

Mechanical properties of a particle-reinforced Zr bulk metallic glass

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Abstract— The mechanical properties of a Zr-based bulk metallic glass were improved via dispersion of graphite particles into the alloy matrix. The resulting material had high plasticity, superior yield strength and good elasticity. The use of reinforcement particles also suppressed heterogeneous nucleation. Increased alloy plasticity of up to 20% was achieved without sacrificing the high yield strength of the metallic glass. The addition of graphite was also found to improve the thermal stability of the reinforced glass compared to that of the monolithic alloy.

Keywords—Zr bulk metallic glass, ZrC, particle-reinforcement.

I. INTRODUCTION

BULK metallic glasses (BMGs) possess as much as quadruple the elasticity [1] and up to double the fracture strength of the crystalline phase [2] and have, thus, high potential as structural materials, albeit at the cost of brittle fracture behaviour [3]. In BMGs the absence of crystalline structure effectively means that deformation via dislocation slip is prohibited, mediating deformation in shear bands of localized nature [4]. BMGs may occasionally exhibit limited ductile character [5] but, overall, they are characterized as brittle materials due to the concentration of fracture energy over a confined microscopic volume. The improvement of BMG plasticity is hence a popular research theme of varied approaches. Of these methods, foreign-particle-reinforcement [6], and in-situ-formed BMG composites [7] have been investigated more widely for the realization of high Poisson ratios. In particular to foreign-particle-reinforcement, the elements utilized include ductile metals such as Nb, Ta and Mo and ceramics like ZrC, TiC and WC. Additionally, reinforcement by carbon fibers or carbon nanotubes has been reported [8, 9]; nonetheless, such techniques mediate mechanical anisotropy and promote heterogeneous crystallization over the nanotube sites. As a result, such materials may be more brittle than monolithic BMGs. On the other hand, in-situ formed BMG composites have been shown to display good combinations of yield strength and plasticity. In particular, such examples for zirconium carbide (ZrC) reinforcement have been disclosed [10-14].

In graphite-particle-reinforcement, the alloy is heated above its liquidus temperature followed by a dispersion of graphite powder into the melt. Following, the melt is rapidly

cooled below its glass transition temperature (involving heat abstraction rates in the range 100-1000 K/s) towards formation of an amorphous composite.

Here, graphite-particle reinforcement is implemented on an amorphous Zr-Cu-Ni-Al-Ti based alloy towards enhancement of the latter's plasticity and yield strength as well as thermal stability.

II. MATERIALS AND METHODS

A master alloy with atomic composition $Zr_{50}Cu_{20}Ni_{15}Al_{10}Ti_5$ (ZCNAT) was prepared by arc melting high-purity elements (> 99%) under an Ar atmosphere, followed by casting the molten ingot into a Cu mould. Graphite at concentrations of 5, 10 and 20 vol.% of particle size ranges of 20-50 μ m (to be referred to as R1) and 51-80 μ m (to be referred to as R2) was dispersed into the mould and the sample was remelted for particle homogenization. The alloy was then chill cast. Monolithic BMG samples were also prepared without induction mixing. X-ray diffraction (XRD) spectra were recorded on a Bruker D8-Focus diffractometer with nickel-filtered Cu-K α radiation ($\lambda=1.5405$ Å), 40 kV and 40 mA. Sample cross sections were examined by scanning electron microscopy (SEM) on a Jeol 6380LV SEM, which also recorded energy dispersive X-ray spectra (EDS). Transmission electron microscopy (TEM) studies were performed on a Jeol 2100 HR microscope.

III. RESULTS AND DISCUSSION

XRD spectra for the ZCNAT composite for a range of graphite concentration and at different casting temperatures (in the R1 range) are shown in Fig.1. The amorphous character of the spectra is owing to the glassy ZCNAT matrix, while the Bragg peaks were indexed as crystalline ZrC (see inset plot in Fig.1a). As can be estimated from a comparison of Fig.1a through to 1c, ZrC concentration was found to increase with increasing casting temperature. Moreover, EDS results suggested that no graphite particles had fully transformed into carbides. Thus, the carbides observed in XRD should be due to interfacial reaction between the matrix material and the reinforcement particles. The results from the DSC scans of both the master ZCNAT alloy and of the composites with reinforcement volume fractions of 10 and 20 vol.% (in the R1 range) are presented in Fig. 2. The increase of graphite particle concentration appears to cause crystallization over higher temperatures, i.e. promotes higher thermal BMG stability. Also with increasing graphite content, the second crystallization peak becomes increasingly faint; this observation is also on a par

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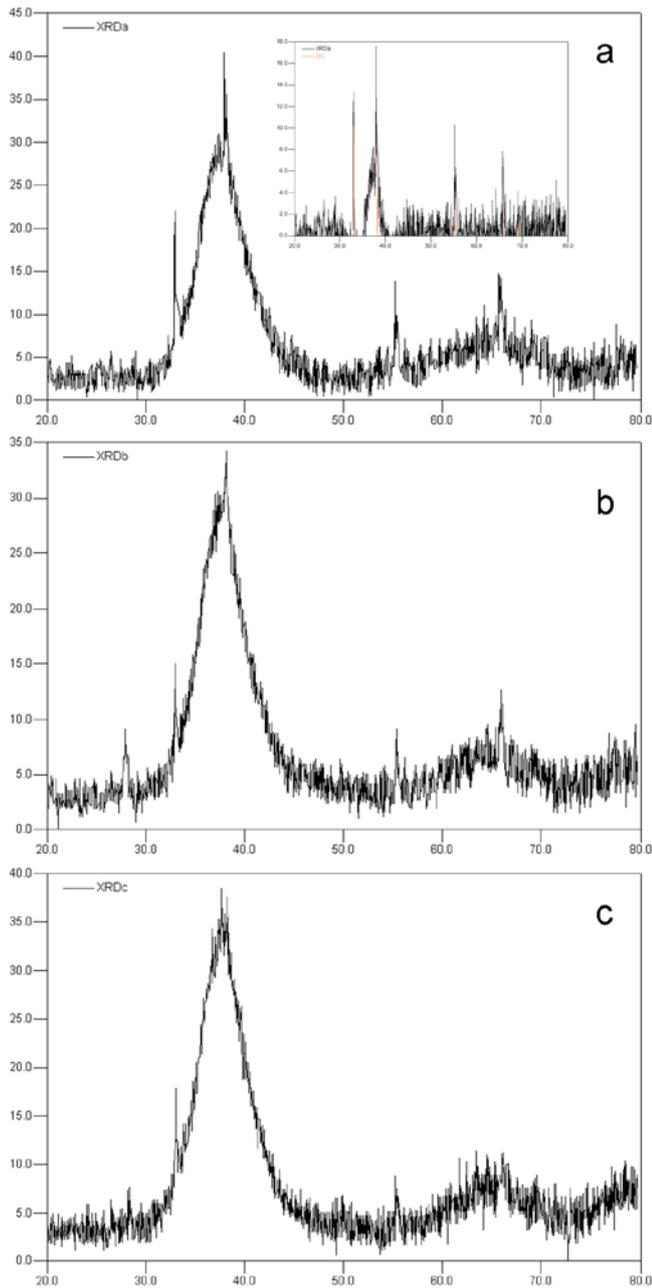


Fig. 1 XRD spectra of graphite-reinforced BMGs with 3.5 vol.% graphite reinforcement cast at various temperatures.

with a Zr-based BMG composite reinforced with SiC [15, 16] and it may be owing to a variance in ZCNAT composition. Reinforced-BMG plasticity also showed improvement at a fractional cost of yield strength, based on compression tests, as shown in Fig.3. All combinations of graphite-BMG resulted in enhancement of the plastic region upwards of 5%, and up to a limit of about 20%, without marked differences in the yield strength between the 10 and 20 vol.% graphite contents. This can be explained by the fact that upon deformation there is a maximum achievable plasticity beyond which an increase of the reinforcement particle concentration (and of the corresponding average distance between particles) will not offer further enhancement towards denser shear bands (for example doubling graphite concentration appears to reduce the average particle distance by sufficiently less than a factor of

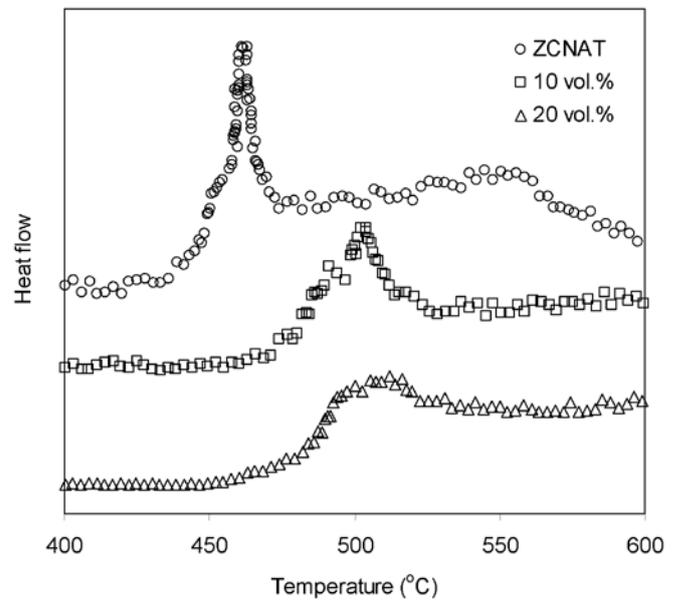


Fig. 2 DSC of master ZCNAT and BMG-graphite composites with varying graphite vol.% content.

two).

The stress-strain behaviour of a composite containing 5 vol.% graphite particles in the R2 range is shown in Fig.3. Overall, larger graphite particles lead to high plasticity, up to 20% of that of the monolithic BMB. However, this improvement was achieved at the cost of yield strength, most probably due to the reduced graphite content involved. Similarly, alloy hardness decreased with increasing graphite volume; a graphite concentration of the order of 5-10vol.% was observed to reduce hardness by as much as 25%.

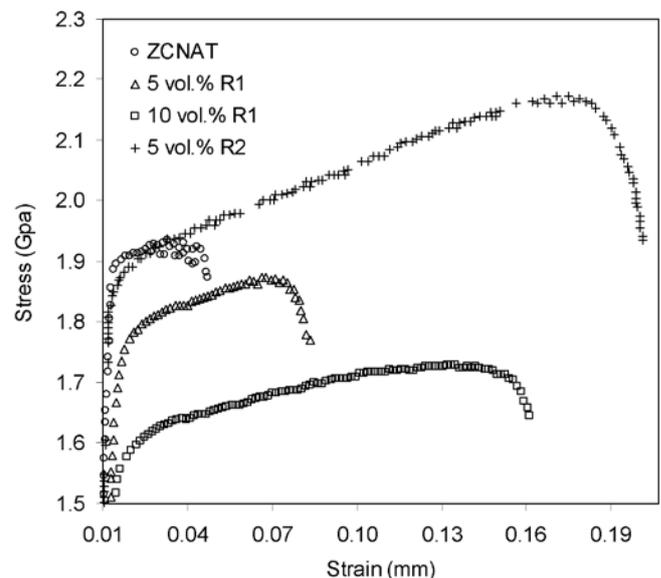


Fig. 3 Stress-Strain plots for various graphite-reinforcement concentrations and particle sizes.

Regarding the effect of interfacial carbide formation on the mechanical properties, it has previously been reported that smaller graphite particles of size below about 10 μm completely transform to ZrC in Zr based BMGs, forming an in-situ composite [17, 18]. In the current study, the changes in carbide content with increasing casting temperature as detected by XRD (not shown) exhibited amorphous humps

which were the result from the glassy ZCNAT matrix. Again, DSC confirmed the glassy structure of the matrix. Bragg peaks were also present and they were attributed to crystalline ZrC, as was the case for the R1 range. ZrC content was observed to increase significantly with increasing casting temperature. Based on EDX, however, no graphite particles were detected to be fully transformed into carbides. Thus, the carbides observed in XRD were deemed to be owing to an interfacial reaction between the matrix graphite. Sample compression tests confirmed that the highest plasticity was achieved for the lowest carbide content (roughly 400 GPa compared to 100 GPa of the matrix material); the mechanism driving the increased plasticity was deemed to be a concentration of tensile stress around the particle interface with the alloy matrix, such that propagating shear is maintained in the vicinity of the reinforcement particles.

IV. CONCLUSION

BMG-graphite composites developed in this study constitute a promising material for structural applications due to their high plasticity, comparable to that of crystalline alloys, combined with the high yield strength typical of metallic glasses. The matrix-particle interface, particularly its hardness, has a major influence on the mechanical properties of these composites. Since the microstructure of these foreign-particle reinforced composites can be tailored and easily reproduced for specific applications, one may expect that these new composites will have a great impact on research efforts in the entire field of amorphous structural materials. While the above examples related to composites based on ZCNAT, it is to be expected that similar results can be achieved also with composites based on BMGs with a different composition.

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