

Response to "Comment on 'Pressure-induced amorphization of ZrTiCuNiBe bulk glass-forming alloy'" [Appl. Phys. Lett. 80, 700 (2002)]

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In our letter,¹ we show that high pressure can promote amorphization of the ZrTiCuNiBe bulk glass-forming alloy, and the formed amorphous under high pressure has a minor composition difference compared with that obtained by the water quenched method, but also has marked structural and properties differences. Jiang² made three comments. The first is the amorphous composition difference between alloy A (quenched from water) and alloy B (quenched under high pressure); the second is the density difference between amorphous phases in alloy A and B; and the third is the effect of pressure on amorphization. We agree that both composition shift and pressure have an effect on the density and properties (such as glass transition temperature, crystallization temperature, and acoustic properties), but pressure plays main role in the effect in our case. The following are our responses.

- (1) The crystallization products under high pressure are markedly different from that obtained by crystallization under an ambient condition.³ This can be clearly seen in Fig. 1 in the letter,¹ alloy A and alloy B have markedly different x-ray diffraction patterns, and more crystalline phases appear in alloy A. The crystalline precipitation under high pressure does not mean definitely the composition shift of the amorphous phase. On the other hand, the amorphous phase, with a composition much different from that of $\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$, can not be formed prior to the $\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ alloy, which is known to have best glass-forming ability (GFA) in ZrTiCuNiBe glass-forming alloy. It is difficult to understand that the alloy with marked different composition, which has a poor GFA in ambient conditions, has an advantage over the $\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ BMG in glass formation under high pressure. So the amorphous phase in alloys A and B should have a similar composition. Furthermore, it is known that the differential scanning calorimetry (DSC) curve of the ZrTiCuNiBe alloy is very sensitive to the composition,^{4,5} e.g., the $\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ and $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ BMGs have completely different DSC curve shapes.⁵ DSC curves of alloys A and B in Fig. 2 of the letter¹ show the very similar shape, demonstrating the similar composition of the two amorphous states.
- (2) The increase in density could be caused both by composition shift and pressure. In our case, the relative density increase of alloy B which contains only about 10% crys-

talline phase, which can also be found in the fully crystallized alloy A and more than 10% in fraction volume, is 1.2%, however the fully crystallized $\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ BMG has only a 1.1% density increase relative to the as-prepared BMG.⁶ This indicates the amorphous phase in alloy B has a higher density compared to alloy A. The composition shift is not the main reason for the density difference. On the other hand, the large increases in v_s (11.5%), θ_D (11.5%), and G (about 26.0%) for alloy B relative to alloy A are comparable to those of fully crystallized alloy A (The changes are 13.5% for v_s , 13.5% for θ_D , and 30.3 % for G , respectively).⁶ These results demonstrate that the amorphous phases in alloys A and B have a minor composition difference but marked differences in structure, properties, and thermal stability.

- (3) In our experiments, the sample was pre-pressed with h -BN powder before melting to guarantee the alloy was tightly covered by h -BN powder, the heterogeneous nucleation environments are identical for the alloy cooling with or without applied pressure. The samples obtained with and without applied pressure show almost the same oxides after melting. The enhanced GFA is a result of high pressure. We have noted that the amorphous fraction volume does not show an obvious increase with pressure an increase in our pressure scale, but the exothermal enthalpy change estimated from DSC curves demonstrates that the amorphous fraction volume shows an obvious increase with an increase in pressure. A much higher pressure may be needed to get full amorphization of the alloy.

In summary, the amorphization process of the ZrTiCuNiBe alloy is obviously enhanced under high pressure. The amorphous phases in alloys A and B have a minor composition difference but marked differences in density, microstructure, properties, and thermal stability. The issue of whether high-density and low-density amorphous phases exist in metallic glasses is under discussion, and we need more evidence to prove the concept.

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