

Characterization of the interface between the bulk glass forming alloy $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ with pure metals and ceramics

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(Received 20 December 1999; accepted 28 April 2000)

The reaction of the bulk glass forming alloy $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ (Vit 1) with W, Ta, Mo, AlN, Al_2O_3 , Si, graphite, and amorphous carbon was investigated. Vit 1 samples were melted and subsequently solidified after different processing times on discs of the different materials. Sessile drop examinations of the macroscopic wetting of Vit 1 on the discs as a function of temperature were carried out *in situ* with a digital optical camera. The reactions at the interfaces between the Vit 1 sample and the different disc materials were investigated with an electron microprobe. The structure and thermal stability of the processed Vit 1 samples were examined by x-ray diffraction and differential scanning calorimetry. The results are discussed in terms of possible applications for composite materials.

I. INTRODUCTION

In recent years there has been a considerable scientific and industrial interest in metal matrix composites as a way to improve mechanical properties compared to the unreinforced alloys.^{1–3} For matrix materials pure metals like, e.g., aluminum⁴ and titanium⁵ and recently bulk metallic glass (BMG) forming alloys,^{6–8} have been studied. BMGs have a high glass forming ability so that cooling rates of less than a 100 K/s are sufficient to circumvent crystallization. They have high yield strength and a high elastic strain limit combined with a good corrosion resistance and relatively high fracture toughness.^{9–12} However, the lack of tensile ductility can be a drawback in many applications. By the addition of particles to the BMG, an improved tensile ductility is expected because the particles encourage the formation of multiple shear bands and hinder the propagation of a single critical shear band.

The properties of a composite are not only defined by the properties of the matrix and the reinforcement material but essentially by the chemical reaction of both. For

particulate-reinforced BMG composites a strong reaction can lead to a dissolution of the particles, which can affect the glass forming ability of the BMG–matrix. On the other hand, a necessary condition for infiltration casting of composites is that the melt wets the particles. Additionally to the wetting condition, an optimized interfacial strength is essential to improve mechanical properties. For example, by the introduction of SiC particles in the bulk metallic glass former $Cu_{47}Ti_{34}Zr_{11}Ni_8$ and $Zr_{57}Nb_5Al_{10}Cu_{15.4}Ni_{12.6}$, it was found that the thermal stability was increased compared to the unreinforced material but no enhancement of the ductility was achieved because the interface between particle and matrix is too weak.^{7,13}

II. EXPERIMENTAL METHODS

$Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ (Vit 1) alloy was used as a matrix material. Samples were prepared by arc melting the constituents with a purity ranging from 99.5% to 99.995% in a titanium-gettered argon atmosphere. The samples were inductively heated either in vacuum ($<5 \times 10^{-6}$ mbar) or in a titanium-gettered argon atmosphere. The temperature was measured using a thermocouple (type K).

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Vit 1 samples were processed as sessile drops on discs of W, Ta, Mo, TiC, ZrC, AlN, Al₂O₃, Si, graphite, and amorphous carbon. The macroscopic wetting was investigated *in situ* with a digital camera as a function of temperature. After melting and processing of the sample under varying conditions, it was cooled with rates between 1 and 20 K/s. The microstructure as well as the interface of the solidified sample were analyzed with a Jeol JXA-733 microprobe. This apparatus is equipped with five wavelength-dispersive spectrometers (WDS) which allowed the determination of the various phases by element concentrations. The beryllium as well as the oxygen contents were not measured but calculated by difference. The carbon content was measured with a Leco C-200 analyzer. In this analyzer, the sample is heated in an oxygen containing atmosphere. The formation of CO₂ content is measured with an infrared absorption cell. X-ray investigations were performed on a Siemens D-500 diffractometer with Cu K_α radiation. Thermal stability studies were carried out with a Perkin-Elmer differential scanning calorimeter (DSC) 7.

III. RESULTS AND DISCUSSION

Figure 1(a) shows images of Vit 1 samples, processed on graphite at four different temperatures. The sample is kept for 500 s at the processing temperature prior to taking the picture. During that time a slow decrease of the wetting angle could be observed. The eutectic temperature of Vit 1 is $T_{\text{eut}} = 937$ K, and the liquidus temperature is $T_{\text{liq}} = 1026$ K.¹⁴ At 1000 K Vit 1 starts wetting

the graphite. The wetting angle, θ , is 90°. By the increasing of the temperature, the wetting angle decreases. Complete wetting occurs at 1200 K.

Figure 1(b) depicts an image of Vit 1 processed on AlN. After the sample is kept for 1000 s at 1100 K, the wetting angle is about 90°. A heat temperature of 1250 K for 500 s does not change the wetting angle noticeably. The interface between the Vit 1 sample and the AlN was extremely weak, as evidenced by the fact that the sample separated from the disc upon removal from the apparatus. No reaction zone could be observed on the AlN disc.

The interface between Vit 1 and the graphite disc was investigated by electron microprobe. A backscattering image of this interface is shown in Fig. 2. Images of the Vit 1 sample show no contrast, DSC as well as x-ray investigations reveal its amorphous state. At the interface between Vit 1 and graphite a layer has formed with a composition close to ZrC. The formation of a ZrC layer has been reported in the past where it formed between Zr₅₇Nb₅Al₁₀Cu_{15.4}Ni_{12.6} and SiC or WC.⁷ Scanning electron microscopy (SEM) and optical microscope investigations reveal that the ZrC layer forms prior to wetting. This can be concluded from the fact that the ZrC layer surrounds the area where Vit 1 has wet the graphite. The wetting angle, θ , is generally determined by the equilibrium of the interfacial energies given here by $\sigma_{\text{V,D}} = \sigma_{\text{Vit 1,D}} + \sigma_{\text{V,Vit 1}} \times \cos(\theta)$, where the subscript V denotes vacuum and D the disc material. In the case of Vit 1 on graphite the wetting angle is not given

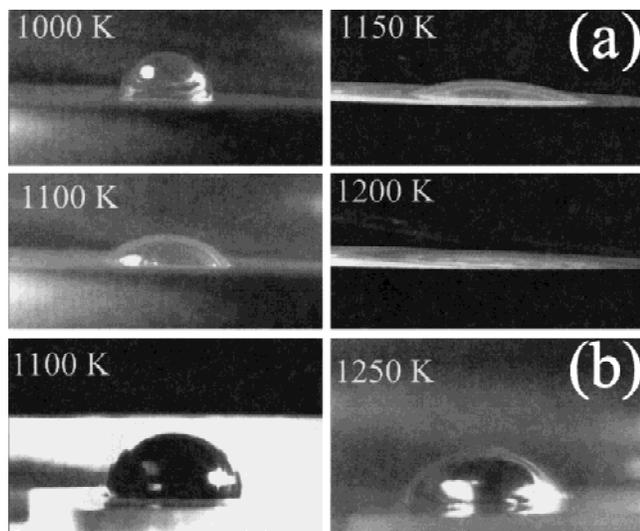


FIG. 1. (a) Images of Vit 1 processed on graphite discs at 1000, 1100, 1150, and 1200 K. The sample was kept 500 s at the processing temperature prior to taking the picture. During that time a slow increase of the wetting behavior was observed. Complete wetting occurs at 1200 K. (b) Vit 1 processed on AlN for 1000 s at 1100 K and for 500 s at 1250 K. The wetting angle is around 90°.

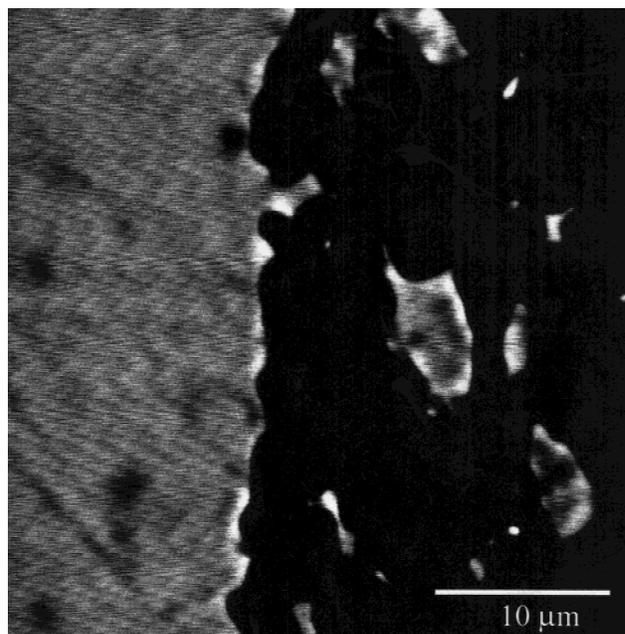


FIG. 2. Backscattering electron image of the interface between Vit 1 (left-hand side) and graphite (right-hand side). At the interface a phase with composition close to ZrC was formed. This phase covers the entire interface between graphite and Vit 1 even in the pores of the graphite disc.

by $\sigma_{V,Graphite} = \sigma_{Vit\ 1,Graphite} + \sigma_{V,Vit\ 1} \times \cos(\theta)$ but by $\sigma_{V,ZrC} = \sigma_{Vit\ 1,ZrC} + \sigma_{V,Vit\ 1} \times \cos(\theta)$ and the kinetics of the wetting are governed by the formation rate of the ZrC layer.

The structure of the Vit 1 material solidified on the different disc materials was investigated by x-ray diffraction (XRD). Figure 3 depicts the diffractograms. For each sample a measurement was performed on the free surface. Subsequently this surface layer (layer between vacuum and the Vit 1 droplet) was removed and the bulk of the sample was measured again. The spectrum measured on the free surface of the Vit 1 sample processed on graphite consists of peaks of ZrC as well as a peak corresponding to graphite. The fact that a peak corresponding to graphite is observed in the spectra may be caused by an uncovered spot of the disc material. A spectrum typical for an amorphous phase was measured after removing the surface layer. The same results were obtained for Vit 1 processed on amorphous carbon as a disc material (not shown). The carbon content of the Vit 1 melt processed on graphite was measured with a Leco C-200 to be around 2 at.%. Thermal analysis of this droplet

performed, using DSC, after processing it on the graphite disc shows no distinctive difference compared to the as-cast Vit 1 (Fig. 4).

The spectra measured on the free surface of Vit 1 processed on Al_2O_3 contain several peaks of crystalline phases that could not be assigned. A broad peak typical for an amorphous phase is superimposed over the sharp crystalline peaks. After removal of the surface layer, a typical diffractogram of an amorphous phase was measured. Figure 5 shows the SEM backscattering image of this particular sample. The bright surface layer (phase 1) with a composition of $Zr_{43}Ti_{15}Cu_{12}Ni_{10}Be_{20}$ which is close to the composition of Vit 1 likely causes the crystalline peaks in Fig. 3. A needlelike phase (2) with a composition of $Zr_{43}Ti_4Cu_4Ni_4(Be,O)_{45}$ is uniformly distributed in the amorphous phase. Its volume fraction of about 1 vol% cannot be detected with x-ray diffractometry. The inset in Fig. 5 shows the formation of a crystalline phase at the interface between Vit 1 and Al_2O_3 with a high content of beryllium and/or oxygen. A DSC run performed with the bulk of this droplet shows a very similar result as for pure Vit 1 (Fig. 4).

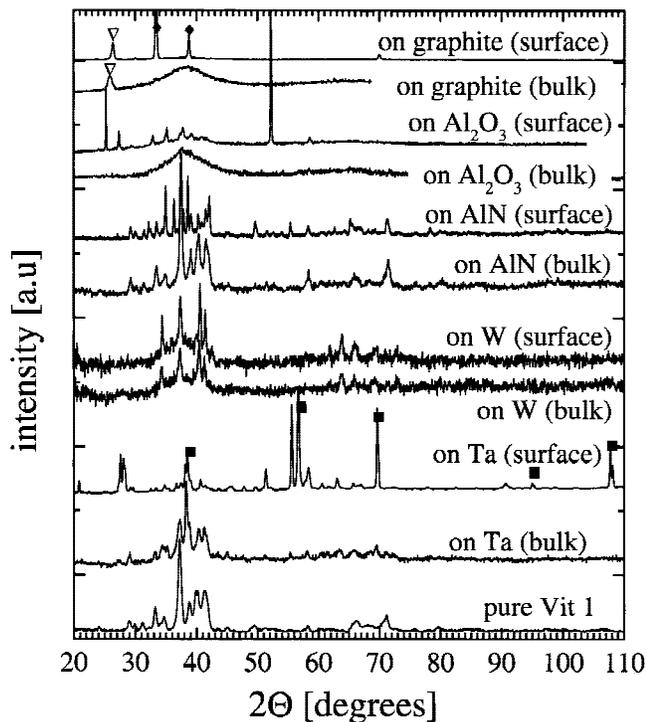


FIG. 3. X-ray diffractograms of Vit 1 samples processed on different disc materials measured with $Cu\ K_{\alpha}$ radiation. The disc material corresponding to each spectrum is noted to the right. The spectra labeled with “surface” are obtained on the free surface (between the Vit 1 sample and vacuum of each sample). Spectra labeled with “bulk” are obtained after this surface layer was removed. A diffractogram of a Vit 1 sample crystallized during constant cooling with 0.5 K/s at a temperature of about 850 K is shown for comparison. Peaks that could be assigned to certain phases are denoted by the following symbols: ■ bcc-Ta; ▽ graphite; ◆ cubic ZrC.

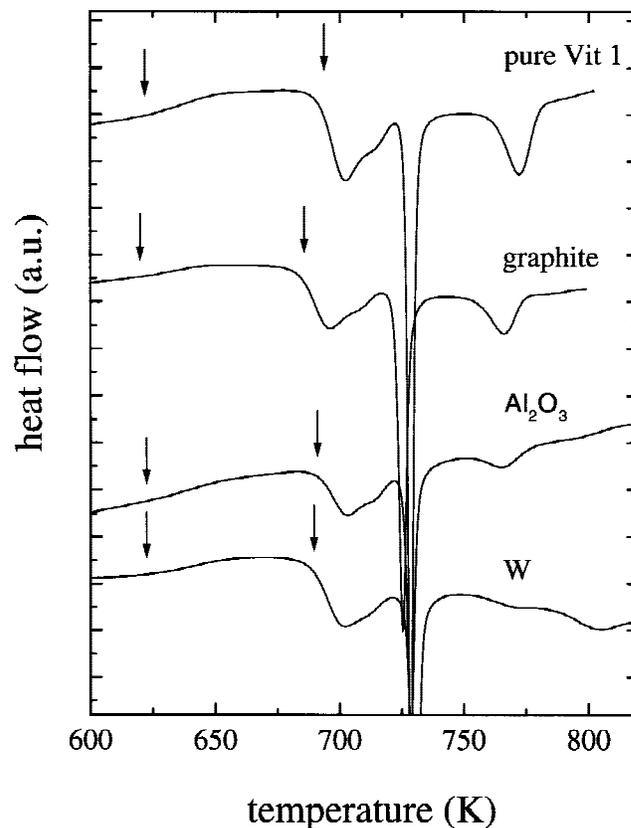


FIG. 4. DSC results of pure Vit 1 and Vit 1 after processing on graphite, Al_2O_3 , and W discs, heated with 20 K/min. The glass transition temperature and the crystallization temperature are not significantly changed compared to pure Vit 1. They are marked by arrows.

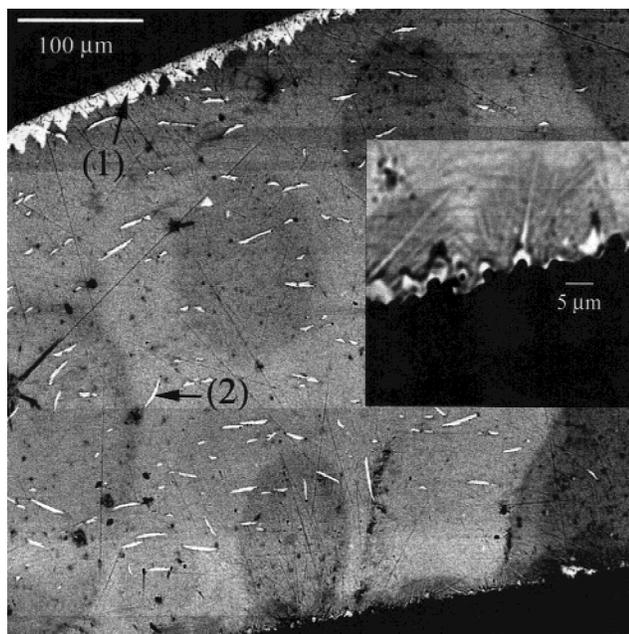


FIG. 5. Backscattering electron image of Vit 1 on Al_2O_3 : top, vacuum; middle, Vit 1; bottom, Al_2O_3 disc. The layer at the free surface (phase 1) has a composition of $\text{Zr}_{43}\text{Ti}_{15}\text{Cu}_{12}\text{Ni}_{10}\text{Be}_{20}$. The Al content was measured to be less than 0.3 at.% in average, which is within the uncertainty of the EDX device. The needlelike phase (2) with a composition of $\text{Zr}_{43}\text{Ti}_4\text{Cu}_4\text{Ni}_4(\text{Be},\text{O})_{45}$ is uniformly distributed all over the Vit 1 sample. The inset gives a closer view of an area at the interface between Vit 1 and Al_2O_3 . A crystalline phase with a high content of about 50 at.% of Be and/or O has formed at the interface.

The spectra of a Vit 1 sample processed on AlN looks similar than that of pure Vit 1 after crystallization during constant cooling with 0.5 K/s at a temperature of about 850 K.

After the processing of Vit 1 on tungsten, a similar XRD spectra as for pure crystalline Vit 1 was observed superimposed by a broad amorphous peak (Fig. 3). Another Vit 1 sample that was processed on tungsten but subsequently cooled with a faster rate of about 20 K/s does not show crystalline peaks anymore (not shown). The DSC run of this postprocessed droplet shows basically the same characteristics as the pure Vit 1 reference sample (Fig. 4).

Tantalum as a disc material leads to a spectra similar to that of pure crystalline Vit 1 when the surface layer is removed. The free surface, however, shows a very different spectra where several peaks can be assigned to the Ta body-centered-cubic (bcc) phase. This is in agreement with microprobe investigations on this sample, shown in Fig. 6, where a Ta-rich phase was found at the free surface. Dissolved in the matrix, an average of about 6 at.% Ta was measured.

In order to test the adhesion after processing between the Vit 1 sessile drop and the discs, we tried to separate the solidified drop from the disc mechanically with a

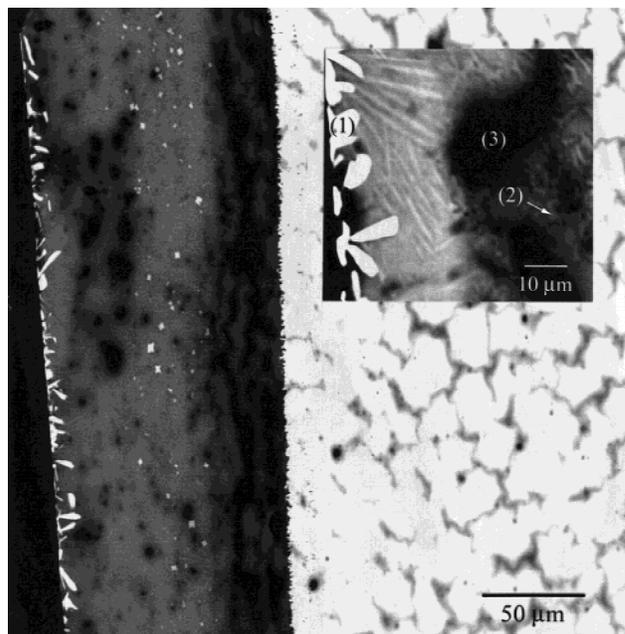


FIG. 6. Backscattering electron image of Vit 1 on tantalum: left, vacuum; middle, Vit 1; right, tantalum disc. The inset gives a closer view of an area at the free surface. The bright phase (1) has a composition of $\text{Zr}_{47}\text{Ti}_{20}\text{Cu}_8\text{Ni}_8\text{Ta}_{17}$ and contains no Be. The composition of the star-shaped phase (2) is $\text{Zr}_{52}\text{Ti}_{16}\text{Cu}_{15}\text{Ni}_{12}\text{Ta}_5$ and contains no Be either. Phase 3 has a Be content of about 60 at.%.

hammer and a chisel. The adhesion was very strong for C and W, less strong for Al_2O_3 and Ta, and not present for AlN and Si.

A summary of the performed experiments and characterizations is given in Table I.

VI. CONCLUSIONS

Among the investigated materials carbon and tungsten are the most promising as a reinforcement material for Vit 1 bulk metallic glass composites. Both materials do not notably alter the glass forming ability of Vit 1 and show an excellent wetting behavior. According to Wang *et al.*¹⁵ a carbon content of 1 at.% increases the microhardness of Vit 1 by 15%. Whether this is desirable or whether it instead leads to embrittlement is currently under investigation. For tungsten the wetting is given by the equilibrium of the interfacial energies between tungsten, Vit 1, and vacuum. The wetting of carbon is controlled by the formation rate of a ZrC reaction layer. Both materials form a strong interface with Vit 1.

A quantitative evaluation of the wetting behavior of Vit 1 on Ta and Al_2O_3 has to be treated with caution because a layer at the free surface between the Vit 1 liquid and the vacuum is formed. In terms of wetting and the formation of a strong interface, tantalum behaves similar to tungsten. However, the drawback of Ta is that it dissolves rapidly in the Vit 1 melt. One possibility to use tantalum as a reinforcement material could be to

TABLE I. Summary of the performed experiments and characterizations. Complete wetting is denoted with a “Yes” for $\theta < 5^\circ$. After complete wetting (or minimum θ for the samples that do not wet completely) the composite was cooled with a rate of about 15 K/s. DSC as well as XRD was carried out to verify the vitreous structure of the sample. The formation of an interface layer between Vit 1 and the disc material as well as the dissolution of disc material in Vit 1 was investigated with an electron microprobe.

Disc material	Wetting	Amorphous	Formation of interface layer	Disc material dissolved in Vit 1
C(graphite)	Yes	Yes	ZrC	2 at.%
AlN	90°	No	No	...
C(amorphous)	Yes	Yes	ZrC	...
			Crystalline	
Al ₂ O ₃	Yes	Yes	phase	...
Ta	Yes	No	No	6 at.%
W	Yes	Yes	No	<1 at.%
Si(001)	40°	No
Mo	Yes	No	...	Yes

process it for much shorter times than performed here. Molybdenum dissolves even faster than tantalum in the Vit 1 melt, so it is a rather unsuitable material for composite synthesis.

Al₂O₃ has promising properties in combination with Vit 1 as a reinforcement for a metallic glass composite. It has good wetting properties, and the Vit 1 melt solidifies amorphous on it. The crystalline phase formed at the interface is mechanically quite strong.

Silicon and AlN do not appear to be useful reinforcement materials. Vit 1 does not wet AlN sufficiently, and the interface is extremely weak. A weak interface was obtained between Vit 1 and Si as well.

The presented method represents a promising route to preselect materials as possible reinforcements for metal matrix composites.

ACKNOWLEDGMENTS

This work was supported by the United States Army Research Office (Grant No. DAAH04-95-1-0233), the Air Force Office of Scientific Research (AFS 5 F4920-97-0323), and the United States Department of Energy (Grant No. DEFG-03086ER45242).

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