Innovative approach to the design of low-cost Zr-based BMG composites with good glass formation

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The high manufacturing cost for metallic glasses hampers actual commercial applications of this class of fascinating materials. In this letter, the effect of oxygen impurity on the glass forming ability and tensile properties of Zr-BMG composites were studied. Our results have demonstrated that oxygen was absorbed and concentrated only in the precipitated β-Zr phase, leading that the remainder molten metal retains good glass forming ability. The high oxygen concentration in the β-Zr phase induces a significant solid-solution strengthening effect, this resulting in an enhanced strength of the BMG composites without sacrificing their overall ductility. Based on this alloying strategy, we have successfully developed the low-cost Zr-based BMG composites with excellent tensile properties and good glass forming ability, using the low grade industrial raw materials processed under industrial vacuum systems. This finding is expected to greatly cut down the manufacturing cost and greatly promote the commercial applications of the BMG composites.

Bulk metallic glasses (BMGs) have been studied extensively in recent years because of their intriguing mechanical, chemical, and physical properties1–3. However, their room-temperature brittleness and high manufacturing cost have been the two stumbling blocks for actual commercial applications. To circumvent the room-temperature brittleness, one effective method is to develop in-situ BMG matrix composites by precipitating out ductile crystalline phases during solidification from the molten state. This method can significantly improve the ductility of several Zr-3–9, Ti-10 and La-based11 BMG composites. However, these BMG composites were prepared in high vacuum systems using high-purity raw materials containing very low level interstitial impurities, such as oxygen. This dramatically increases the manufacturing cost. Therefore, for widespread applications of BMGs, it is vitally important for us to develop innovative ways to manufacture BMG composites using industrial-grade raw materials and processing in conventional industrial systems.

It is well known that requirements of high-purity charge materials and high vacuum condition are primary for eliminating the detrimental effect of oxygen, which is a major impurity in low-grade raw materials and basically unavoidable during the production of BMGs. In general, oxygen has been known to be the major reason for the formation of intermetallic oxide particles12 or metastable phases such as quasicrystalline phases13,14, leading to a sharp decrease of glass forming ability (GFA). Moreover, dissolution of even small amounts of oxygen also severely deteriorates the mechanical properties of BMGs, especially ductility12,15,16.

To alleviate the harmful effect of oxygen impurities, Liu et al.12 show that microalloying with B had a marginal beneficial effect on the suppression of crystalline-phase formation. Lu et al.17 reported that yttrium can act as an oxygen scavenger to purify the molten liquid to a certain extend and enable the formation of the glass matrix in Fe-based BMGs. Similar results were also reported by Heinrich et al.18 in Zr-based BMGs with aluminum as an oxygen scavenger. Like the yttrium and aluminum, zirconium also has a strong affinity for oxygen atoms as compared with other alloying elements added in Zr-based alloys19. Moreover, it is well known that oxygen has a high solubility (~ 30 at. %) in crystalline Zr20. Based on these considerations, it appears to be feasible for using Zr precipitates as oxygen scavengers to remove oxygen from the glass matrix, even the matrix is active and is based on Zr.

To demonstrate the beneficial role of Zr precipitates, we had systematically added various levels of oxygen sources to the Zr-Ti-Nb-Cu-Ni-Be glass composite containing Zr particles. The key finding of our study is that the
Oxygen is essentially absorbed by Zr precipitates, and the remaining molten liquid with much lower oxygen content (< 200 wt. ppm) readily forms the glass matrix with high GFA. Furthermore, we also found that the intentionally added oxygen impurities have a strong solid-solution hardening effect when absorbed by \( \beta \)-Zr precipitates in the liquid state, resulting in the significant enhancement of the overall yield strength without lowering the tensile ductility of the glass-matrix composite. It is important to note that our finding opens a new window to produce ductile but strong BMG composites with good GFA, using low-grade raw materials and being processed in industrial vacuum systems. Enabling their industrial production should tremendously boost the engineering application of BMG composites.

**Results**

Table 1 shows the inert gas fusion (IGF) analysis results of the oxygen content in the 11 mm as-cast rods doped with different amounts of \( \text{ZrO}_2 \). As indicated in Table 1, the measured oxygen concentration is well consistent with the nominal content, confirming that the addition of \( \text{ZrO}_2 \) as an oxygen source is successful. Moreover, the low-purity alloy made from Zr sponges has an oxygen concentration of 980 ppm, which is much higher than 0-added alloy.

Figure 1 shows the representative cross section of the current alloys doped with different oxygen contents. It can be seen that there are two kinds of BMG composite microstructures. The 0-added, low-purity and 4000-added alloys have the similar microstructures which contain the coarse and spherical crystalline phases homogeneously embedded in the glass matrix. The average diameter of the spherical particles is approximately 42.5 µm, and the volume fraction of the primary phase is 50%~55%. It is worthy of noting that there exist another crystal phase (denoted by arrows in Fig. 1(d)) precipitates in the center of primary phase in the 10000-added alloy. Moreover, no obvious oxides can be detected for all the alloys, indicating that oxygen is homogeneously dissolved in the glass matrixes or crystalline phases.

XRD patterns of the present BMG composites are shown in Fig. 2(a). The XRD traces of the alloys 0-added, low-purity and 4000-added are typical for the BMG composites with body-centered cubic (bcc) \( \beta \)-Zr precipitates uniformly embedded in the BMG matrix.

| Alloys number | IGF (wt. ppm) | Structure | EPMA (wt. ppm) | H (GPa) | E (GPa) |
|---------------|--------------|-----------|---------------|---------|---------|
| 0-added       | 210          | Glass matrix | < 200  | 8.4     | 112     |
|               |              | \( \beta \)-Zr phase | 500    | 5.3     | 92      |
| Low purity    | 980          | Glass matrix | < 200  | 8.5     | 110     |
|               |              | \( \beta \)-Zr phase | 1800   | 5.8     | 98      |
| 2000-added    | 2400         | Glass matrix | < 200  | 8.5     | 113     |
|               |              | \( \beta \)-Zr phase | 4300   | 6.1     | 107     |
| 4000-added    | 4400         | Glass matrix | < 200  | 8.6     | 115     |
|               |              | \( \beta \)-Zr phase | 8200   | 6.8     | 117     |
| 10000-added   | 10600        | Glass matrix | < 200  | 8.5     | 114     |
|               |              | \( \beta \)-Zr phase | 15000  | 7.2     | 121     |
|               |              | \( \alpha \)-Zr phase | 32300  | 7.6     | 127     |

**Figure 1** Optical micrographs of (a) 0-added alloy, (b) low-purity alloy, (c) 4000-added alloy (inset shows composition profile of oxygen in the selected line using the WDS line scan) prepared by SSPS, and (d) 10000-added alloy prepared by arc-melting master alloy. Arrow indicates the \( \alpha \)-Zr phase in the center of \( \beta \)-Zr precipitates.
matrix, which is consistent with the microstructures shown in Fig. 1(a-c). However, besides the \(\beta\)-Zr phase, some other sharp diffraction peaks corresponding to the hexagona close-packed (hcp) \(\alpha\)-Zr phase are observed in 10000-added alloy. This is again consistent with the microstructural observation (Fig. 1(d)). The Zr-O phase diagram indicates that, under high temperatures, oxygen could completely dissolve into the \(\beta\)-Zr phase. As the temperature decreases, the saturated oxygen would induce the \(\beta\)-Zr \(\rightarrow\) \(\alpha\)-Zr phase transformation and result in the precipitation of the \(\alpha\)-Zr phase from the \(\beta\)-Zr phase precipitates.

The typical DSC curves for the alloys with different oxygen contents are shown in Fig. 2(b). As can be seen, the entire alloys exhibit the similar glass transition and crystallization behavior, the glass transition temperature (T_g) and the onset crystallization temperature (T_x) keep almost the same, and they are independent of the oxygen contents. This not only demonstrates the amorphous characteristic of the composite matrixes, but also indicates the composition of the glass matrixes is nearly the same. Based on these results, we believe that oxygen mainly dissolves into the \(\beta\)-Zr and \(\alpha\)-Zr phases, and the glass matrixes contain a very limited oxygen level.

### Discussion

To provide with more evidences to our claims, electron probe micro-analysis (EPMA) measurements were carried out to analyze the oxygen distribution in the composites. Table 1 lists the oxygen concentration in both the glass matrixes and crystalline phases. As can be seen, although the oxygen content is increased to 10,000 ppm, the glass matrix still contains very low oxygen level less than the detection limit of the EPMA analyzer (\(~200\) wt. ppm). However, the oxygen concentration in the \(\beta\)-Zr phase increases significantly. The inset in the Fig. 1(c) shows the oxygen distribution obtained by line scanning in the 4000-added alloy. It clearly reveals that the oxygen is only absorbed and dissolved homogeneously into the \(\beta\)-Zr particles, and the glass matrix contains very low oxygen level.

To further investigate the GFA of the glass matrixes, the microstructure evolution for 0-added, low-purity and 4000-added alloy was studied experimentally by the Bridgman technique. As shown in Fig. 3, all the alloys have the same critical withdraw rate (which is related to a cooling effect) of 0.46 mm/s during solidification, at which the eutectic cells are precipitated out from the glass matrix. In the other words, the glass formation of the matrix is not affected by

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**Figure 2** | XRD patterns (a) and DSC curves (b) for the composites added with different amounts of oxygen.

**Figure 3** | OM micrographs of alloys subjected to Bridgman solidification at withdrawal velocities of (a) 1.0 mm/s, (b) 0.46 mm/s for 0-added alloy and (c) 1.0 mm/s, (d) 0.46 mm/s for 4000-added alloy. Arrows indicate the eutectic cell precipitates.
the oxygen levels. This strongly suggests that the GFA of the glass matrix is independent of the oxygen level and can be obtained using the low-grade industrial raw materials at a low vacuum condition. This is vitally important for BMG manufacturing used for commercial applications.

It is interesting to point out that this oxygen segregation in the $\beta$-Zr phase has also a strong effect on the mechanical properties of the composites. The hardness (H) and elastic modulus (E) of the $\beta$-Zr phases and the glass matrix in the BMG composites with different oxygen contents were measured by a nanoindentor. The results are summarized in Table 1. It is clear that the hardness and elastic modulus of the glass matrixes are invariable with whatever the oxygen contents added. This result further confirms that the compositions and structures of the glass matrixes in the BMG composites with different oxygen content are similar. However, the hardness and elastic modulus of the crystalline $\beta$-Zr phase increase significantly with the increase in oxygen content. It is reasonable to rationalize that this increase is due to solid-solution strengthening induced by solute oxygen in the $\beta$-Zr particles.

Figure 4 shows the results of the tensile properties of the composites prepared by semi-solid progressive solidification (SSPS). It is exciting to see that the low-purity and 2000-added alloys exhibit the optimum mechanical properties. In comparison with the 0-added composite, the low-purity composite shows a substantial increase in the yield strength from 1080 to 1220 MPa without any reduction of the ductility, and the yield strength is further increased to 1302 MPa for the 2000-add composite. This result is very interesting and important for the industrial use of BMG materials. With a further increase in oxygen from 2000 to 4000 ppm, the ductility decrease sharply. As indicated in Fig. 4, the composite loses all the tensile ductility when the oxygen reaches 4000 ppm. Hofmann et al. proposed that soft precipitated phases with lower shear moduli were necessary to design BMG composites with tensile ductility. Therefore, the brittle of 4000-added composite may be attributed to the result of excessive solid-solution hardening effect of oxygen which induces the high elastic modulus and hardness of $\beta$-Zr phase. Another possible reason is the direct embrittlement of the $\beta$-Zr phase. The oxygen embrittlement has been observed in some Ti, Ta and Mo alloys containing excessive oxygen. Figure 5 shows the fractographs of the low-purity and 4000-added alloys. The low-purity alloy exhibits a classic cup-and-cone fracture, as shown in the inset of Fig. 5(a). Many ductile tear-off marks can be observed on the fracture surface, in agreement with the ductile behavior of $\beta$-Zr particles. However, the 4000-added alloy shows typical brittle fracture morphology.

It is worth to note that, similar to the Zr element, Ti also has a strong affinity and large solubility for oxygen. Thus, we think that the current approach could be readily extended to Ti-BMG composites. Moreover, some other interstitial elements such as N, C and H, which have been regarded as common impurities in Zr, Ti and their alloys, also may act as alloying elements/impurities to improve the mechanical properties of BMG composites, rather than deteriorate their glass forming ability.

In summary, the Zr-BMG composites with different oxygen levels were fabricated. Our results show that Zr precipitates act as an effective scavenger to remove oxygen from the molten liquid, resulting in a very limited oxygen concentration in the BMG matrix. This retains the good glass forming ability of BMG matrix in the BMG composites manufactured from impure raw materials. The solubility of oxygen in the $\beta$-Zr phase induces a significant solid-solution strengthening effect, which enhances the strength of the BMG composites without sacrificing their overall ductility. The BMG composites with optimum mechanical properties can then be obtained using the low grade industrial raw materials processed under industrial vacuum systems. This finding is expected to greatly cut down the manufacturing cost and greatly promote the commercial applications of the BMG composites.

**Methods**

$Zr_{60.1}Ti_{45.9}Nb_{1.2}Cu_{35.3}Ni_{44.6}Be_{10}$ (at. %) alloys with different oxygen concentration (0 ppm, 2000 ppm, 4000 ppm and 10000 ppm wt. %) were prepared by arc-melting a mixture of high purity (> 99.9%) raw metals and ZrO$_2$ of 99.99 purity under a Ti-gettered argon atmosphere. Some alloys were also prepared using low grade raw materials (commercial sponge Zr and Ti with purity ~99.2% containing 1300 ppm oxygen) under a low vacuum condition (a vacuum of 10 Pa). We refer to these alloys as 0-added, 2000-added, 4000-added, 10000-added and low-purity alloys. Samples with 11 mm diameter were prepared using the semi-solid progressive solidification (SSPS) method. The detail experiments were shown elsewhere.

![Figure 5](image1.png)  
**Figure 5** | SEM images of the fracture surfaces for (a) low-purity alloy and (b) 4000-added alloy, the insets show their macroscopic necking.
The microstructure and phase identification in the as-cast samples with different oxygen contents were carried out using an optical microscopy and an X-ray diffractometer (XRD) with a Cu Kα radiation, respectively. An average value of oxygen concentration in the samples was measured using a LECO-TC436 inert gas fusion (IGF) nitrogen/oxygen analyzer. Oxygen contents at the precipitate crystals and the BMG matrix were also analyzed using electron probe micro-analysis (EPMA) equipped with wavelength dispersive spectroscopy (WDS). Thermal property measurements were conducted using a differential scanning calorimeter (DSC) at a heating rate of 20 K/min. Specimens for tensile test with a gauge length of 36 mm and 6 mm in diameter were prepared according to the ASTM E8M standard. Tensile tests were carried out at room temperature using an initial engineering strain rate of 2 × 10−4 s−1 and a strain gauge was used to measure the engineering strain. CSM-NHT2 nanoindentation instrument was used to measure the hardness and elastic modulus of the primary crystal phases and the glass matrix with different oxygen contents.

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Author contributions
J.L.C., G.C., C.T.L. and Y.L. designed the experiments. J.L.C. carried out the experiments. All authors analyzed the data and wrote the paper.

Additional information
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