Vickers hardness and compressive properties of bulk metallic glasses and nanostructure-dendrite composites

X.F. Pan
Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, People’s Republic of China; and School of Materials Science and Engineering, Tianjin University, Tianjin 300072, People’s Republic of China

H. Zhang and Z.F. Zhang
Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, People’s Republic of China

M. Stoica
Leibniz Institute for Solid State and Materials Research Dresden, Institute of Metallic Materials, D-01171 Dresden, Germany

G. He
School of Materials Science and Engineering, Shanghai Jiaotong University, Shanghai 200030, People’s Republic of China

J. Eckert
Physical Metallurgy Division, Department of Materials and Geo Sciences, Darmstadt University of Technology, D-64287 Darmstadt, Germany

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The compressive properties and the Vickers hardness of Cu-, Fe-, Mg-, and Zr-based monolithic bulk metallic glasses (BMGs) as well as Ti-based nanostructure-dendrite composites were investigated and compared. The monolithic BMGs exhibit nearly the same yield strength \( \sigma_y \) and fracture strength \( \sigma_f \) but poor plasticity. The Vickers hardness \( H_V \) of the monolithic BMGs follows the empirical relationship \( H_V/3 \approx \sigma_y \approx \sigma_f \). The Ti-based composites yield at a relatively low stress level (less than 850 MPa) but fail at a very high fracture stress (2 GPa) and exhibit a large strain hardening ability. Accordingly, the Vickers hardness \( H_V \) of the Ti-based nanostructure-dendrite composites obeys the relationship \( \sigma_y < H_V/3 < \sigma_f \). Based on these results, the relationship between the Vickers hardness and the compressive properties of the investigated materials will be discussed by taking the yield and fracture strength (\( \sigma_y \) and \( \sigma_f \)), the strain hardening exponent \( n \), and the elastic and plastic energy stored upon deformation (\( \delta_E \) and \( \delta_P \)) into account.

I. INTRODUCTION

In 1960, an Au–Si metallic alloy with amorphous structure was first discovered.\(^1\) After that, many attempts have been devoted to amorphization of a variety of alloys.\(^2\)–\(^4\) Finally, starting at the at the beginning of the 1990s and continuing since then, Zr-, Cu-, and Pd-based bulk metallic glasses and also other classes of easy glass-forming alloys were discovered and successfully fabricated.\(^5\)–\(^7\) A large amount of investigations in the recent decade has demonstrated that bulk metallic glasses (BMGs) possess novel physical, chemical, and mechanical properties and have a large potential for a variety applications,\(^8\)–\(^10\) which has created extensive interest among scientists and engineers. Normally, metallic materials with glassy structure exhibit very high strength and hardness value, a relatively low Young’s modulus, and almost perfect elastic-plastic behavior upon room temperature deformation.\(^11\),\(^12\) Therefore, the discovery of BMGs opens up new opportunities to reveal the basic deformation and fracture mechanisms of matter.\(^13\)

In addition to monolithic metallic glasses, in situ formed Zr- and Ti-based metallic glass matrix composites with ductile dendritic precipitates as well as nanostructure/dendrite composites have recently been obtained, which
exhibit a dramatic increase in plastic deformability under quasi-static compression.14–18 The enhanced ductility of such composites is attributed to the blocking effects of the dendrites dispersed in the matrix, acting as obstacles hindering the propagation of shear bands.14,15,17–20

Compressive testing and Vickers hardness measurements are two typical and convenient methods for revealing the deformation and fracture mechanisms of BMG materials. By employing these techniques, one can easily measure the yield and fracture strength ($\sigma_y$ and $\sigma_f$), the ductility, Young’s modulus, and the hardness of the materials. A large amount of investigations have shown that there is an empirical relationship, i.e., $\sigma_f = H_v /3$,21 between the fracture strength $\sigma_f$ and the Vickers hardness $H_v$ of monolithic bulk metallic glasses.22–25 However, so far there is no report about such a relationship for BMGs or nanostructured composites containing ductile dendrites. In this work, we investigated a series of metallic glasses with a wide range of fracture strength and Young’s modulus and compare the data with the results obtained for Ti-based nanostructure-dendrite composites. The main purpose of this work is to reveal the factors affecting the hardness of the materials by taking their compressive properties into account.

II. EXPERIMENTAL PROCEDURE

Five different metallic glassy alloys or nanostructure-dendrite composites were used for the current investigations, i.e., (i) monolithic metallic glasses, including Mg65Cu7.5Ni7.5Zn5Ag5.5Y10, Zr59Cu20Al10Ni8Ti3, Cu60Zr30Ti10, and Fe65.5Cr4Mo4Ga4P12C5B5.5, and (ii) Ti50Cu22Ni20Sn3Si2B3 nanostructured composites with ductile body-centered-cubic (bcc) type dendrites. The monolithic BMGs were prepared by arc melting the mixture of the pure elements in a Ti-gettered argon atmosphere to obtain master ingots. These master ingots were then remelted several times to ensure the homogeneity. To prepare the Ti50Cu22Ni20Sn3Si2B3 composites, one method was to cast the master alloy ingots into a copper mold of dimensions $3 \times 100$ mm. Alternatively, the composites were prepared by arc-melting the master alloy ingots several times and cooling on the copper hearth at a slower rate. The Ti50Cu22Ni20Sn3Si2B3 composites fabricated by both arc-melting and casting consisted of a nanostructured matrix and ductile bcc-type dendritic precipitates.30 The details of the fabrication processes of the BMGs and the nanostructure-dendrite composites have already been described elsewhere.17,18,30–33

The Vickers hardness was measured using a MVK-H3 Vickers microhardness tester. For these measurements, the specimen surfaces were carefully polished before testing. The tests were preformed using a typical diamond indenter in the form of pyramid with square base and an angle of 136° between opposite faces. A load of 4.9 N was applied for 10 s. The diagonal of the indentation as well as the hardness was calculated using a digital video measuring system.

Two kinds of samples, i.e., rectangular bars with dimensions of $3 \times 3 \times 6$ mm or rods with dimensions of $\Phi 3 \times 6$ mm, were machined from the as-solidified specimens for compression testing. The tests were performed using a MTS810 test system at a strain rate of $10^{-4}$ s$^{-1}$ at room temperature. From the compression stress–strain curves, the yield strength $\sigma_y$, the yield strain $\varepsilon_y$, the fracture strength $\sigma_f$, the fracture strain $\varepsilon_f$, and Young’s modulus $E$ were derived. To investigate the effects of indentation on the formation of the shear bands, the Vickers hardness tester was used to induce a series of indentations on the polished surfaces of some of the samples before compression testing. The characteristics of the fracture surfaces as well as the features of the indents after the hardness tests were studied by using a Cambridge S360 scanning electron microscope (SEM).

III. RESULTS AND DISCUSSION

Figure 1 shows the room-temperature compressive stress–strain curves of all the BMGs and the Ti-based composites. The mechanical properties of all the samples (A–F) are listed in Table I. It can be seen that the fracture strength $\sigma_f$ of the different alloys spans over a wide range of 851–2840 MPa; Young’s modulus $E$ also varies greatly between 49 and 161 GPa, as shown in Table I. The plastic strain at failure for the monolithic metallic glass samples A, D, E, and F is less than 1.0%, but the Ti-based composites exhibit a relatively high ductility of 4.4% (B) or 11.5% (C), respectively. Another feature is that the yield strength $\sigma_y$ of all the monolithic metallic glasses is quite close to the fracture strength $\sigma_f$, indicating that there is no obvious strain hardening before
failure. The yield strength of the Ti-based composites B and C are 647 and 817 MPa. These alloys display a pronounced strain-hardening ability, and their final fracture strength reaches values of 1880 MPa (B) or 1970 MPa (C), respectively.

The fracture surfaces of the Zr$_{59}$Cu$_{20}$Al$_{10}$Ni$_{8}$Ti$_{3}$ monolithic metallic glass and of the as arc-melted Ti$_{50}$Cu$_{22}$Ni$_{20}$Sn$_{3}$Si$_{2}$B$_{3}$ composite are shown in Fig. 2. For the fully amorphous alloy, failure occurs in a shear mode, and the shear fracture surface makes an angle of approximately 43° with respect to the compression axis. The shear fracture surface exhibits typical veinlike patterns [Figs. 2(a) and 2(b)], as reported also for different metallic glasses. A similar fracture feature was also observed in A, D, E, and F monolithic BMG samples. The fracture surface of the arc-melted Ti-based composite sample (B) displays a relatively rough feature in comparison with the fully amorphous alloys [Fig. 2(c)]. The rough fracture surface of the composite can be attributed to the strong interactions between shear bands and the dendrites, resulting in a high ductility. The typical shear fracture surfaces of the composites still contain veinlike features, as displayed in Fig. 2(d), indicating the occurrence of melting during shear fracture.

Figure 3(a) shows the dependence of Vickers hardness $H_v$ on the applied load for Zr$_{50}$Cu$_{20}$Al$_{10}$Ni$_{8}$Ti$_{3}$ (D) and Ti$_{50}$Cu$_{22}$Ni$_{20}$Sn$_{3}$Si$_{2}$B$_{3}$ (B) samples, respectively. It can be seen that the hardness decreases with increasing the applied load $P$. When the applied load is higher than 1 N, the hardness approximately remains constant. These results for the metallic glasses are similar to the experimental results reported by Li et al. They found that the indenter/specimen interfacial friction in Vickers indentation testing has a minimal effect in the high load regime whereas it has a significant effect in the low load regime. Therefore, a load in the range of 1–10 N, i.e., 4.9 N was selected for the current hardness tests.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metallic glasses</th>
<th>$\sigma_y$ (MPa)</th>
<th>$\epsilon_y$ (%)</th>
<th>$\sigma_f$ (MPa)</th>
<th>$\epsilon_f$ (%)</th>
<th>$E$ (GPa)</th>
<th>$H_v$ (GPa)</th>
<th>$\delta_E$ (MJ/m$^3$) (%)</th>
<th>$\delta_f$ (MJ/m$^3$) (%)</th>
<th>$\delta_E/\delta_f$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Mg$<em>{62}$Cu$</em>{13}$Ni$_{7}$Zn$_3$Ag$<em>8$Y$</em>{10}$</td>
<td>851</td>
<td>1.76</td>
<td>851</td>
<td>0</td>
<td>49</td>
<td>2.35</td>
<td>7.37</td>
<td>7.37</td>
<td>100</td>
</tr>
<tr>
<td>B</td>
<td>Ti$<em>{50}$Cu$</em>{22}$Ni$_{20}$Sn$_3$Si$_2$B$_3$ (arc-melting)</td>
<td>647</td>
<td>2.9</td>
<td>1880</td>
<td>11.5</td>
<td>68</td>
<td>3.44</td>
<td>25.99</td>
<td>155.3</td>
<td>17.3</td>
</tr>
<tr>
<td>C</td>
<td>Ti$<em>{50}$Cu$</em>{22}$Ni$_{20}$Sn$_3$Si$_2$B$_3$ (as-cast)</td>
<td>817</td>
<td>2.0</td>
<td>1970</td>
<td>4.4</td>
<td>70</td>
<td>4.38</td>
<td>27.72</td>
<td>69.4</td>
<td>40.1</td>
</tr>
<tr>
<td>D</td>
<td>Zr$<em>{50}$Cu$</em>{20}$Al$<em>{10}$Ni$</em>{8}$Ti$_{3}$</td>
<td>1610</td>
<td>1.0</td>
<td>1710</td>
<td>0.8</td>
<td>78</td>
<td>4.69</td>
<td>18.74</td>
<td>29.81</td>
<td>62</td>
</tr>
<tr>
<td>E</td>
<td>Cu$<em>{60}$Zr$</em>{50}$Ti$_{10}$</td>
<td>1720</td>
<td>1.9</td>
<td>2010</td>
<td>0.4</td>
<td>99</td>
<td>5.78</td>
<td>20.16</td>
<td>27.14</td>
<td>74.3</td>
</tr>
<tr>
<td>F</td>
<td>Fe$<em>{65}$Cr$</em>{30}$Ti$_{5}$</td>
<td>2820</td>
<td>1.76</td>
<td>2840</td>
<td>0.15</td>
<td>161</td>
<td>8.67</td>
<td>25.05</td>
<td>28.5</td>
<td>87.9</td>
</tr>
</tbody>
</table>

FIG. 2. Typical fracture surface features of some metallic glasses: (a, b) Zr$_{50}$Cu$_{20}$Al$_{10}$Ni$_{8}$Ti$_{3}$ and (c, d) Ti$_{50}$Cu$_{22}$Ni$_{20}$Sn$_3$Si$_2$B$_3$ (as-arc-melted).
The hardness values for all the samples studied here increase in the order of A–F from 2.35 to 8.67 GPa, as listed in Table I. For all the monolithic BMGs, their yield strength and fracture strength are almost the same. Therefore, the ratios of $H_V/3\sigma_y$ or $H_V/\sigma_f$ for various metallic glasses available$^{22–29}$ are shown in Figs. 4(a) and 4(b). The data for the BMGs investigated in our study are also plotted in Figs. 4(a) and 4(b) for comparison. First, $H_V$ follows an approximately linear relationship with Young’s modulus $E$ for a large number of metallic glasses over a wide range of $E$, as shown in Fig. 4(a). This indicates that the hardness $H_V$ is proportional to the Young’s modulus $E$ for a variety of metallic glasses.$^{22–29}$ Secondly, the hardness of all the monolithic BMGs follows the relationship $\sigma_f = H_V/3$ because their yield and fracture strength are nearly the same, as shown in Fig. 4(b). Since the Ti-based composites B and C exhibit higher ductility and strong strain hardening, their yield and fracture strength have a great difference. Therefore, the ratios of $H_V/\sigma_y$ or $H_V/\sigma_f$ for the Ti-based composites B and C always deviate from the trend line in Fig. 4(b). This gives rise to the question of what is the major factor affecting the hardness of the Ti-based composites in the regime between the yield and the fracture strength. This issue will be discussed below.

The SEM micrographs of the indentations on the surfaces of the samples C and D before and after compression testing are shown in Fig. 5. For the monolithic metallic glass D, “coronet” shear bands are observed at the edge of the indentation put down before the compression test [Fig. 5(a)]. The newly formed shear bands introduced during compression pass through the indentation and the “coronet” shear bands. However, the shape and propagation direction of the initial shear bands introduced by indentation do not change after compression [Fig. 5(b)]. Also the indentations on the surfaces of the as-cast Ti-based composite (C) maintain the same shape after the compressive test [see Figs. 5(c) and 5(d)]. This indicates that the existing indentations on the surfaces of both the monolithic BMGs and the Ti-based composites do not affect the formation and development of the new shear bands introduced upon compression.

### Table II. Relationship between tensile strength and hardness of some nano-materials$^{36}$

<table>
<thead>
<tr>
<th>Materials</th>
<th>Grain size (nm)</th>
<th>Yield strength $\sigma_y$ (MPa)</th>
<th>Fracture strength $\sigma_f$ (MPa)</th>
<th>Hardness (GPa)</th>
<th>$H_V/\sigma_y$</th>
<th>$H_V/\sigma_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultra-fine-grained Al</td>
<td>250</td>
<td>135</td>
<td>220</td>
<td>1.0</td>
<td>7.4</td>
<td>4.5</td>
</tr>
<tr>
<td>Nano-Cu</td>
<td>26</td>
<td>535</td>
<td>880</td>
<td>2.4</td>
<td>4.5</td>
<td>2.7</td>
</tr>
<tr>
<td>Nano-Ni</td>
<td>28</td>
<td>1150</td>
<td>1550</td>
<td>4.8</td>
<td>4.2</td>
<td>3.1</td>
</tr>
</tbody>
</table>
In addition, the yield strength of these samples are equal to 647 MPa (B), 817 MPa (C), and 1720 MPa (E), respectively. It seems that the material with higher yield strength has a higher hardness. For the Ti-based composites, their hardness follows the relationship \( \sigma_y < \frac{H_V}{3} < \sigma_f \). This indicates that the hardness of these materials with strong strain-hardening ability is not only affected by the fracture strength \( \sigma_f \), but also by the yield strength \( \sigma_y \). For simplicity, it is assumed that the hardness \( H_V \) of such materials can be expressed as a function of the yield strength \( \sigma_y \) and the fracture strength \( \sigma_f \), i.e.,

\[
H_V/3 = x\sigma_y + (1-x)\sigma_f \quad (0 < x < 1),
\]

where \( x \) represents the contribution of yield strength \( \sigma_y \) to the hardness, and \( (1-x) \) reflects the contribution of fracture strength \( \sigma_f \) to the hardness. In the present study, the values of \( x_B \) and \( x_C \) for the samples B and C are 0.59 and 0.44, respectively, as calculated by Eq. (1) and the data in Table I. This indicates that the yield strength plays a more important role in the hardness for sample B than for sample C. In addition, the strain hardening exponent \( n \) represents the hardening rate of a material after yielding. Therefore, the strain hardening exponent \( n \) of the samples B and C was calculated from their stress–strain curves in Fig. 1. The calculated strain hardening exponents \( n \) of the samples B and C are 0.5 and 0.54, respectively. This means that the hardness of the samples with strong strain hardening ability will be higher although they have nearly the same fracture strength \( \sigma_f \). Therefore, the strain hardening exponent \( n \) is also one of the factors affecting the hardness of the materials.

During the compression testing, the total applied energy can be transformed into elastic and plastic energy. The hardness of a material represents its ability to resist permanent plastic deformation. Therefore, the elastic and plastic energy absorbed by a compressed sample should be considered. The normal elastic energy density \( \delta_E \) at failure is given by the shadowed area as illustrated in Fig. 6, and the total energy density \( \delta_T \) is defined as the area below the stress-strain curve. Hence, the difference between \( \delta_T \) and \( \delta_E \) is the plastic energy density \( \delta_p \), and \( \delta_T, \delta_E, \delta_p \) as well as \( \delta_E \) can be expressed as

\[
\delta_T = \int_0^{\sigma_f} \sigma dv, \quad (2)
\]

\[
\delta_E = \frac{\sigma_f^2}{2E}, \quad (3)
\]

\[
\delta_p = \delta_T - \delta_E. \quad (4)
\]

The values of \( \delta_E \) and \( \delta_p \) as well as the ratios of \( \delta_E / \delta_T \) to \( \delta_T \) and \( \delta_p / \delta_T \) were calculated by Eqs. (2)–(4), and are listed in Table I. For the investigated BMG materials, when \( \delta_E / \delta_T \) is larger, the corresponding hardness is
higher. It seems that the relative magnitudes of $PH_{9254}$ and $PH_{9254}$ during the deformation process can also affect the hardness of the Ti-based composites. The hardness will increase with increasing $PH_{9254}$ for samples B, C, D, E, and F. When $PH_{9254}$ is higher, the applied energy related to the plastic deformation is smaller. Thus, the ability of the materials resisting permanent deformation is relatively stronger, resulting in a higher hardness. This might be one of reasons why the hardness of samples B, C, D, E, and F increases with increasing value of $PH_{9254} / PH_{9254}$, if not considering the atomic bonding properties of different composites in the materials above.

From the above discussion, the monolithic metallic glasses were found to obey the well-known empirical relationship $H_{9268} / 3 \approx \sigma_f$. However, the deformation of the Ti-based composites with larger ductility deviates from this relationship. It can be concluded that the hardness of all the BMGs and their composites cannot simply be expressed as $H_{9268} / 3 = \sigma_f$, but other compressive properties, such as $\sigma_y$, $E$, $n$, and $PH_{9254} / PH_{9268}$ also play significant roles in determining the hardness. Therefore, one can assume that the hardness of a material should be a function of these properties, i.e.,

$$H_{9268} / 3 = \sigma_y + f(\sigma_f, E, \delta_E, \delta_T, n) \quad (5)$$

However, the detailed relationship between these parameters is not clear yet, but needs further investigation.

IV. CONCLUSIONS

The monolithic metallic glasses materials exhibit high yield and fracture strength, but poor ductility. Their hardness $H_{9268}$ follows the empirical relationship $H_{9268} / 3 = \sigma_f = \sigma_y$.

The Ti-based nanostructure-dendrite composites exhibit a high fracture strength (~2.0 GPa) and distinct ductility in contrast to the monolithic metallic glasses. They yield at a relatively low stress level (less than 850 MPa) and display a strong strain-hardening ability. Their hardness $H_{9268}$ follows the relationship $\sigma_y < H_{9268} / 3 < \sigma_f$. Accordingly, the hardness of such materials is not only affected by the fracture strength, but also by yield strength.

The elastic energy $\delta_E$ and the plastic energy $\delta_p$ represent the ability of a material to resist the elastic and plastic deformation. The contribution of the elastic and plastic energy $\delta_E$ and $\delta_p$ may also affect the hardness of


FIG. 5. Typical micrograph of indentation: (a, b) the indentations of sample D before and after compressive testing and (c, d) the indentations of sample C before and after compressive testing.
a material. When $\delta_p/\delta_B$ increases, the contribution of the applied energy to the plastic deformation is smaller. As a result, the ability of the material to resist plastic deformation is higher, resulting in a high hardness.

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