

Chapter 13 High-Entropy Metallic Glasses

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Abstract This chapter applies the concept of high entropy to metallic glasses (MGs), in particular, to those in a bulk shape: bulk metallic glasses (BMGs). The resultant target materials in this chapter are mainly high-entropy bulk metallic glasses (HE-BMGs), which have recently been developed as alloys with characteristics of both high-entropy alloys (HEAs) and BMGs. The contents in this chapter start by introducing historic background of HE-BMGs and by summarizing the differences between HEAs and BMGs. Then, the fundamental properties of representative HE-BMGs found to date are described mainly in terms of thermodynamic and mechanical behaviors. Besides the experiments, the latest computational approach for clarifying the features of HE-BMGs are described based on the results using *ab initio* molecular dynamics simulations for the atomic structure, chemical interaction, and diffusivity in this unique class of materials. The current status and future prospects of the HE-BMGs by utilizing their unique features are outlined for their future applications.

13.1 Introduction

In this chapter, the focus is put on the formation mechanisms, mechanical properties and atomic structure of metallic glasses (MGs) that are associated with high-entropy alloys (HEAs) [1,2]. In particular, descriptions principally include MGs in a bulk form named bulk metallic glasses (BMGs), with a compositional feature of HEAs: high-entropy bulk metallic glasses (HE-BMGs) [3]. The HE-BMGs are mathematical intersection of sets of bulk metallic glasses (BMGs) and HEAs. Specifically, HE-BMGs possess both features of MGs with sample dimensions of a couple of millimeter or more and of HEAs for exact or near equi-atomic composition. In fact, BMGs and HEAs possess different crystallographic structure—BMGs as well as MGs and HEAs, respectively, are formed into a glassy and a crystalline phase. However, HE-BMGs that have been recently discovered have academically contributed in a major way to widening the definition of HEAs from crystalline solid solutions only to whole solid solutions including a glassy phase. Furthermore, new BMGs as well as MGs have been developed by utilizing the unique nature of HEAs. Thus, HE-BMGs play a role in leading HEAs and BMGs towards their future research orientations.

This introduction starts with describing similarities and differences in characteristics of BMGs and HEAs, leading to the resultant HE-BMGs with characteristics of both HEAs and BMGs. Subsequent sections in this chapter deal with the alloy design of HE-BMGs, followed by individual characteristics of the HE-BMGs found to date.

13.1.1 Differences between BMGs and HEAs

It has long been believed that the BMGs differ from HEAs because many different characteristics between these alloys. For instance, BMGs differ from HEAs in terms of (1) crystallographic structure, (2) thermodynamic state and (3) compositional feature. First, BMGs are defined as bulk-shaped non-crystalline metallic solids that exhibit the so-called glass transition temperature (T_g). Conversely, HEAs are crystalline materials. Although some HEAs can be fabricated into a non-crystalline structure in thin film form, these thin-film HE-MG will not covered in this chapter. Secondly, the BMGs are formed into a non-equilibrium state through quenching at a cooling rate of the order of $\sim 10^3$ K/s or slower by avoiding nucleation and growth of crystalline phases during solidification. On the other hand, the HEAs are thermo-

dynamically stable state, and so far HEAs in bcc and fcc structures [4] are frequently reported, and those in hcp structures [5,6] have very recently been reported. Thirdly, the BMGs possess one or two principal elements from Zr, La, Fe, Mg, Pd, Cu and Ca [7], whereas there is no dominating element in HEAs with equal molar ratio among elements. These fundamental differences between BMGs and HEAs have promoted their separate development since the early 1990s.

13.1.2 Historical background of HE-BMGs and Derivation of HE-BMGs from BMGs

The widely-accepted belief regarding the differences between BMGs and HEAs mentioned above, however, has been broken due to the appearance of new alloys that have both features of HEAs for their composition and those of metallic glasses for their non-crystalline structure. These new alloys are regarded as HE-BMGs or high-entropy bulk glassy alloys. At present, several HE-BMGs have been found in sequence, since the first report in 2002 in a $\text{Cu}_{20}\text{Hf}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ alloy [8]. These HE-BMGs found to date are summarized in Table 13.1, together with representative BMGs that include the prototypical ones for HE-BMGs. The $\text{Cu}_{20}\text{Hf}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ alloy is the first HE-BMG fabricated by referring to the “confusion principle” proposed by Greer in 1993 [9]. Specifically, Greer argued that the confusion principle works for glass formation in such a way that the more elements involved, the lower the chance that the alloy can select viable crystal structures, and the greater the chance of glass formation. In contrast, Cantor [10] reported in 2004 that “the confusion principle does not apply, and other factors are more important in promoting glass formation”, based on experimental results that glassy structures are not formed by casting or melt spinning of late transition metal rich equi-atomic multi-component alloys. After these arguments, researchers overlooked HE-BMGs for years.

However, the subsequent HE-BMGs have been found in sequence in 2011 in a $\text{Ca}_{20}(\text{Li}_{0.55}\text{Mg}_{0.45})_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{20}$ alloy [11] and a $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ alloy [12], and the two alloys [13] related to the Ca-(Li,Mg)-Sr-Yb-Zn of $\text{Ca}_{20}\text{Mg}_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{20}$ and $\text{Ca}_{20}\text{Cu}_{10}\text{Mg}_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{10}$, [11] and an $\text{Al}_{20}\text{Er}_{20}\text{Dy}_{20}\text{Ni}_{20}\text{Tb}_{20}$ alloy [13]. Here, $\text{Ca}_{20}\text{Mg}_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{20}$ has been studied for biomedical applications [14]. Furthermore, $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ [15] and $\text{Be}_{16.7}\text{Cu}_{16.7}\text{Ni}_{16.7}\text{Hf}_{16.7}\text{Ti}_{16.7}\text{Zr}_{16.7}$ [16] alloys have very recently been reported as the latest HE-BMGs. These findings of HE-BMGs are achieved by selecting five or more principal alloying elements in equal molar ratio but still forming BMG. As frequently applied to MGs and BMGs, the HE-

BMGs can be classified into two sets of metal-metal and metal-metalloid, depending on whether or not the alloys includes metalloid elements, such as B, C, Si, P, Ge. The HE-BMGs in metal-metalloid type have only been found in $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ alloy. The lineups of HE-BMGs are shown in Table 13.1. The constituent elements of the HE-BMGs are mixtures of early- and late-transition metals, s-block elements, metalloids, lanthanides, and p-block metallic elements. These combinations of constituent elements indicate that classification of BMGs [7] can be used as a guide for finding out unprecedented BMGs as well as HE-BMGs.

Some of the HE-BMGs mentioned above resemble prototypical BMGs in their constituent elements and compositions. As usual in alloy development, the elements in the same group in the periodic table or those with chemical properties are added or substituted in order to search for new alloys. Taking HE-BMGs for example, $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ and $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ HE-BMGs, respectively, were developed by referring to $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ [17] and $\text{Zr}_{41.2}\text{Ti}_{13.9}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ [18] BMGs, by modifying the compositions of the constituent elements to meet the equi-atomicity.

Table 13.1 HE-BMGs found to date and representative BMGs that include the prototypical ones for HE-BMGs for their maximum sample thickness (d_c) and year published. The HE-BMGs from Nos. 1 to 8 are sorted according to the year published, whereas the BMGs with d_c over 10 mm from Nos. 1 to 24 are in the order of d_c .

No	Alloy	d_c/mm	Year published	Reference
HE-BMG-1	$\text{Cu}_{20}\text{Hf}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$	1.5	2002	[8]
HE-BMG-2	$\text{Ca}_{20}(\text{Li}_{0.55}\text{Mg}_{0.45})_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{20}$	3	2011	[11]
HE-BMG-3	$\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$	10	2011	[12]
HE-BMG-4	$\text{Ca}_{20}\text{Mg}_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{20}$	$2 \times 5 \text{ mm}^2$ (sheet sample)	2011	[13]
HE-BMG-5	$\text{Ca}_{20}\text{Cu}_{10}\text{Mg}_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{10}$	5	2011	[13]
HE-BMG-6	$\text{Al}_{20}\text{Er}_{20}\text{Dy}_{20}\text{Ni}_{20}\text{Tb}_{20}$	2	2011	[13]
HE-MGB-7	$\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$	3	2013	[15]
HE-BMG-8	$\text{Be}_{16.7}\text{Cu}_{16.7}\text{Ni}_{16.7}\text{Hf}_{16.7}\text{Ti}_{16.7}\text{Zr}_{16.7}$	>15	2014	[16]
BMG-01	$\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$	72	1997	[19]

BMG-02	$\text{Zr}_{41.2}\text{Ti}_{13.9}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ (Vit1)	>50	1996	[18]
BMG-03	$\text{Pd}_{35}\text{Pt}_{15}\text{Cu}_{30}\text{P}_{20}$	30	2005	[20]
BMG-04	$\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$	30	1996	[21]
BMG-05	$\text{Mg}_{59.5}\text{Cu}_{22.9}\text{Ag}_{6.6}\text{Gd}_{11}$	27	2007	[22]
BMG-06	$\text{Mg}_{54}\text{Cu}_{26.5}\text{Ag}_{8.5}\text{Gd}_{11}$	25	2005	[23]
BMG-07	$\text{Zr}_{48}\text{Cu}_{36}\text{Ag}_8\text{Al}_8$	25	2008	[24]
BMG-08	$\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$	25	1996	[17]
BMG-09	$\text{Y}_{36}\text{Sc}_{20}\text{Al}_{24}\text{Co}_{20}$	25	2003	[25]
BMG-10	$(\text{La}_{0.7}\text{Ce}_{0.3})_{65}\text{Co}_{25}\text{Al}_{10}$	25	2007	[26]
BMG-11	$\text{La}_{62}(\text{Cu}_{5/6}\text{Ag}_{1/6})_{14}\text{Ni}_5\text{Co}_5\text{Al}_{14}$	>20	2006	[27]
BMG-12	$\text{Zr}_{57}\text{Ti}_5\text{Cu}_{20}\text{Ni}_8\text{Al}_{10}$	20	1997	[28]
BMG-13	$\text{Pt}_{42.5}\text{Cu}_{27}\text{Ni}_{9.5}\text{P}_{21}$	20	2004	[29]
BMG-14	$(\text{Fe}_{0.8}\text{Co}_{0.2})_{48}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Tm}_2$	16	2008	[30]
BMG-15	$\text{Pt}_{60}\text{Cu}_{16}\text{Ni}_2\text{P}_{22}$	16	2004	[29]
BMG-16	$\text{Mg}_{54}\text{Cu}_{28}\text{Ag}_7\text{Y}_{11}$	16	2005	[23]
BMG-17	$\text{Ca}_{65}\text{Mg}_{15}\text{Zn}_{20}$	>15	2004	[31]
BMG-18	$\text{Zr}_{58.5}\text{Nb}_{2.8}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}$	15	1998	[32]
BMG-19	$\text{Ni}_{50}\text{Pd}_{30}\text{P}_{20}$	21	2009	[33]
BMG-20	$\text{Pd}_{40}\text{Ni}_{40}\text{Si}_4\text{P}_{16}$	20	2011	[34]
BMG-21	$\text{Zr}_{61}\text{Ti}_2\text{Nb}_2\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$	20	2009	[35]

BMG-22	Zr ₆₀ Ti ₂ Nb ₂ Al _{7.5} Ni ₁₀ Cu _{18.5}	20	2009	[35]
BMG-23	Ti ₄₀ Zr ₂₅ Cu ₁₂ Ni ₃ Be ₂₀	14	2005	[36]
BMG-24	Fe ₄₈ Cr ₁₅ Mo ₁₄ Er ₂ C ₁₅ B ₆	12	2004	[37]

13.1.3 Similarities between BMGs and HEAs in their alloy designs

Interestingly, some of the BMGs and HEAs have been developed under the same alloy design principles, including the following factors:

1. the number of elements (N),
2. atomic size mismatch (difference in atomic size), and
3. heat of mixing (mixing enthalpy, ΔH_{mix}).

The details of the three factors for the development of BMGs and HEAs are described as follows. The BMGs are usually restricted to $N \geq 3$, excepting a couple of binary BMG alloys, such as Cu-Zr [38,39] and Ni-Nb [40], whereas HEAs have $N \geq 5$, together with an additional restriction requiring equi-atomic or near equi-atomic composition. The second and third factor for BMGs are simply described as 12% or more mismatch and negative heat of mixing, respectively [41]. On the other hand, the second and third factor for HEAs are more complicated than BMGs and are associated with values of parameter (δ) and ΔH_{mix} in δ - ΔH_{mix} diagrams [42], to form zone S for disordered and zone S' for ordered HEAs as detailed in Chapter 2 of this book. Here, it should be noted that the order and disorder mentioned above refers to chemical species (elements), and not the atomistic positions in crystallography. In addition, zones for BMGs are also indicated as zone B's in the δ - ΔH_{mix} diagram.

Furthermore, a new parameter (Ω) comprising average melting temperature multiplied by configurational entropy and divided by mixing enthalpy has been proposed to form δ - Ω diagrams [43] for predicting HEAs as well as BMGs. The details of these criteria for HEAs are described in Chapter 2, "Formation Rules", in this book. As mentioned above, all three factors in the alloy design for HEAs and BMGs deal with numerical and thermodynamic quantities, enabling alloy design of HEAs as well as BMGs. Here, it should be noted that there are several ways to calculate the values of ΔH_{mix} , such as thermodynamic method based on CALPHAD

[44] as described in Chapter 2 of this book, as well as electronic density functional theory as described in Chapter 8 of this book. Besides, Miedema's empirical method [45] is also widely utilized for evaluating ΔH_{mix} for BMGs as well as HEAs. The exact data on ΔH_{mix} for 2,628 atomic pairs from combination of 73 elements that are available in Miedema's model taken 2 at a time (${}_{73}\text{C}_2$) at equi-atomic binary alloy composition are provided in the authors' previous work [7].

Classifications of BMGs as well as MGs were reported since 1980s by Hafner [46], Masumoto [47], and Inoue [41], and Takeuchi and Inoue [7,48]. Inoue [41] has summarized the BMGs with five groups comprising (1) Zr- and La-based, (2) Fe-ETM base, (3) Fe-(Al,Ga) base, (4) Mg-based, (5) Pd- and Pt-based where ETM stands for early-transition metals, and the following two supplemental groups have been added later by Takeuchi and Inoue [7,48]: (6) LTM (Late-transition Metals)-based, and (7) Ca-based BMGs. The classifications by Takeuchi and Inoue [7] were made basically by taking into account the sub-groups of ETM, Ln, LTM, BM and IIA corresponding to early transition, lanthanide, late transition, group IIIB-IVB and group IIA-group metals, respectively. On the other hand, the latest classification of BMGs proposed by Takeuchi and Inoue [48] was based on four sub-groups of s, d_{Ef} , d_{Lp} and p from s-, d-, f- and p-block elements on the periodic table that correspond to s-block elements, early-transition metals and lanthanides, late-transition metals and p-block metallic elements, and metalloids in p-block. These classifications provide a hint to discover unknown HE-BMGs. The HE-BMGs have been found by referring to and modifying the components and compositions of the BMGs. Takeuchi and Inoue [48] eventually succeeded in obtaining a universal trend of BMG formation on the basis of the regular tetrahedral composition diagram comprising s, d_{Ef} , d_{Lp} and p. It appears that a compositional band connects BMGs on the surface of the regular tetrahedral composition diagram.

The guiding principle of the alloy design for HE-BMGs has two stages. First, one should find out the prototypical alloy compositions from the early studies of BMGs. Second, one should approximate the compositions of the prototypical BMGs by taking into account the chemical similarities in elements, such as the same group of the periodic table. Table 13.2 [49] summarizes the relationships between the representative BMGs and the corresponding HE-BMGs found to date summarized by class, sub-groups as well as the relative atomic size for BMGs, s- d_{Ef} - d_{Lp} -p description and corresponding HE-BMGs.

Table 13.2 Relationships between seven classes of BMGs and HE-BMGs. The letters “L, M and S” indicate the relative atomic size (Large, Medium, or Small) of the constituent elements. The bold and underlined letter in each class indicates the main constituent element. It should be noted that C-VI-I is not the result of classification of BMGs, but is shown for comparison for $\text{Cu}_{20}\text{Hf}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ HE-BMG. The BMGs do not list their constituents alphabetically, but in an empirical way to show the principal element. Reproduced with permission from Ref. [49].

Class	Sub-Group s d _{ef} d _{Lp} p				Representative BMGs	Ref. s-d _{ef} -d _{Lp} -p de- scription	Corresponding HE- BMGs	Ref.
I	M	<u>L</u>	S	—	$\text{La}_{60}\text{Al}_{15}\text{Ni}_{25}$	[50] (d _{ef}) ₆₀ s ₁₅ (d _{Lp}) ₂₅	$\text{Al}_{20}\text{Er}_{20}\text{Dy}_{20}\text{Ni}_{20}\text{Tb}_{20}$	[13]
	S	<u>L</u>	M	—	$\text{Zr}_{41.2}\text{Ti}_{13.9}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$	[18] (d _{ef}) ₅₅ (d _{Lp}) _{22.5} s _{22.5}	$\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$	[15]
II	—	L	<u>M</u>	S	$(\text{Fe}_{0.8}\text{Co}_{0.2})_{48}\text{Cr}_{15}\text{Mo}_{14}\text{Ti}_{12}\text{C}_{15}\text{B}_6$	[30] (d _{Lp}) ₄₈ (d _{ef}) ₃₁ p ₂₁	—	—
III	L	—	<u>M</u>	S	$\text{Fe}_{73}\text{Al}_{15}\text{Ga}_{2}\text{P}_{11}\text{C}_5\text{B}_4$	[51] (d _{Lp}) ₇₃ p ₂₀	—	—
IV	<u>M</u>	L	S	—	$\text{Mg}_{59.5}\text{Cu}_{22.9}\text{Ag}_{6.6}\text{Gd}_{11}$	[23] s _{59.5} (d _{Lp}) _{29.5} (d _{ef}) ₁₁	$\text{Ca}_{20}\text{Mg}_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{20}$	[13]
V	—	—	<u>L</u>	S	$\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$	[17] (d _{Lp}) ₈₀ p ₂₀	$\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$	[12]
	—	—	<u>L</u>	S	$\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$	[19]		
VI	—	L	<u>S</u>	—	$\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$	[52] (d _{Lp}) ₆₀ (d _{ef}) ₄₀	—	
VI-I	—	<u>L</u>	S	—	—	— (d _{ef}) ₆₀ (d _{Lp}) ₄₀	$\text{Cu}_{20}\text{Hf}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$	[8]
VII	<u>L</u>	—	S	—	$\text{Ca}_{65}\text{Mg}_{15}\text{Zn}_{20}$	[31] s ₈₀ (d _{Lp}) ₂₀	—	

d_{ef}: Early-transition metals from d-block, and lanthanides from f-block

d_{Lp}: Late-transition metals from d-block and metallic elements in p-block,

p: Metalloid elements in p-block,

s: s-block elements where Al and Sn are supposed to belong to either s or d_{Lp} depending on the other constituent elements

$\text{Al}_{20}\text{Er}_{20}\text{Dy}_{20}\text{Ni}_{20}\text{Tb}_{20}$ and $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ are chemically near $\text{La}_{60}\text{Al}_{15}\text{Ni}_{20}$ [50], $\text{Ca}_{20}\text{Mg}_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{20}$ between $\text{Mg}_{50}\text{Ni}_{30}\text{La}_{20}$ [53] and $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ [54], $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ near $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ [17] and $\text{Cu}_{20}\text{Hf}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ near $\text{Cu}_{23}\text{Ni}_{11}\text{Fe}_7\text{Ti}_{52}\text{Mo}_7$ [55]. These HE-BMGs surely possess exact or near equi-atomicity, but chemical similarity among the constituent elements reduces HE-BMGs to conventional BMGs.

13.2 HE-BMGs, relevant alloys and their characteristics

This subsection deals with three types of alloys: $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$, $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ and $\text{Ca}_{20}\text{Mg}_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{20}$ based HE-BMGs. The thermodynamic properties are mainly explained for the $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ HE-BMG and its relevant HEAs. The mechanical properties are explained for $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ and $\text{Ca}_{20}\text{Mg}_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{20}$ based HE-BMGs that belong to the metal-metal type comprising metallic elements only, while the $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ HE-BMG from metal-metalloid type including metalloid elements from B, C, Si P and Ge is eliminated for its mechanical properties due to the brittle nature inherent to the inclusion of the metalloid element.

13.2.1 $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ HE-BMG and relevant alloys

Of the HE-BMGs found to date, the $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ [12] as well as $\text{Be}_{16.7}\text{Cu}_{16.7}\text{Ni}_{16.7}\text{Hf}_{16.7}\text{Ti}_{16.7}\text{Zr}_{16.7}$ [16] HE-BMGs exhibit sample dimensions reaching a centimeter. The outer appearance and the XRD profile taken from a cross-sectional area of the $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ HE-BMG are shown in Fig. 13.1.

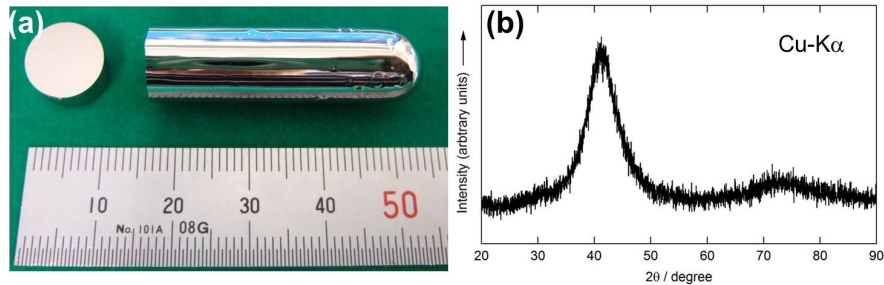


Fig. 13.1 (a) Outer appearance and (b) XRD profile taken from the cross-sectional area of $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ HE-BMG with a diameter of 10 mm. Reproduced with permission from Ref. [12].

The $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ HE-BMG was designed from a prototypical BMG of $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ with $d_c = 25$ mm [17] by replacing half moles of Pd with Pt and those of Ni with Cu. These replacements, ironically, degrade glass-forming ability (GFA), resulting in decreasing d_c from 25 for the $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ BMG to 10 mm for the $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ HE-BMG. The degrading GFA indicates that the best BMG compositions are not always the ones for HEAs. Another peculiar feature of the $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ HE-BMG is seen for the reduced glass transition temperature (T_g/T_l), which is evaluated by glass transition temperature (T_g) normalized with liquidus temperature (T_l). It is widely-accepted that $T_g/T_l \geq 0.6$ is a condition for an alloy with a high GFA. The value of T_g/T_l of the $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ HE-BMG is as high as 0.71, which is the highest value among BMGs with d_c 's ≥ 10 mm, but it seemingly contradicts the low $d_c = 10$ mm. Including T_g/T_l , 12 GFA parameters in all have been proposed to evaluate GFA where the features of each parameter are well-summarized in literature [56]. The representative GFA parameters include T_g/T_l , supercooled liquid region ($\Delta T_x = T_x - T_g$) exhibiting the temperature interval between onset temperature of crystallization (T_x) and T_g , γ parameter defined by $T_x/(T_g + T_l)$. However, these GFA parameters exhibit a critical issue that there is no absolutely-reliable GFA parameter that makes it possible to evaluate GFA universally over different kinds of BMGs with different composition. Accordingly, the 12 GFA parameters each preferentially characterize BMG families with specific base elements. For instance, the evaluation of GFA with T_g/T_l provides the best fit for Co-based BMGs [56]. In this sense, the GFA parameters fall into utter confusion. The existence of preferential base element for each GFA parameter prevents description of HE-BMGs with no principal elements, and raises a question on the utility of presently known GFA parameters. Further study of the GFA parameters is required in near future.

In a process of fabricating the $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ HE-BMG, other possible combinations were examined by fixing Pd, Pt and P and changing LTMs from Cu and Ni, found that the $\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}\text{TM}_{120}\text{TM}_{220}$ alloys form into a glassy phase only by $(\text{TM}_1, \text{TM}_2) = (\text{Cu}, \text{Ni})$ as shown in Fig. 13.2 [57]. Besides, Takeuchi et al. examined three types of alloys with $\text{ETM}_{60}\text{LTM}_{40}$, $\text{ETM}_{50}\text{LTM}_{50}$ and $\text{ETM}_{40}\text{LTM}_{60}$ alloys, such as (a) $\text{Hf}_{20}\text{Ni}_{20}\text{Pd}_{20}\text{Ti}_{20}\text{Zr}_{20}$, (b) $\text{Cu}_{16.7}\text{Ni}_{16.7}\text{Hf}_{16.7}\text{Pd}_{16.7}\text{Ti}_{16.7}\text{Zr}_{16.7}$, and (c) $\text{Cu}_{20}\text{Ni}_{20}\text{Pd}_{20}\text{Ti}_{20}\text{Zr}_{20}$ alloy ribbons, and found that the $\text{Cu}_{20}\text{Ni}_{20}\text{Pd}_{20}\text{Ti}_{20}\text{Zr}_{20}$ alloy from $\text{ETM}_{40}\text{LTM}_{60}$ type can be a candidate for HE-BMGs because of a formation of a glassy phase in the ribbon specimen. However, it was impossible to obtain

$\text{Cu}_{20}\text{Ni}_{20}\text{Pd}_{20}\text{Ti}_{20}\text{Zr}_{20}$ HE-BMGs even with a sample diameter as small as 1 mm. Instead, it was found that that half mole of addition of Al ($\text{Al}_{0.5}$) to an $\text{ETM}_{40}\text{LTM}_{60}$ type, $\text{Al}_{0.5}\text{CuNiPdTiZr}$ alloy, is formed into a HEA with bcc structure when prepared by a cylindrical alloy with a diameter of 1.5 mm as shown in Fig. 13.3 [58]. It should be noted in Fig. 13.3 that $\text{Al}_{0.5}\text{CuNiPdTiZr}$ alloy resulted in failure to obtain HEAs, although $\text{Cu}_{20}\text{Hf}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ alloy is a HE-BMG [8]. The XRD profiles in Fig. 13.3 indicate that the $\text{Al}_{0.5}$ addition, which works efficiently to obtain HEA, does not always works well for enhancing GFA. In any case, the $\text{Al}_{0.5}\text{CuNiPdTiZr}$ alloy exhibits unique forming-ability to be into a glassy phase as well as crystalline HEA depending on the sample size and the cooling rate. Thus, it is considered that $\text{Al}_{0.5}\text{CuNiPdTiZr}$ alloy can be a high-entropy metallic glass to bridge HEAs and MGs (BMGs) scientifically.

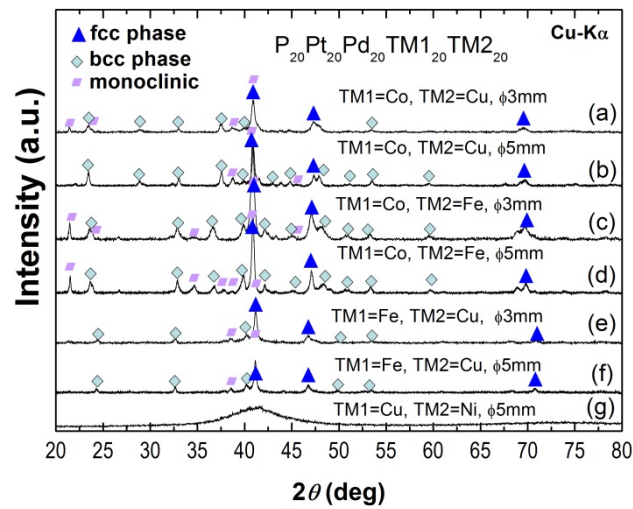


Fig. 13.2 XRD profiles of $\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}\text{TM1}_{20}\text{TM2}_{20}$ cylindrical alloys cast into diameters of 3 and 5 mm [57].

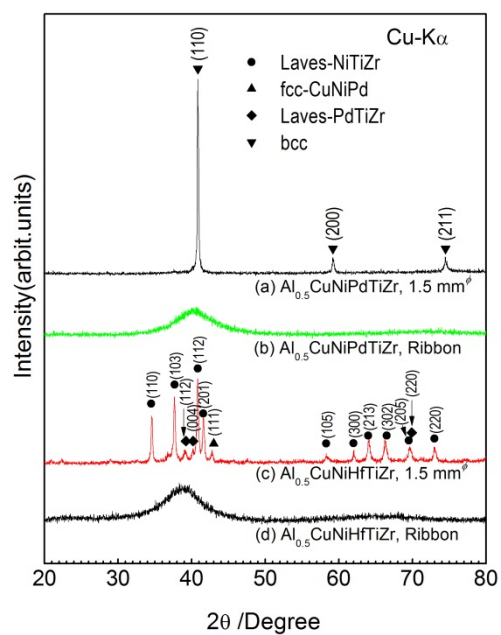


Fig. 13.3 XRD profiles of (a) and (b) $\text{Al}_{0.5}\text{CuNiPdTiZr}$ and (c) and (d) $\text{Al}_{0.5}\text{CuNiHfTiZr}$ alloys formed into (a) and (c) cylindrical specimens with 1.5 mm in diameters and (b) and (d) ribbons. Reproduced with permission from Ref. [58].

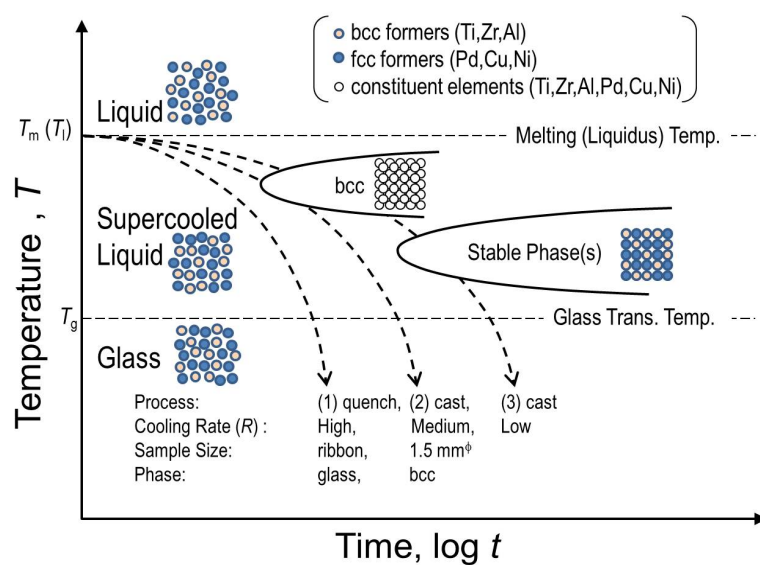


Fig. 13.4 A schematic illustration of the continuous-cooling-transformation (C.C.T.) diagram of the $\text{Al}_{0.5}\text{CuNiPdTiZr}$ alloy with different processes (1) to (3). Atomic arrangements in 2-dimensions for phases of liquid, supercooled liquid, glass, bcc and stable phases are given to demonstrate the statuses of atomic bonding of the $\text{Al}_{0.5}\text{CuNiPdTiZr}$ alloy for bcc (Ti, Zr and Al) and fcc (Pd, Cu and Ni) formers. The atomic arrangements exhibit a tendency that the bcc and fcc formers are separately percolated in an atomistic level in liquid, supercooled liquid, glassy and stable crystalline phases statistically. The bcc and fcc formers occupy the sites in the bcc structure randomly where the bcc structure is drawn as a hypothetical layered structure intentionally to distinguish it from the stable phase(s). Reproduced with permission from Ref. [58].

The possible reason for the peculiar characteristics of the $\text{Al}_{0.5}\text{CuNiPdTiZr}$ alloy to appear in two different phases, either glassy or bcc depending on the cooling rate, is considered with a schematically illustrated continuous-cooling transformation (C.C.T.) diagram shown in Fig. 13.4. A C-curve for a bcc phase is drawn at a high temperature range in Fig. 13.4. This is due to allotropic transformation of pure Ti and Zr [59] as well as a widely-accepted fact that the bcc structure is often the high-temperature structure of a metal that has a close-packed structure at lower temperature [59]. Thus, the present authors think that the allotropic transformation of pure Ti and Zr could provide a symptom of the $\text{Al}_{0.5}\text{CuNiPdTiZr}$ alloy to be formed into a bcc phase at high temperatures. One such symptom would be provided as formulae of nucleation sites or embryos. In casting the alloy in the process (2) in Fig. 13.4, the alloy remains a bcc phase because of limited diffusions of atoms at a medium cooling rate (R). On the other hand, a glassy phase is obtained in the process (1) at a high R , whereas a bcc phase may transform into stable phases at a low R in the process (3). In addition to Ti and Zr, it should be noted that Al can be regarded as a bcc former in HEAs [60] [60], supporting the presence of a bcc phase at a high temperature.

The peculiarity of the $\text{Al}_{0.5}\text{CuNiPdTiZr}$ HEA can be seen in Table 13.3 for the values of δ and ΔH_{mix} for the $\text{Cu}_{20}\text{Ni}_{20}\text{Pd}_{20}\text{Ti}_{20}\text{Zr}_{20}$, $\text{Al}_{0.5}\text{CuNiPdTiZr}$ and $\text{Al}_{0.5}\text{CuNiHfTiZr}$ alloys. It is also important that $\text{Al}_{0.5}\text{CuNiPdTiZr}$ HEA is located in a less dense area in the δ - ΔH_{mix} diagram covered by the ternary amorphous alloys [42]. These features of the $\text{Al}_{0.5}\text{CuNiPdTiZr}$ HEA encourage us to search for new HEAs by referring to the δ - ΔH_{mix} diagram.

Table 13.3 Mixing enthalpy (ΔH_{mix}), Delta parameter (δ), phases in the forms of ribbon and 1.5mm rod specimens and reference of the HEAs. Reproduced with permission from Ref. [58].

	$\Delta H_{\text{mix}} / \text{kJ mol}^{-1}$	δ	Phase in a form of Ribbon /(1.0)* 1.5mm rod
$\text{Cu}_{20}\text{Ni}_{20}\text{Pd}_{20}\text{Ti}_{20}\text{Zr}_{20}$	-45.1	9.2	Glass/(fcc + hcp + Laves + unknown)*
$\text{Cu}_{20}\text{Hf}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$	-27.4	10.3	Glass/Glass
$\text{Al}_{0.5}\text{CuNiPdTiZr}$	-46.7	8.8	Glass/bcc
$\text{Al}_{0.5}\text{CuNiHfTiZr}$	-31.6	9.9	Glass/(fcc + Laves)

The $\text{Cu}_{20}\text{Ni}_{20}\text{Pd}_{20}\text{Pt}_{20}$ HE-BMG exhibits poor mechanical properties. In short, it is mechanically brittle. This is expected from the fact that some of the BMGs belonging to metal-metalloid type are brittle in the as-cast state. It is possible that local atomic arrangements of HE-BMGs are associated with those of intermetallic compounds. Other treatments can worsen the brittleness including structural relaxation and crystallization upon annealing.

13.2.2 $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ HE-BMG and its Mechanical Properties

One can list the $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ HE-BMG as a representative HE-BMG of metal-metal type based on the prototypical BMG $\text{Zr}_{41.2}\text{Ti}_{13.9}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ (Vit1) [18]. The $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ HE-BMG was prepared by arc-melting the mixture of the pure Zr, Ti, Be, Cu, and Ni in a water-cooled Cu crucible under a Ti-gettered high purity argon atmosphere. Rod-like samples with a diameter of 3 mm and a length of about 70 mm were obtained. Fig. 13.5 shows the SEM of the $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ high-entropy alloys (HEAs). The contrast is featureless, indicating an amorphous structure for the present alloy. Thermodynamic characteristics of the $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ HE-BMG were reported as follows: $T_g = 683$ K and $T_x = 729$ K. High thermal stability and strength is attributed to the high entropy (equal atomic) nature of this HE-BMG as well as an increase in Ni concentration. After annealing under vacuum at 813 K for 1 h, three phases including fcc, bcc solid solutions together with Ni_7Zr_2 intermetallic phase precipitated.

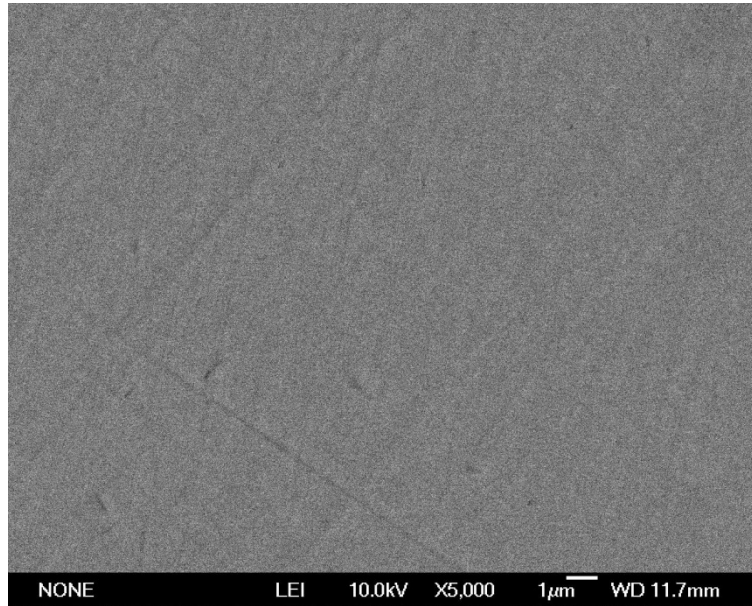


Fig. 13.5 SEM of Be₂₀Cu₂₀Ni₂₀Ti₂₀Zr₂₀ HEA.

Examples of the uniaxial compressive tests are shown in Fig. 13.6 that were performed on 6 mm long sections cut from the 2 mm diameter cylinders using the MTS 809 material testing machine at room temperature (RT) with a strain rate of $2 \times 10^{-4} \text{ s}^{-1}$. For the compression testing, the samples were sandwiched between two WC platens, and two blades were mechanically fixed on the side surface of the WC platens. Figure 13.6(a) exhibits the engineering stress-strain curve of Be₂₀Cu₂₀Ni₂₀Ti₂₀Zr₂₀ at RT. This HEA has a brittle fracture, and no plasticity can be observed from Fig. 13.6(a). It is noted that it exhibits the maximum strength of about 2600 MPa and elastic limit of about 1.9 %. Figure 13.6(b) presents the fractographies of the current amorphous HEA. From Fig. 13.6(b), it is seen that multiple faces are dominant features, suggesting that more fracture energy is needed to convert to surface energy during fracture. A high magnification of a localized fracture surface is shown in Fig. 13.6(c) revealing a radiating pattern. In the front of this pattern, profuse molten liquids could be found, associated with shear adiabatic heating. Besides, a mirror area is present in the core of the radiating pattern.

In contrast to Zr-based BMGs, the Be₂₀Cu₂₀Ni₂₀Ti₂₀Zr₂₀ HE-BMG exhibits a brittle behavior, although the fracture strength is as high as over 2000 MPa. In part, this brittle nature is due to the precipitation of Ni₇Zr₂ intermetallic phase besides the conventional simple solid solutions with fcc and bcc structures. The brittle nature of

the $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ HE-BMG is supported by the value of $\Delta H_{\text{mix}} = -30.24$ kJ/mol, which is extremely large and negative relative to that for HEAs. The large and negative nature of ΔH_{mix} suggests the tendency to form intermetallic compounds which leads to the brittle nature of the alloy.

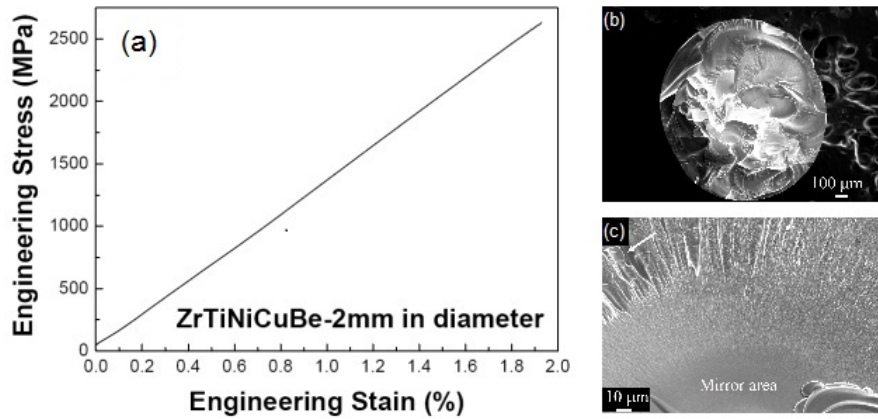


Fig. 13.6 (a) the engineering stress-strain curve of $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ and (b–c) presents the fractographies of the current amorphous HEA.

13.2.3 $\text{Ca}_{20}\text{Mg}_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{20}$ base HE-BMGs and their Unique Mechanical Properties

This subsection describes the peculiar mechanical properties of $\text{Ca}_{20}\text{Mg}_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{20}$ base HE-BMGs. In principle, crystalline and glassy alloys reveal different mechanical properties when subjected to forces. The appearance of different mechanical properties are caused by some factors, such as chemical bonding, macroscopic morphology with and without grain boundaries and dislocations as a result of the atomic arrangements and so on. These factors determine the properties of materials. Among various properties, mechanical properties are the most sensitive to the inhomogeneity included in the materials where the inclusions here are represented by defects, cracks, secondary phases, pores and so on. The key phenomenon to determine the mechanical properties of materials can be a stress concentration generated at the sharp corners and edges by the inclusions, such as dislocations and cracks for crystalline and glassy alloys, respectively.

In principle, HE-BMGs behave as a glassy material in mechanical tests. As is similar to oxide and other glassy materials, HE-BMGs with a macroscopic dense random packing structure without long range atomic periodicity exhibit the brittleness in mechanical tests at room temperature. This brittle nature of HE-BMGs originates from the absence of dislocations inherent to crystalline alloys, and thus, crack propagations via shear band formation and propagation lead to fracture without exhibiting plastic deformation. In contrast to the crystalline alloys with dislocations that release the stress concentrations by their movements by forming networks with resultant macroscopic deformations, in glassy alloys stress concentration takes place at the points of inclusions, leading to crack propagation and resultant fracture. As a result, the stress-strain curves of glassy materials in tensile test is very brittle or exhibits a strain (ϵ) of $\sim 0.2\%$, which is extremely smaller than ductile metallic crystalline alloys with ϵ reaching a couple of tens % or more. As an exceptional case, some glassy alloys, such as $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ BMG [52] exhibit plastic deformation at room temperature, but its deformation can be observed in compression tests only. The comparison of representative features of glassy alloys with crystalline alloys is summarized as follows: (1) relatively higher tensile strength and lower Young's modulus and (2) absence of distinct plastic elongation at room temperature due to inhomogeneous deformation modes. Here, one can see the relatively low Young's modulus of HE-BMG in Fig. 13.7.

In general, the latter feature of glassy alloys in mechanical tests makes it difficult to utilize the glassy alloys as structural materials. In contrast, glassy alloys exhibit advantageous aspects at relatively high temperature near T_g , which can be widely-accepted as viscous flow. The viscous flow of glassy materials takes place as a result of a homogeneous deformation mode at a temperature range called the supercooled liquid region ΔT_x defined as the temperature interval between T_g and T_x . Thus, HE-BMGs as well as BMGs with extremely low T_g provide us an opportunity to overcome the brittle nature in mechanical tests. An example can be seen in $\text{Ca}_{20}\text{Mg}_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{20}$ base HE-BMGs tested at RT in Fig. 13.8. The latest results of HE-BMGs regarding mechanical properties including the ones in Figs. 13.7 and 8 are also summarized in Ref. [61].

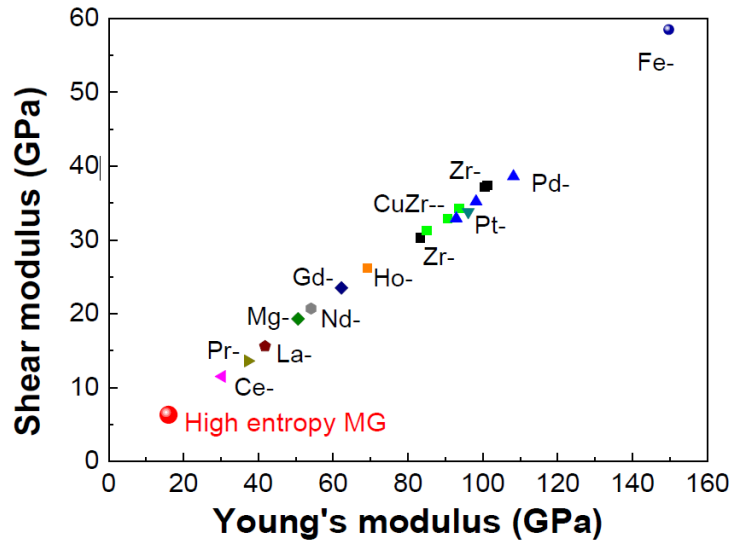


Fig. 13.7 The comparison of the Young's modulus and shear modulus of a series MGs. The $\text{Ca}_{20}(\text{Li}_{0.55}\text{Mg}_{0.45})_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{20}$ BMG has the smallest elastic constant among other typical BMGs. Reproduced with permission from Ref. [11].

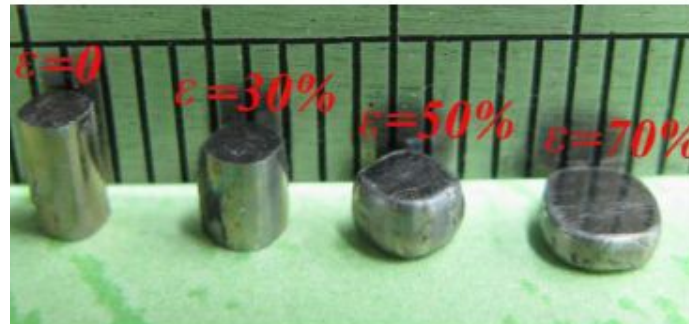


Fig. 13.8 The photo image of the compressed $\text{Ca}_{20}(\text{Li}_{0.55}\text{Mg}_{0.45})_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{20}$ HE-BMG, which can be compressed up to 70% of its original height without shear banding and cracking [11]. Reproduced with permission from Ref. [11].

13.2.4 Factors Affecting the Mechanical Properties of HE-BMGs

This subsection focuses on two factors that would affect the mechanical properties of HE-BMGs. The first one is the types of HE-BMGs, MGs and BMGs; metal-

metal and metal-metalloid types. In principle, metal-metalloid type MGs and BMGs comprising metallic elements only tend to be more brittle than metal-metal type including metalloids [62] because of the presence of covalent-like atomic bonding and easiness in occurring chemically-induced structural relaxation as well as topological ones. The second one is the values of ΔH_{mix} [63], which indicate the tendency of forming glassy and intermetallic phases. Generally, HE-BMGs as well as MGs possess larger and more negative ΔH_{mix} and larger δ than HEAs in the δ - ΔH_{mix} diagram [42]. In reality, the values of ΔH_{mix} are approximately in the range of 0 to -10 kJ/mol, which forms zone S in the δ - ΔH_{mix} diagram. On the other hand, $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ HE-BMG has $\Delta H_{\text{mix}} = -30.24$ kJ/mol and $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ HE-BMG has $\Delta H_{\text{mix}} = -25$ kJ/mol, which are considerably larger and negative than those for HEAs. However, $\text{Ca}_{20}\text{Mg}_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{20}$ base HE-BMGs have $\Delta H_{\text{mix}} = -10$ to -12 kJ/mol, which are nearly the same grade to those of HEAs. These feature of ΔH_{mix} of the HE-BMGs could determine the mechanical properties for ductility or brittleness to some extent. The values of ΔH_{mix} are closely related to the interatomic interaction and bonding in the alloys, which are explained in next subsection by showing the results of *ab initio* molecular dynamics (AIMD) simulations for model HE-BMGs.

13.2.5 AIMD simulations

The atomic structure of model HE-BMG alloys including $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$, $\text{Al}_{20}\text{Er}_{20}\text{Dy}_{20}\text{Ni}_{20}\text{Tb}_{20}$, $\text{Cu}_{20}\text{Hf}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$, and $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$, were studied using canonical ensemble (NVT) AIMD simulations at $T = 1400$ K. A cell of 200 atoms was used except 100 for $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$, and the data were collected over 50 ps. The calculated partial pair distribution functions (PDF) are presented in Fig. 13.9. As is similar to the classification of BMGs described in subsection 13.1.3, we group chemically similar elements as a "single element". In the case of CuNiPPdPt , we group Ni, Pd and Pt as "N" for "Nickel group". The partial CuN PDF was obtained by averaging over CuNi, CuPd and CuPt pairs, and likewise for partial PDFs over NN and PN pairs. Clearly, P binds more strongly to the Nickel group than to Cu. This follows expectation, as the enthalpies of formation of P with the Ni group are approximately four times larger than with Cu. Equally dramatic is the absence of a P-P near neighbor peak, reflecting the strong preference of P to surround itself with metal atoms. A complete presentation of the partial PDF's of $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ at $T = 1200$ K was shown in ref. [64].

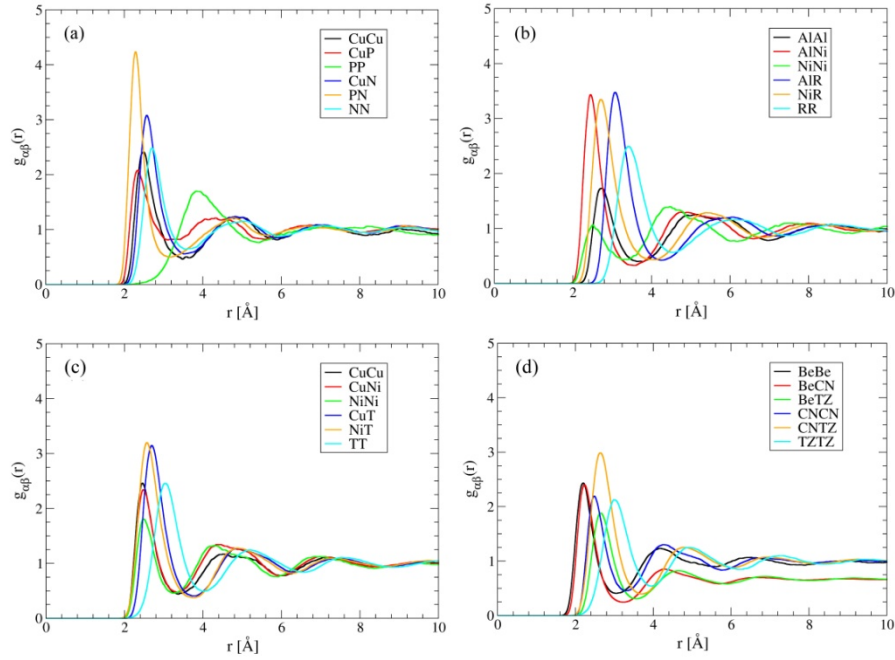


Fig. 13.9 Calculated partial PDF pertaining to Ni in (a) $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ (where $\text{N} = \text{Ni}, \text{Pd}, \text{Pt}$) (b) $\text{Al}_{20}\text{Er}_{20}\text{Dy}_{20}\text{Ni}_{20}\text{Tb}_{20}$ (where $\text{R} = \text{Dy}, \text{Er}, \text{Tb}$), (c) $\text{Cu}_{20}\text{Hf}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ (where $\text{T} = \text{Hf}, \text{Ti}, \text{Zr}$) and (d) $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ (where $\text{TZ} = \text{Ti}, \text{Zr}$, and $\text{CN} = \text{Cu}, \text{Ni}$)

It is well known that the rare earth lanthanide series consists of chemically similar elements, because the strongly localized 4f electrons hardly participate in chemical bonding. Hence the RX ($\text{R} = \text{Er}, \text{Dy}, \text{Tb}$; $\text{X} = \text{Al}, \text{Ni}$) correlations exhibit little dependence on rare earth element "R" in $\text{Al}_{20}\text{Dy}_{20}\text{Er}_{20}\text{Ni}_{20}\text{Tb}_{20}$, and we choose to average the correlation functions over the R elements. The strongest correlations occur between chemically dissimilar pairs of elements. Hence the rare earths strongly bind both Al and Ni, while the AlNi correlation is also strong, consistent with the strong compound formation and chemical ordering prevalent in solid Al-Ni alloys. The preference for binding with unlike elements leads to strong reductions in the strength of the nearest-neighbor Al-Al and Ni-Ni peaks.

The Ti group shares a common valence of 4+, and a relatively large radius and low electronegativity since they are positioned early in the transition metal rows. Hence we group these elements under the label "T" and average their correlation functions. This group binds strongly to both of the strongly electronegative and relatively small late transition metals Cu and Ni. The relative sizes of atoms are evi-

dent in the positions of the peaks, starting with the late-late pairs at the shortest distances, followed by late-early pairs and finally early-early.

For the last compound, $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$, we separately group the early transition metals Ti and Zr (label “TZ”) and the late transition metals Ni and Cu (label “CN”). A hierarchy of sizes is apparent, in the order Be, CN, TZ. The strongest binding occurs between CN and TZ, again reflecting their large electronegativity difference, with Be intermediate in both electronegativity and in binding strength to CN and to TZ.

The diffusion constants were obtained by plotting the mean square displacement (MSD) versus time. The plot is fairly linear for all species, and the obtained diffusion constants are shown in Fig. 13.10 and Table 13.4. With the smallest atomic size, P has the slowest diffusivity at $T = 1400$ K due to strong chemical bonding between P and metallic elements. For the rest 3 alloys, the atomic diffusivity largely is inversely correlated to their atomic size, namely, element of large atomic radii diffuses slowly. Note that atomic diffusivity is also system sensitive. The diffusivity of Ni in $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ is nearly twice that in $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$.

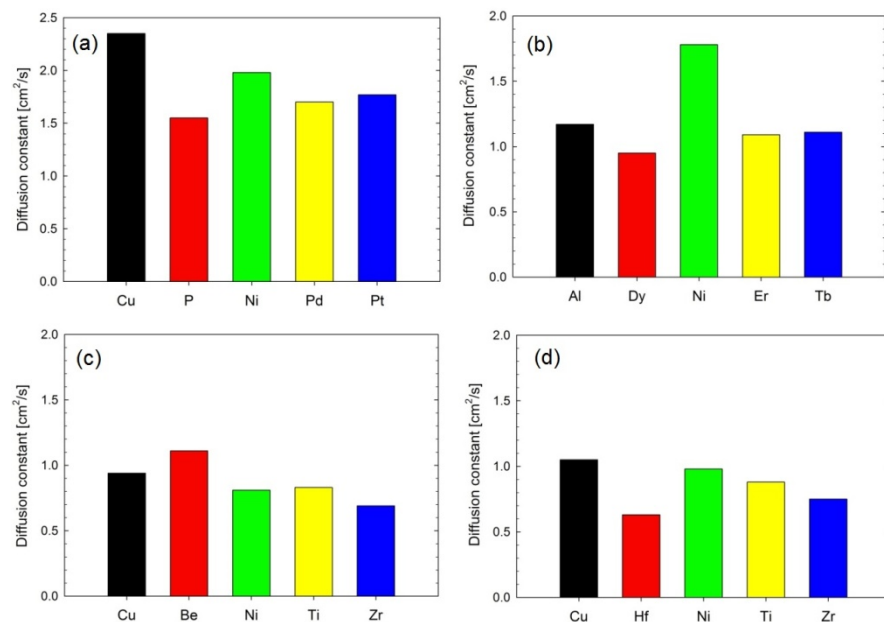


Fig. 13.10 Diffusion constants obtained from MSD plots for (a) $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$, (b) $\text{Al}_{20}\text{Er}_{20}\text{Dy}_{20}\text{Ni}_{20}\text{Tb}_{20}$, (c) $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$, and (d) $\text{Cu}_{20}\text{Hf}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ from AIMD simulations at $T = 1400$ K.

Table 13.4 Diffusion constants [$10^{-5} \text{ cm}^2/\text{s}$] at $T = 1400$ K obtained from AIMD simulations.

$\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$	Cu	Ni	P	Pd	Pt
	2.35	1.98	1.55	1.70	1.77
$\text{Al}_{20}\text{Er}_{20}\text{Dy}_{20}\text{Ni}_{20}\text{Tb}_{20}$	Al	Er	Dy	Ni	Tb
	1.17	1.09	0.95	1.78	1.11
$\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$	Be	Cu	Ni	Ti	Zr
	1.11	0.94	0.81	0.83	0.69
$\text{Cu}_{20}\text{Hf}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$	Cu	Hf	Ni	Ti	Zr
	1.05	0.63	0.98	0.88	0.75

The glass structure of $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ was obtained by quenching the liquid at $T = 1200$ K to 500 K at a cooling rate of 8.75×10^{13} K/s followed by full relaxation at $T = 0$ K. The resulting partial PDF and atomic structure are shown in Fig. 13.10. In consistent with liquid simulation, the PNi pair ordering has the highest probability at shortest bond length.

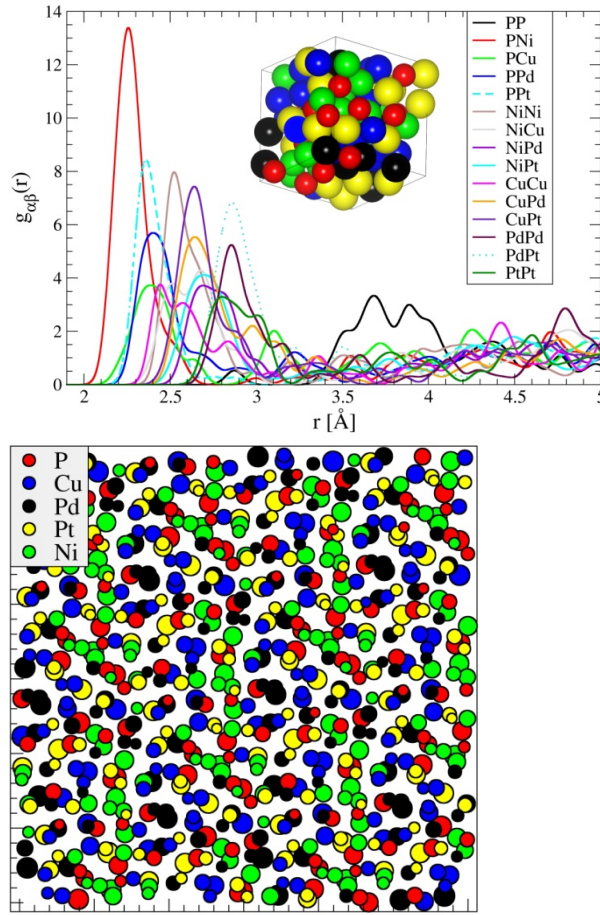


Fig. 13.10 Partial PDF of $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ glass and the cross section along [100] projection.

13.3 Expected Applications of HE-BMGs

A recent report on the application of products of BMGs [3] focused on the mechanical properties of BMGs for Zr-, Ti-based and Fe-based alloys where the former two are metal-metal and the last one is metal-metalloid type. Of these three alloys, there is little prospect to discover new HE-BMGs as magnetic alloys comprising iron-group elements because of the limited selection of metal and metalloid elements with approximate composition of $(\text{metal})_{80}(\text{metalloid})_{20}$. Exceptionally, it has re-

cently reported [65] that alloys comprising iron-group-element and metalloids with compositions of $\text{Al}_{x/2}\text{FeCoNiSi}_{x/2}$ ($0 \leq x \leq 0.8$) can be formed into HEAs as soft magnetic alloys, but the magnetization of these soft magnetic HEAs is restricted to around 1.3 T due to the limited content of iron-group-elements. Thus, it is expected that new HE-BMGs belonging to metal-metal type could be used as materials in the application fields where the BMGs have already reached to date. The expected applications depend on the characteristics of porous behavior, imprintability in nanoscale and so forth which all are achieved by utilizing the viscous behavior of BMGs. In fact, it was reported that the $\text{Ca}_{20}(\text{Li}_{0.55}\text{Mg}_{0.45})_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{20}$ alloy was applied to imprinted material [11]. Besides, low Young's modulus can also be utilized for applications of HE-BMGs where it was previously applied to head materials of golf clubs made of Zr-based BMGs [41]. In addition to the unique mechanical properties of HE-BMGs, HE-BMGs as well as BMGs can be used as coating materials [3] by utilizing the glassy nature of the alloys that do not contain defects. It is expected that HE-BMGs will find both similar and new applications by making the most of the unique properties inherent to glassy materials.

CONCLUSIONS

High-entropy BMGs have been successfully produced by substituting chemically similar elements to known BMG. For example, the $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ and $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ HE-BMGs are derived from the prototypical BMGs of $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ and $\text{Zr}_{41.2}\text{Ti}_{13.9}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$, respectively. However, the glass forming ability of HE-BMG to date is significantly poorer than conventional BMG. These HE-BMGs exhibit brittle nature inherited from the glass materials. Their enthalpy of mixing (ΔH_{mix}) much more negative than the threshold in forming HEAs, suggesting a preference to form intermetallic compounds. Besides, inclusion of metalloid elements in the $\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}\text{Pd}_{20}\text{Pt}_{20}$ HE-BMG also leads to its brittle characteristic. In sharp contrast, $\text{Ca}_{20}\text{Mg}_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{20}$ base HE-BMGs are ductile and are characterized by peculiar mechanical properties exceeding those of the HEAs and BMGs. An extremely low glass transition temperature near RT of the $\text{Ca}_{20}\text{Mg}_{20}\text{Sr}_{20}\text{Yb}_{20}\text{Zn}_{20}$ base HE-BMGs leads to deformation at RT, which cannot be achieved by any metals and alloy and even BMGs. Unlike single-phase HEAs, AIMD simulations reveal preferred near-neighbor interaction in these HE-BMGs, showing strong tendency in forming intermetallic compounds. The current and upcoming HE-BMGs have a potential to be used as application products which have

been accomplished by BMGs. In addition, it is possible that HE-BMGs have a potential to open a new research field by utilizing the unique properties of HEAs and BMGs in near future.

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