

Interface characterization in tungsten fiber/Zr-based bulk metallic glass matrix composite

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Abstract

In this research, $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk metallic glass (BMG) alloy is used as the base material to form tungsten fiber reinforced BMG composites. The composites are synthesized using melt infiltration casting method and their microstructure and compressive properties are investigated. Two different infiltration times of 10 min and 15 min are used to produce the composites. The microstructural evaluation of the interface between tungsten fiber and BMG matrix reveals that a narrow reaction band emerges between the tungsten wires and BMG alloy. Some portions of this layer are broken into the fine Zr/W-rich particles and eventually are dispersed in the BMG matrix, when the infiltration time is 15 min. The results also showed that increasing the infiltration time from 10 min to 15 min improves the compression strength of the composite from 1333 MPa to 1396 MPa and also increases the compression strain of the composite from 0.11 to 0.13. This is attributed to the lack of porosities and better metallurgical bonding between tungsten fibers and BMG matrix.

1. Introduction

Bulk metallic glasses (BMGs) are new type of materials with excellent properties including high strength and hardness, large elastic strain and almost high fracture toughness. They have also good wear and corrosion resistance [1-4]. However, the critical cooling rate for fabricating BMGs is a major factor that limits the size of as fabricated parts [5]. Due to the relatively excellent glass forming ability, good thermal stability and favorable mechanical properties, Zr based glass forming alloys have become one of the materials which are promising for the large-scale preparation. Inoue *et al.* [6] found that the critical cooling rate of $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG was only $10 K \cdot s^{-1}$. The diameter of $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG bar could reach up to 30 mm using copper casting method.

The BMGs do not have a considerable plastic strain which limits their applications [6,7]; but the development of ex-situ and in-situ composites based on BMGs have promising results for structural engineering applications [8-11]. Unlike the monolithic BMGs, the BMG matrix composites can tolerate plastic deformation in the compression [12-14]. Adding second phase particles or fibers to the BMGs increases the plastic deformation by hindering the propagation of shear bands and formation of multiple shear bands [15-18]. The W fiber/Zr-based bulk metallic glass composite (W/BMGC), as one kind of the earliest BMGCs, has been investigated widely due to the excellent mechanical properties and potential armor application [1,18]. The bonding characteristics and interfacial status between the two phases are the key factors to determine whether the W/BMGCs fail by shearing or splitting [19].

The matrix and the reinforcement phase have the crucial effect on the BMG composites, but the production method also plays an

important role. One of the most important factors in the melt infiltration casting method is the infiltration time. A strong reaction at the interfaces influences the glass-forming ability (GFA) of the BMG matrix and also deteriorates the properties of the fiber. On the other hand, in the infiltration cast composites, it is crucial that the melted material wets the fiber to make a strong metallurgical bond. There is a large volume of liquid/solid interface during casting a BMG composites, especially when a high amount of reinforcement fibers is used. The interfaces act as the nucleation sites for crystallites and decrease the capability of the melted alloy to become amorphous solid. At the liquid/solid interfaces, the chemical reaction and atomic diffusion occurs easily, and the resulting properties of the composite is severely affected by these interfacial layers [11,18].

During casting, diffusion and reaction at the interface are inevitably, excessive diffusion and reaction will weaken reinforcements and cause the loss of strength [20]. For the metallic glass matrix composites, these diffusion and reaction are more noticeable because they will alter the composition of the metallic glass matrix and reduce its glass forming ability. It was found that the W fibers yielded firstly and then transferred load to the metallic glass phase during deformation, the bonding characteristics and the interfacial status between the two phases are the key factors to determine whether the W/BMGCs shear or split [21]. Diffusion at the interface is a thermally activated process where time and temperature of infiltration are predominant variables.

It is known that the interface plays an important role in the mechanical properties of composites [22]. Wang *et al.* [23] and Li *et al.* [24] optimized the interface between the metallic glass matrix and the tungsten fiber by adding alloy element to the glass matrix, which significantly increased the compressive mechanical properties of BMGCs. Besides the interface, Conner *et al.* [8] and Dragoi *et al.* [25]

found that the thermal residual stresses also influenced the mechanical properties and deformation behaviors of the BMGCs. Wang *et al.* studied the interface reaction in W fiber/Zr-based bulk metallic glass composites were prepared by melt infiltration casting infiltrated at different temperatures for different times [23].

Although the W/BMGs have been investigated and discussed widely, those works so far mainly focus on the synthesis and deformation. Thus the effect of the infiltration time on diffusion and reaction at the interface is still unclear. In this paper, the effect of infiltration time on the microstructure and compression strength of the $Zr_{55}Cu_{30}Al_{10}Ni_5$ alloy reinforced by tungsten fibers is studied. The matrix alloy is a beryllium-free Zr-based glass former, which is not harmful for the health. Tungsten has a high melting point and limited reactivity with the liquid matrix material. Tungsten fibers also have a high density and self-sharpening behavior during dynamic deformation. Therefore, these kinds of composites are new candidates in the aerospace and defense applications such as tungsten-based kinetic-energy penetrators [26,27].

2. Experimental procedure

In this study, the $Zr_{55}Cu_{30}Al_{10}Ni_5$ alloy was selected as the matrix material because of its high glass forming ability. The base amorphous alloy was prepared by alloying the constitutive elements together in an arc furnace under a titanium-gettered argon atmosphere. The high-purity metals were used as the raw materials to prevent the formation of undesirable phases. The oxygen content of the raw materials was very low and in the range of 30~35 ppm.

Unidirectional tungsten wires with a diameter of 0.8 mm were cut into 70 mm (length) and degreased by ultrasonic cleaning in a bath of acetone and followed by cleaning in a bath of ethanol. The melt infiltration casting [28] was used to manufacture the W/BMG composite. A schematic sketch of the procedure is represented in Figure 1. The tungsten wires were placed in the sealed end of a quartz tube with an inner diameter of 7 mm. A necked tube was set up about 10 mm above the tungsten wires, and then the BMG ingot was inserted in the tube above the neck. The necked tube is necessary to minimize

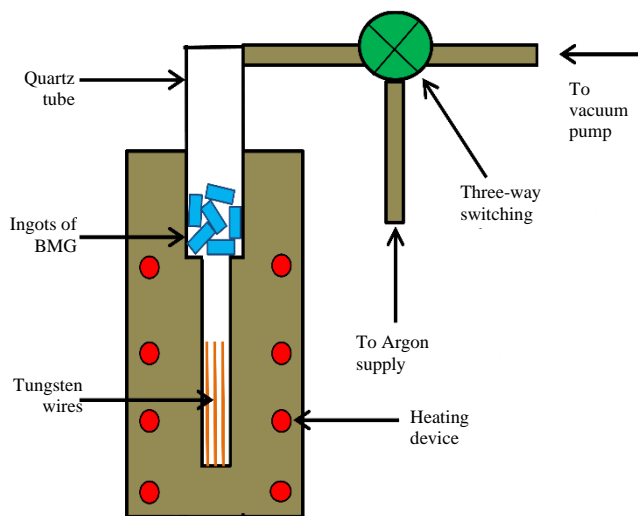


Figure 1. Schematic sketch showing the set up for the W/BMG composite fabrication.

the premature contact between the BMG melt and the tungsten wires to prevent excessive reactions. Before heating and melting the ingots, the tube was evacuated and then filled with the argon gas. The assembly of tube was heated up to approximately 1223 K, which is higher than the liquidus temperature of the BMG, and then held for 10 min to allow the material to melt completely. After that, the argon gas with a positive pressure of 0.24 MPa was applied to push the melt to infiltrate through the bundle of the tungsten wires and the pressure was maintained for two infiltration times of 10 min and 15 min. Then the assembly of tube was quickly removed from the furnace and quenched in brine (8% NaCl/H₂O solution). The microstructure of the W-BMG composite was observed by scanning electron microscope (SEM).

The W/BMG specimens were prepared by means of an electrical discharge machining for compressive tests. Cylindrical specimens with the dimension of 3 mm diameter and 6 mm length were used for compression tests, and ends of the specimens were mechanically polished. Uniaxial compression tests were conducted on an Instron-5500 testing machine at room temperature using an engineering strain rate of $2 \times 10^{-4} \text{ s}^{-1}$. At least three samples for mechanical testing were measured to ensure that the results are reproducible and statistically meaningful.

3. Results and discussion

The SEM micrographs of the cross section of W/BMG composites produced at 1223 K is shown in Figure 2. The cross-section shows a structure of close packed tungsten wires in the BMG matrix. The quality of the composite samples produced by this technique varied with the time of infiltration. When the infiltration time is 15 min, a sound composite with no porosity is produced due to the sufficient time for molten material to penetrate between the tungsten wires (Figure 2(a)). However, when the infiltration times is 10 min, some porosities are observed in the microstructure, due to insufficient time for penetration of the liquid between the tungsten fibers (Figure 2(b)).

Figure 3 shows SEM micrographs of interfacial region of the composites. The samples are produced at temperature of 1223 K and two infiltration times of 10 min and 15 min. The grey part in each picture is tungsten fiber while the darker one is the $Zr_{55}Cu_{30}Al_{10}Ni_5$ matrix. At lower infiltration time of 10 min, there is a limited interfacial reaction (Figure 3(a)) and a sharp interface is obtained, with no crystalline phase in the matrix. By increasing the infiltration time to 15 min, a reaction layer is formed around the tungsten wires and some white particles were eroded away from the wires (Figure 3(b)). The EDS results of the particle near the tungsten wire are shown in Figure 4. The existence of high amount of Zr and W in this particle indicates the formation of Zr/W-rich phase. There are also little amounts of Ni, Cu and Al elements in this phase. This proves the occurrence of metallurgical reaction between the W wires and $Zr_{55}Cu_{30}Al_{10}Ni_5$ base alloy during the casting process.

To preserve the mechanical properties of the metallic glass in the composite, the crystallization of the metallic glass and formation of the brittle intermetallics should be avoided [29]. However, the interface reaction during casting process cause the formation of some intermetallics such as Zr_3W_2 . Figure 5(a) shows some of these particles indicated with arrows. This is in accordance with the study of Wang *et al.* [23]. They concluded that the interface peritectic

reaction becomes more intensive with increasing infiltration temperature and infiltration time. They reported the formation of some Zr-W intermetallics such as W_2Zr and W_5Zr_3 . The interface reaction product breaks off W fiber after peritectic reaction, in this way, the new fiber surface is exposed to the liquid melt and the interface peritectic reaction can proceed, which will weaken the mechanical properties of W fiber severely, so this peritectic reaction must be controlled effectively. On the other hand, it is reported that the dispersion of intermetallics in the metallic glass matrix can improve the mechanical properties of the matrix due to the second phase strengthening effect [30]. Figure 5(b) shows the average particle size versus distance from the tungsten wire. As can be seen in Figure 5(b), the particles size decreases when the distance from the tungsten wire increases (with an exponential equation). The liquid metal near the tungsten wires experiences fast cooling because of the heat sink effect of the wires, therefore these particles do not have enough time to dissolve in the liquid phase again. The particles farther from the wires have more time and enough temperature to dissolve in the molten matrix and finally become smaller in size.

Figure 6 shows the higher magnification SEM micrograph of the interface between tungsten wire and BMG matrix. As can be seen,

there is a narrow band with about 4–6 μm width. The EDS line scan results show the concentration profile of Zr and W; this indicates the formation of Zr/W intermetallic at the interface.

The tungsten content in the reaction layer is decreased with increasing the infiltration time and also by getting away from the tungsten wires. The Zr content of the particles also increases by getting away from the wires (Figure 6). It can be deduced that the elements Zr, Al, Cu and Ni diffuse toward the reaction layer and tungsten diffuse out of the wire to form layers of about 3–4 μm as shown in Figure 7. The diffusion coefficients of those elements are higher than that of the tungsten, thus they diffuse more rapidly toward the tungsten wires. When the tungsten content in the reaction layer is reduced under a certain amount, its grain boundaries strength reduces; therefore the layer is broken into the separated grains during the infiltration process. The broken particles are dispersed between the wires inside the metallic glass material (Figure 7). By increasing the temperature and the infiltration time, the Zr/W-rich layer formation is facilitated and the broken particles are more dispersed inside the composite. The formation of the Zr/W-rich layer or particles decreases the Zr content of the glass former liquid, therefore this can stimulate the formation of some crystalline nuclei which grow from the particles into the glass metallic matrix.

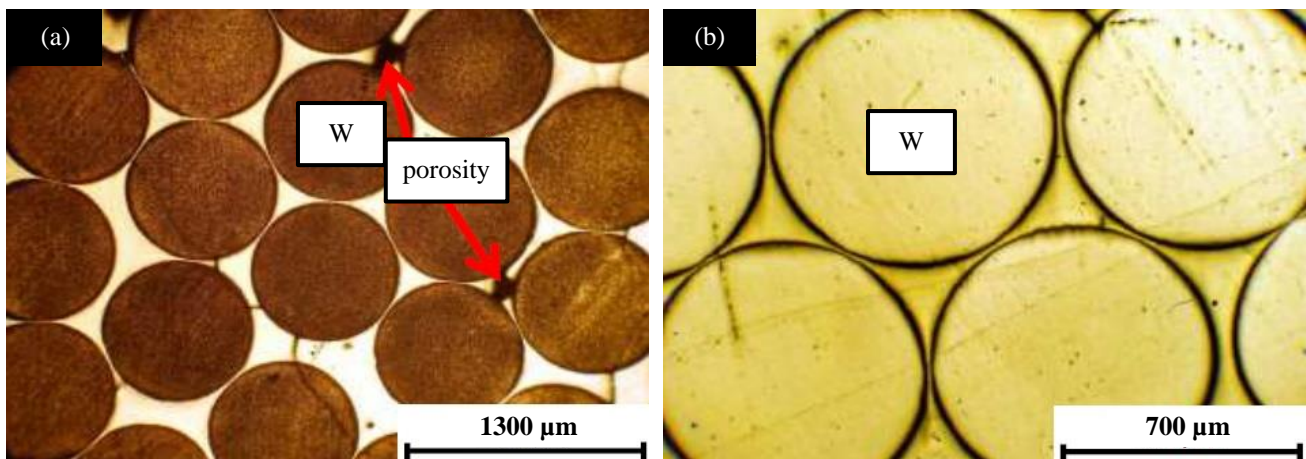


Figure 2. Low magnification micrograph of the W/BMG composite cross section produced at 1223 K and infiltration time of (a) 10 min and (b) 15 min.

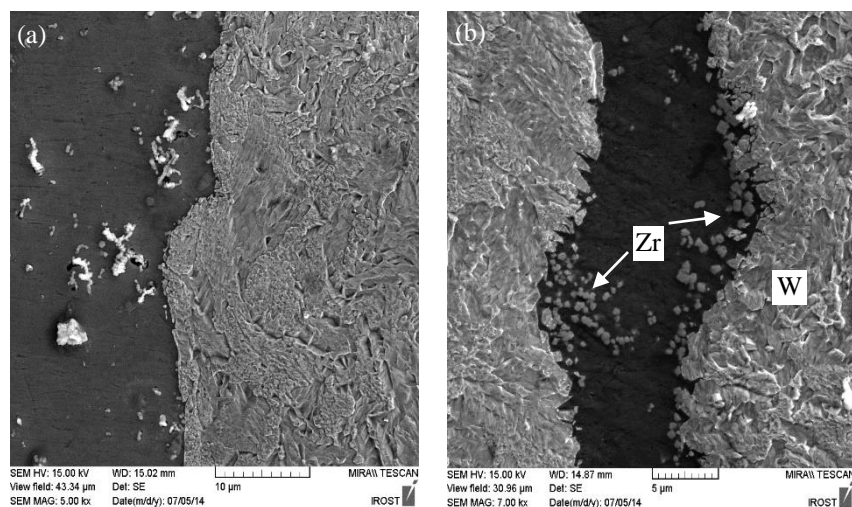


Figure 3. SEM micrograph of W fiber/ $Zr_{55}Cu_{30}Al_{10}Ni_5$ composites synthesized at 1223 K and infiltration time of (a) 10 min and (b) 15 min.

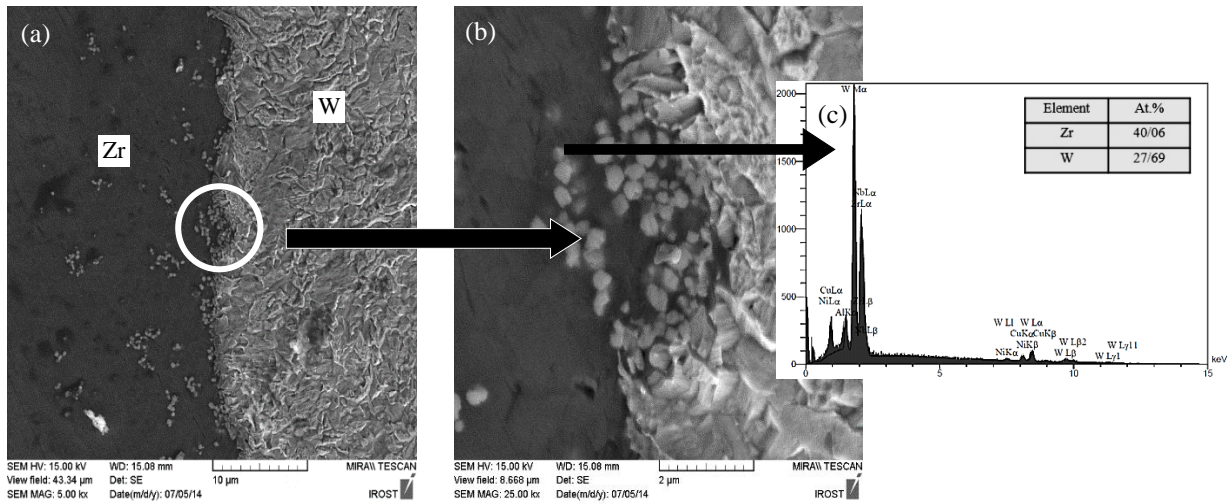


Figure 4. (a), (b) Formation of Zr/W-rich particles at the interface of W wire and Zr₅₅Cu₃₀Al₁₀Ni₅ (infiltration time of 15 min) and (c) corresponding EDS results.

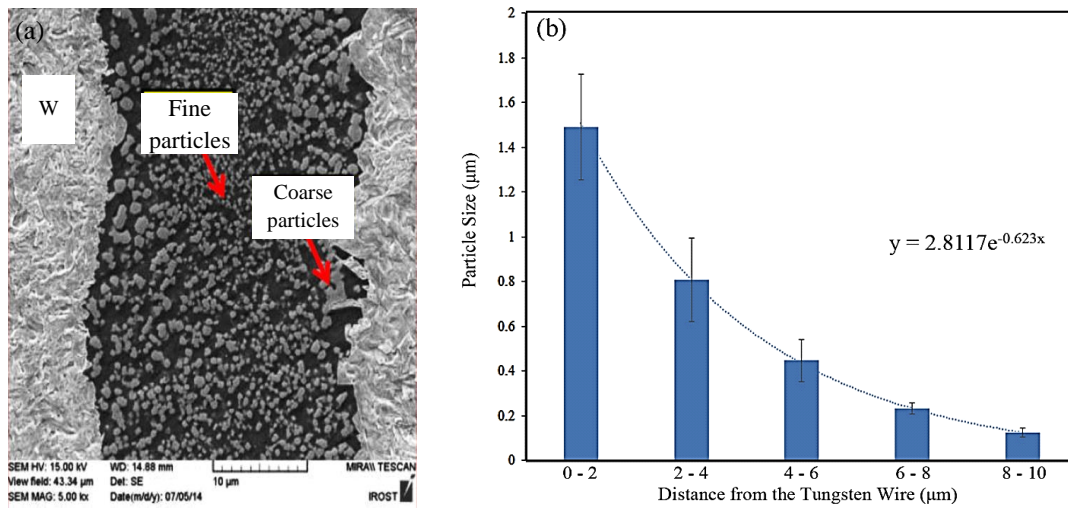


Figure 5. (a) Formation of W/Zr intermetallics in the W/BMG composite (infiltration time of 15 min) and (b) average particle size versus distance from the tungsten wire.

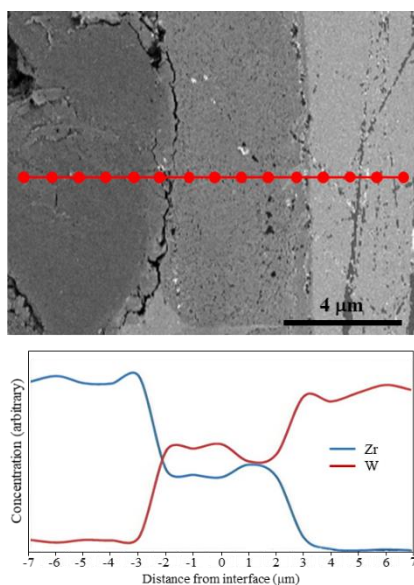


Figure 6. SEM micrograph of the interface of W/BMG and EDS line-scan of the Zr and W distribution across the interface (infiltration time of 15 min).

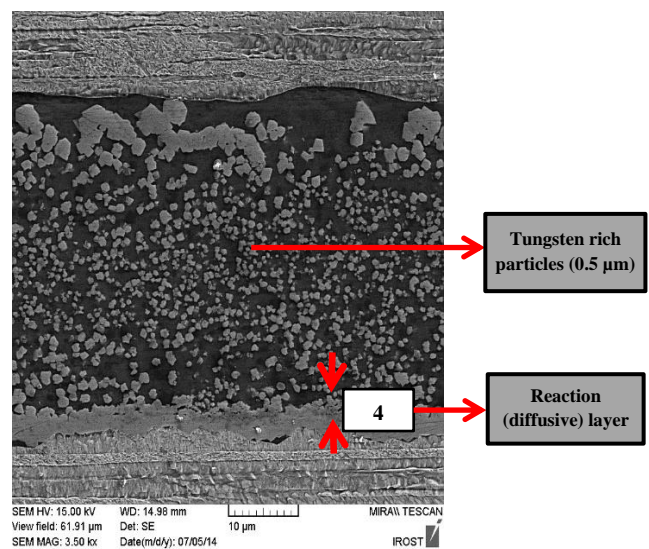


Figure 7. Formation of reaction layers and tungsten rich particles in the interface of W/BMG for composite processed at time period of 15 min and infiltration temperature of 1223 K.

Figure 8 shows the reaction layers attached to the tungsten wire and the particles eroded away from the wires. The presence of reaction layer is useful for inter-diffusion and interaction of atoms at the interface which produces a strong metallurgical bond between W wires and BMG base alloy. But in extended infiltration time with increasing the thickness of this intermetallic layer some cracks are formed and the layer is detached from tungsten wire (Figure 8).

The results of the compression test of the produced W/BMG composites are represented in Figure 9. The monolithic BMG has slightly greater fracture strength (1517 MPa) compared to the W/BMG composites.

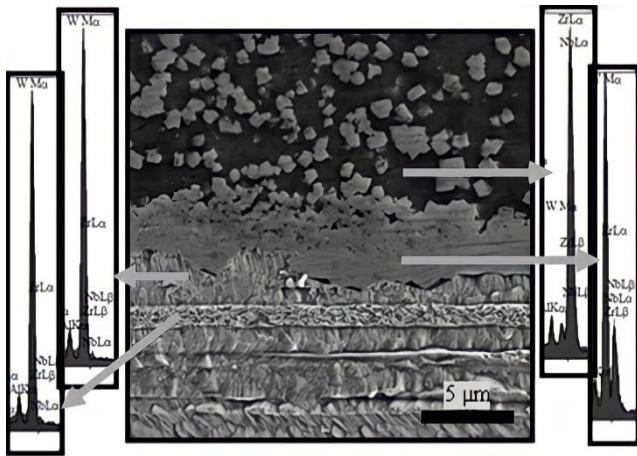


Figure 8. The reaction layer near the tungsten wire and the particles eroded away in the composite processed at infiltration time of 15 min.

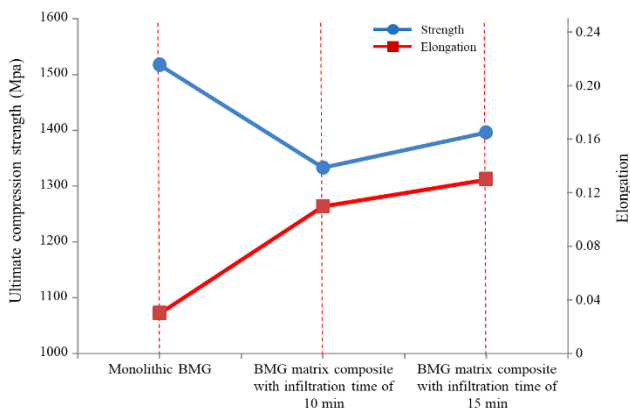


Figure 9. Compression test results of the monolithic BMG and W/BMG composites

Increasing the infiltration time causes higher compression strength of the composite (1333 MPa for infiltration time of 10 min and 1396 MPa for infiltration time of 15 min), which is attributed to the lack of porosities and distribution of small intermetallics inside the matrix. The compression strain of W/BMG composites is 0.11 for infiltration time of 10 min and 0.13 for infiltration time of 15 min, which is almost three times higher than the monolithic BMG (0.03). The presence of long tungsten fibers in the composite prevents the rapid propagation of shear bands in the matrix and leads to formation of multiple shear bands. This can improve the

plasticity of the composite, similar to the particle-reinforced MGMCs [31]. The plasticity of the composite is slightly increased when the infiltration time is increased, which can be a result of better metallurgical bond between the W fibers and BMG matrix.

4. Conclusions

In this study, the infiltration casting method is used to produce tungsten fiber reinforced Zr-based BMG composites with two different infiltration times.

1. At lower infiltration time of 10 min, a limited interfacial reaction is seen and a sharp W/BMG interface is obtained. Increasing the time to 15 min causes the formation of a Zr/W-rich reaction layer around the tungsten wires.

2. Some equiaxed Zr/W-rich particles are found inside the BMG matrix, when the infiltration time is 15 min. The size of the particles decreases exponentially by getting away from the tungsten wires because the particles farther from the wires have more time and enough temperature to dissolve in the molten matrix and finally become smaller in size.

3. Increasing the infiltration time from 10 min to 15 min leads to a higher compression strength. This is due to the lack of porosities and existence of equiaxed particles which have strengthening effect.

4. The compression strain of the composites is at least three times more than the monolithic BMG, due to the existence of tungsten wires. Increasing the infiltration time leads to increasing the strain which can be attributed to the better metallurgical bond between the W fibers and BMG matrix.

References

- [1] R.D. Conner, A.J. Rosakis, W.L. Johnson, and D.M. Owen, "Fracture toughness determination for a beryllium-bearing bulk metallic glass," *Scr Mater*, vol. 37, pp.1373-1378, 1997.
- [2] C.J. Gilbert, R.O. Ritchie, and W.L. Johnson, "Fracture toughness and fatigue-crack propagation in a Zr-Ti-Ni-Cu-Be bulk metallic glass," *Appl Phys Lett*, vol. 71, pp. 476-478, 1997.
- [3] J. Jayaraj, D.J. Sordellet, D.H. Kim, Y.C. Kim, and E. Fleury, "Corrosion behaviour of Ni-Zr-Ti-Si-Sn amorphous plasma spray coating," *Corrosion Science*, vol. 48, pp. 950-964, 2006.
- [4] M. Chen, "Mechanical behavior of metallic glasses: microscopic understanding of strength and ductility," *Annual Review of Materials Research*, vol. 38, pp. 445-469, 2008.
- [5] Z.P. Lu, C.T. Liu, J.R. Thompson, and W.D. Porter, "Structural amorphous steels," *Phys. Rev. Lett*, vol. 92(24), pp. 245-503, 2004.
- [6] A. Inoue, "Stabilization of metallic supercooled liquid and bulk amorphous alloys," *Acta Materialia*, vol. 48(1), pp. 279-306, 2000.
- [7] H. Choi-Yim, R. Busch, U. Koster, and W.L. Johnson, "Synthesis and characterization of particulate reinforced $Zr_{57}Nb_5Al_{10}Cu_{15.4}Ni_{12.6}$ bulk metallic glass composites," *Acta Materialia*, vol. 47, pp. 2455-2462, 1999.
- [8] R.D. Conner, R.B. Dandliker, V. Scruggs, and W.L. Johnson, "Dynamic deformation behavior of tungsten-fiber/metallic-glass matrix composites" *Inter J Impact Eng*, vol. 24 (5), pp. 435-444, 2000.

- [9] B. Clausen, Y. Lee S, E. Üstündag, C.C. Aydiner, R.D. Conner, and M.A.M. Bourke, "Compressive yielding of tungsten fiber reinforced bulk metallic glass composites," *Scripta Materialia*, vol. 49(2), pp. 123-128, 2003.
- [10] K.Q. Qiu, A.M. Wang, H.F. Zhang, B.Z. Ding, and Z.Q. Hu, "Mechanical properties of tungsten fiber reinforced ZrAlNiCuSi metallic glass matrix composite," *Intermetallics*, vol. 10(11-12), pp. 1283-1288, 2002.
- [11] J. Qiao, H. Jia, and P.K. Liaw, "Metallic glass matrix composites" *Materials Science and Engineering R*, vol. 100, pp. 1-69, 2016.
- [12] Y.L. Huang, A. Bracchi, T. Niermann, M. Seibt, D. Danilov, B. Nestler, and S. Schneider, "Dendritic microstructure in the metallic glass matrix composite $Zr_{56}Ti_{14}Nb_5Cu_7Ni_6Be_{12}$," *Scripta Materialia*, vol. 53(1), pp. 93-97, 2005.
- [13] W. Löser, J. Das, A. Güth, H.J. Klauß, C. Mickel, U. Kühn, J. Echert, S.K. Roy, and L. Schultz, "Effect of casting conditions on dendrite-amorphous/nanocrystalline Zr-Nb-Cu-Ni-Al in situ composites," *Intermetallics*, vol. 12(10-11), pp. 1153-1158, 2004.
- [14] Z. Bian, G. He, and G.L. Chen, "Investigation of shear bands under compressive testing for Zr-base bulk metallic glasses containing nanocrystals," *Scripta Materialia*, vol. 46(6), pp. 407-412, 2002.
- [15] G. He, W. Loser, and J. Eckert, "In situ formed Ti-Cu-Ni-Sn-Ta nanostructure-dendrite composite with large plasticity" *Acta Materialia*, vol. 51(17), pp. 5223-5234, 2003.
- [16] H. Kato, T. Hirano, A. Matsuo, Y. Kawamura, and A. Inoue. "High strength and good ductility of $Zr_{55}Al_{10}Ni_5Cu_{30}$ bulk glass containing ZrC particles," *Scripta Materialia*, vol. 43, pp. 503-507, 2000.
- [17] B.Y. Zhang, X.H. Chen, S.S. Wang, D.Y. Lin, and X.D. Hui, "High strength tungsten wire reinforced Zr-based bulk metallic glass matrix composites prepared by continuous infiltration process," *Materials Letters*, vol. 93, pp. 210-214, 2013.
- [18] H. Choi-Yim, R.D. Conner, F. Szuets, and W.L. Johnson, Quasistatic and dynamic deformation of tungsten reinforced $Zr_{57}Nb_5Al_{10}Cu_{15.4}Ni_{12.6}$ bulk metallic glass matrix composites, *Scr. Mater*, vol. 45, pp. 1039-1045, 2001.
- [19] B.P. Wang, B.Q. Yu, Q.B. Fana, J.Y. Liang, L. Wang, Y.F. Xue, H.F. Zhang, and H.M. Fue, "Anisotropic dynamic mechanical response of tungsten fiber/Zr-based bulk metallic glass composites," *Materials and Design*, vol. 93, pp. 485-493, 2016.
- [20] M.L. Wang, G.L. Chen, X. Hui, Y. Zhang, and Z.Y. Bai, "Optimized interface and mechanical properties of W fiber/ Zr-based bulk metallic glass composites by minor Nb addition," *Intermetallics*, vol. 15, pp. 1309-1315, 2007.
- [21] C. Du, D. Shu, Z. Du, G. Gao, M. Wang, Z. Zhu, and L. Xu, "Effect of L/D on penetration performance of tungsten fibre/ Zr-based bulk metallic glass matrix composite rod," *International Journal of Refractory Metals & Hard Materials*, vol. 85, pp. 105042, 2019.
- [22] Y. Mao, J.W. Coenen, J. Riesch, S. Sistla, J. Almanstötter, B. Jasper, A. Terra, T. Höschen, H. Gietl, C. Linsmeier, and C. Broeckmann, "Influence of the interface strength on the mechanical properties of discontinuous tungsten fiber-reinforced tungsten composites produced by field assisted sintering technology," *Compos. Part A Appl. Sci. Manuf*, vol. 107, pp. 342-353, 2018.
- [23] M.L. Wang, G.L. Chen, X. Hui, Y. Zhang, and Z.Y. Bai, "Optimized interface and mechanical properties of W fiber/ Zr-based bulk, metallic glass composites by minor Nb addition," *Intermetallics*, vol. 15(10), pp. 1309-1315, 2007.
- [24] Z.K. Li, H.M. Fu, P.F. Sha, Z.W. Zhu, A.M. Wang, H. Li, H.W. Zhang, H.F. Zhang, and Z.Q. Hu, "Atomic interaction mechanism for designing the interface of W/Zr-based bulk metallic glass composites," *Sci. Rep*, vol. 5, pp. 8967, 2015.
- [25] D. Dragoi, E. Ustundag, B. Clausen, and M.A.M. Bourke, "Investigation of thermal 544 residual stresses in tungsten-fiber/bulk metallic glass matrix composites," *Scripta. 545 Mater*, vol. 45(2), pp. 245-252, 2001.
- [26] Z.Q. Hu, A.M. Wang, and H.F. Zhang, "Amorphous Materials," In: Xu R, Xu Y, editors. *Modern Inorganic Synthetic Chemistry*. second ed. Netherlands: Elsevier; 2017. pp. 641-667.
- [27] Z. Xiaoping, L. Shukui, L. Jinxiu, W. Yingchun, and W. Xing. "Self-sharpening behavior during ballistic impact of the tungsten heavy alloy rod penetrators processed by hot-hydrostatic extrusion and hot torsion," *Materials Science and Engineering A*, vol. 527, pp. 4881-4886, 2010.
- [28] R. Luo, D. Huang, M. Yang, E. Tang, M. Wang, and L. He, "Penetrating performance and "self-sharpening" behavior of fine-grained tungsten heavy alloy rod penetrators," *Materials Science and Engineering: A*, vol. 675, pp. 262-270, 2016
- [29] R.B. Dandliker, R.D. Conner, and W.L. Johnson, "Melt infiltration casting of bulk metallic-glass matrix composites," *Journal of Materials Research*, vol. 13, pp. 2896-2901, 1998.
- [30] W.L. Johnson, "Bulk glass-forming metallic alloys: Science and technology," *MRS Bulletin*, vol. 24, pp. 42-56, 1999.
- [31] T. Liu, P. Shen, F. Qiu, T. Zhang, and Q. Jiang, "Microstructures and mechanical properties of ZrC reinforced (Zr-Ti)-Al-Ni-Cu glassy composites by an in situ reaction," *Advanced Engineering Materials*, vol. 11, pp. 392-398, 2009.