Reply to "Comment on 'High Mixing Entropy Enhanced Energy States in Metallic Glasses'"

Juntao Huo(霍军涛)[1], Kangyuan Li(李康源)[2], Bowen Zang(臧博闻)[1], Meng Gao(高萌)[1], Li-Min Wang(王利民)[3], Baoan Sun(孙保安)[4], Maozhi Li(李茂枝)[2*], Lijian Song(宋丽建)[1*], Jun-Qiang Wang(王军强)[1*], and Wei-Hua Wang(汪卫华)[4]

[1]*CAS Key Laboratory of Magnetic Materials and Devices, and Zhejiang Province Key Laboratory of Magnetic Materials and Application Technology, Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, Ningbo 315201, China*
[2]*Department of Physics, Renmin University of China, Beijing 100872, China*
[3]*State Key Lab of Metastable Materials Science and Technology, and College of Materials Science and Engineering, Yanshan University, Qinhuangdao 066004, China*
[4]*Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*

(Received 19 July 2022; accepted manuscript online 17 October 2022)

DOI: 10.1088/0256-307X/39/11/119902

We thank Dr. Ristić and Dr. Babić for their interests in our work and for reminding us about their works on metallic glasses.

Metallic glasses are a family of materials with disordered atomic packing structure, which makes it quite challenging to design new advanced metallic glasses and makes it charming to understand the relative physical mechanisms. For metallic glasses (also for crystalline alloys), composition is a key parameter that controls the material properties.[1–5] For a given alloy system, many parameters, such as atomic radius difference and mixing enthalpy, are directly related to its chemical compositions. However, we could still make some more universal conclusion by using these parameters. For example, increasing the Nb content of a $Fe_{85}B_{14}Nb_1$ alloy can improve its glass-forming ability. Besides describing this as "Nb improves the glass-forming ability of Fe–B alloy", we could also say that "alloy with a larger atomic radius difference has better glass-forming ability".

For a regular solution, its mixing entropy is composition dependent. In our paper,[6] we found that the energy state of metallic glasses increases along with the mixing entropy, especially for the Zr–Ti–Cu–Ni–Be system we studied. The result was supported by both DSC measurements and simulations. In addition, it was found that the yielding strength has a positive correlation with the mixing entropy. In this reply, we neither dismissed the relation between mixing entropy and composition nor proposed that the change in thermal stability and physical properties has no compositional contribution.

We further surveyed the relationship between glass transition temperature (T_g) and mixing entropies (S_{mix}) in other alloy systems. For the Ti–Zr–Hf–Be–Cu–Ni system,[7,8] as shown in Fig. 1(a), the HEMG with the chemical compositions of $Ti_{16.7}Zr_{16.7}Hf_{16.7}Be_{16.7}Cu_{16.7}Ni_{16.7}$ possesses the largest S_{mix} and the highest T_g. It is noticeable that the T_g of $Ti_{20}Zr_{20}Hf_{20}Be_{20}Cu_{17.5}Ni_{2.5}$ and $Ti_{20}Zr_{20}Hf_{20}Be_{20}Cu_{2.5}Ni_{17.5}$,[8] which has the same S_{mix}, are equal. For the Pt–Pd–Cu–Ni–P system[9,10] shown in Fig. 1(b), the T_g obviously increases with the increasing S_{mix}. The HEMG possesses the highest T_g. All these results demonstrate the strong correlation between the thermal stability and ΔS_{mix} in multiple metallic glass systems.

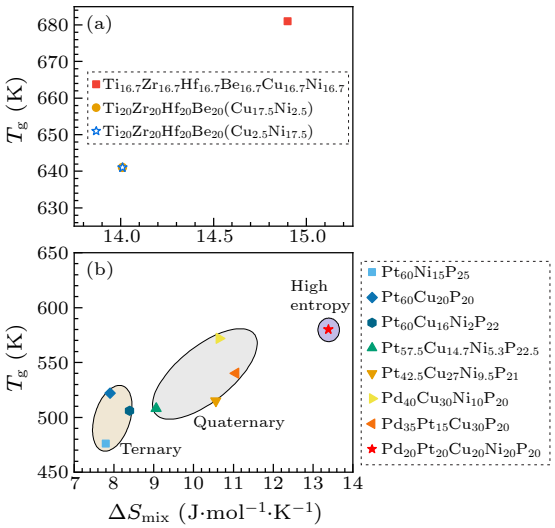

Fig. 1. (a) The glass transition temperature versus the mixing entropy of Ti-based MGs. (b) The glass transition temperature change with the mixing entropy of Pt-based MGs. For the same elements, the senary Ti–Zr–Hf–Be–Cu–Ni system shows a positive correlation between T_g and ΔS_{mix}. Similarly, the T_g also increases with the increases of the ΔS_{mix} when the system elements increase from ternary to quinary. All these results suggest that there is a strong correlation between the thermal stability and ΔS_{mix}.

*Corresponding authors. Email: jqwang@nimte.ac.cn; songlj@nimte.ac.cn; maozhili@ruc.edu.cn
© 2022 Chinese Physical Society and IOP Publishing Ltd

In the comment of Ristić and Babić's, they put Ni and Cu together. However, it may not be appropriate to consider Ni and Cu as a family of elements when they are alloyed with Ti. It is well known that the deep eutectic points in phase diagram are beneficial for glassy forming ability. The Ti–Ni binary phase diagram has deep eutectic points, while there is no deep eutectic point in the Ti–Cu phase diagram. Thus, it may be not proper to draw a relationship between mechanical properties with the concentration of Cu and Ni. It is not difficult to understand that the properties of metallic glass will be linked with different elements for different alloy systems.

About their suggestion of adding a new metallic glass composition for comparison, we think this is a nice idea. However, since Be element is prohibited now, the experiments of $Ti_{40}Zr_{12}Cu_{25}Ni_3Be_{20}$ cannot be carried out. We believe that adding one specific composition is not a complete work to support or oppose our observations. This should be systematically studied both experimentally and theoretically. We admit their previous works on relative topics. There remains much work to do to know how to design advanced metallic glasses and to unravel the underlying mechanisms.

References

[1] Li M X, Zhao S F, Lu Z, Hirata A, Wen P, Bai H Y, Chen M, Schroers J, Liu Y, and Wang W H 2019 *Nature* **569** 99

[2] Li Y, Guo Q, Kalb J A, and Thompson C V 2008 *Science* **322** 1816

[3] Jilani S, Koloadin L S, Miskovic D M, and Laws K J 2021 *Scr. Mater.* **204** 114120

[4] Ristić R, Figueroa I A, Salčinović F A, Zadro K, Mikšić T V, Pervan P, and Babić E 2021 *J. Appl. Phys.* **130** 195102

[5] Wang F, Inoue A, Han Y, Zhu S L, Kong F L, Zanaeva E, Liu G D, Shalaan E, Al-Marzouki F, and Obaid A 2017 *J. Alloys Compd.* **723** 376

[6] Huo J T, Li K Y, Zang B W, Gao M, Wang L M, Sun B A, Li M Z, Song L J, Wang J Q, and Wang W H 2022 *Chin. Phys. Lett.* **39** 046401

[7] Ding H Y, Shao Y, Gong P, Li J F, and Yao K F 2014 *Mater. Lett.* **125** 151

[8] Zhao S F, Shao Y, Liu X, Chen N, Ding H Y, and Yao K F 2015 *Mater. & Des.* **87** 625

[9] Takeuchi A, Chen N, Wada T, Yokoyama Y, Kato H, Inoue A, and Yeh J W 2011 *Intermetallics* **19** 1546

[10] Kohda M, Haruyama O, Ohkubo T, and Egami T 2010 *Phys. Rev. B* **81** 092203