic conditions:
- at the level of fracture surface appearance, the fluid layer is distinctly thicker. Solidified particles (around 30μm in diameter) could possibly overflow.
- the random orientation of the veins suggests that the flow was inhomogeneous because of important variations of viscosity during the tests, and due to disturbances of the fluid inhomogeneous layer on the specimen and localization shear phenomenon.

Although viscosity changes are responsible for a localized deformation and lead to an inhomogeneous flow, under quasistatic as well as dynamic conditions, the latter case, the changes in local viscosity are intense. Thus, the increase of the strain rate could favour the inhomogeneous flow and also strong strain variations through an increase in the viscosity.

5. CONCLUSION

The mechanical behaviour of the metallic glass Vit 6 proved uneasy to highlight at room temperature. It appeared difficult to follow the evolution of mechanical properties with the strain rate. Even though the quasistatic compression test showed that Vit 6 is characterized at room temperature by a yield stress around 1760MPa, followed by a viscous flow, under dynamic loading, the characterization is more difficult. For the further studies, it seems more judicious to work near the glass transition temperature and to study the temperature influence on the mechanical behaviour for different strain rates, for instance through DSC (Differential Scanning Calorimetry) measurement, which would allow to follow the crystallization phenomenon stemming from the loading.

Under quasistatic conditions, the fracture appears via main shear band along a plane lightly smaller than the one corresponding to a maximal shear (45°). Besides, under dynamic loading, the fracture does n't happen along a privileged direction. The fracture appearance is characterized by 2 veins types stemming from a shear fracture for the first one and from fluidized coat fracture appearing in the material curing the loading for the second one. Under quasistatic compression, the first vein type predominates, while the second type is more frequently observed under dynamic conditions. The deformation and fracture seem directly associated with viscous flow. The different vein shapes and directions depend on the disturbances appearing in the fluidized layers, especially in case of strong variations of viscosity. Then the strain rate has an effect on the fracture, improving the viscous flow via a strong and localized warming of more or less thick material layers.

References


