Al0.5TiZrPdCuNi High-Entropy (H-E) Alloy Developed through Ti20Zr20Pd20Cu20Ni20 H-E Glassy Alloy Comprising Inter-Transition Metals

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An Al0.5TiZrPdCuNi high-entropy (H-E) alloy with a bcc single phase was found through a Ti20Zr20Pd20Cu20Ni20 H-E glassy alloy designed based on equi-atomicity inherent to H-E alloys. The constituent elements and the composition of the Ti20Zr20Pd20Cu20Ni20 alloy were determined by regarding a binary Cu40Zr60 bulk metallic glass as Cu40Zr60 alloy and subsequent replacements of the Cu and Zr atoms with other late- and early-transition metals, respectively. The Ti20Zr20Pd20Cu20Ni20 alloy in a ribbon shape forms into a glassy single phase. The addition of 0.5Al to the Ti20Zr20Pd20Cu20Ni20 H-E glassy alloy resulted in forming a bcc single phase for a rod specimen with a diameter of 1.5 mm. The analysis revealed that the Al0.5TiZrPdCuNi H-E alloy is characterized by mixing enthalpy of 46.7 kJ·mol−1 and Delta parameter of 8.8, which are considerably larger and negative for the former and larger for the latter against the conventional H-E alloys.

Keywords: high-entropy alloy, metallic glass, mixing enthalpy, atomic size ratio, alloy design, body centered cubic phase, Laves phase

1. Introduction

Recently, high-entropy (H-E) alloys1,2) and bulk metallic glasses (BMGs)3) have accumulated increasing academic and engineering interests in the field of advanced metallic materials. Here, H-E alloy is a multicomponent alloy with the number of elements (N) ≥ 5 and with principally or nearly the same fraction of the constituent elements in a class of multi-principal element alloy.1,2) On the other hand, BMGs are a metallic glass comprising N ≥ 2 formable in a bulk shape with a diameter or thickness of a couple of millimeter or more. A common feature of H-E alloys and BMGs is that both alloys are formed in a chemically-disorder solid solution, in which the H-E alloys are formed in a single crystalline phase of bcc, fcc or their mixture, whereas BMGs are in a single glassy phase. As a guiding principle, heat of mixing and atomic size ratio of the constituent elements are frequently used in their alloy design, suggesting that one could have succeeded in fabricating the alloys with both features of H-E alloys and BMGs as HE-BMGs. In reality, however, only a few results have been reported to date about the HE-BMGs.4−7) In part, small number of HE-BMGs is due to a different feature of H-E alloys and BMGs in terms of the fractions of the constituent elements. Specifically, the fractions of the constituent elements are principally equi-atomic for the H-E alloys, such as a senary CuTiVFeNiZr H-E alloy with a fraction of 1/6,2) or its modification by adding half mole of Al to the other constituent elements, such as Al0.5CuTiVFeNiZr H-E alloy. On the other hand, BMGs usually possess a main constituent element with the maximum fraction, such as a Pd40Cu30Ni20Zn10Cu10 alloy in Pd-based BMGs.3) Thermodynamic explanation for the above difference between H-E alloys and BMGs can be given by calculating configurational entropy (Sconfig) normalized with the gas constant (R), Sconfig/R, for a solution expressed by eq. (1),

\[ S_{\text{config}}/R = - \sum_{i=1}^{N} c_i \ln c_i. \]  

The maximum value of Sconfig/R, which is lnN as shown in eq. (2), is obtained when the fraction of i-component denoted by ci has an equi-atomicity expressed by ci = 1/N,

\[ S_{\text{config}}/R = \ln N. \]  

Thus, the thermodynamic explanation demonstrates that H-E alloys and BMGs are different types of advanced metallic materials in terms of the fractions of the constituent elements. Despite the difficulty in obtaining HE-BMGs, a few HE-BMGs have been reported to date: Ti20Zr20Hf20Cu20Ni20,4) Zr20Ca20Sr20Yb20(Li0.55Mg0.45)20 BMGs5,7) and its relevant alloys of Sr20Ca28Yb28Mg28Zn20, Sr20Ca28Yb28Mg28Zn10Cu10, and Pd32Pt28Cu23Zn20P20 BMGs.6) Among these HE-BMGs, the authors have recently come to know of the Ti20Zr20Hf20Cu20Ni20 HE-BMG with a critical diameter of 1.5 mm reported by Ma et al. in 2002 in a huge number of relevant papers on BMGs. A reason for difficulty in finding the literature5) is due to the fact that it was reported without referring to the term “high-entropy” in the paper, in which the authors just use a term of “confusion principle”6) that is related to H-E alloys. After about one decade had passed since 2002, the other HE-BMGs have almost simultaneously been found in 2011 based on the alloy design of H-E alloys.5,7) Among all the H-E alloys found to date, the Pd32Pt28Cu23Zn20P20 HE-BMG5) is the only one in Metal-Metalloid type. In other words, almost all the HE-BMGs are Metal-Metal type comprising metallic elements only, suggesting that one may find out new HE-BMGs in Metal-Metal type easier.

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The present study aims (1) to investigate a formation of H-E glassy alloy comprising early-(E) and late (L)-transition metals (ETM and LTM), (2) to analyze the thermal stability and glass-forming ability of the H-E glassy alloys comprising inter-transition metals with and without Al, and (3) to examine the relationships between the H-E alloys and H-E glassy alloys.

2. Methods

Specimens with a nominal composition of Ti$_{20}$Zr$_{20}$Pd$_{20}$Cu$_{20}$Ni$_{20}$ (at%) were prepared by melt-spinning and conventional Cu mold casting from raw materials of pure Ti, Zr, Pd, Cu and Ni. The system and composition of the Ti$_{20}$Zr$_{20}$Pd$_{20}$Cu$_{20}$Ni$_{20}$ alloy was determined by referring to a Cu$_{64}$Zr$_{36}$ alloy with a critical diameter ($d_{\text{prot}}$) of 2 mm$^3$ with an approximate fraction of ETM: LTM = 40:60. Besides, Ti$_{16.7}$Zr$_{16.7}$Hf$_{16.7}$Pd$_{16.7}$Cu$_{16.7}$Ni$_{16.7}$ and Ti$_{20}$Zr$_{20}$Hf$_{20}$Pd$_{20}$Cu$_{20}$Ni$_{20}$ alloys (at%) with fractions of ETM: LTM = 50:50 and 60:40 were also studied for comparison where their prototypes, respectively, were Ti$_{40}$Zr$_{10}$Cu$_{36}$Pd$_{14}$ BMG and Ti$_{20}$Zr$_{20}$Cu$_{20}$Ni$_{20}$ HE-BMG$^{(5)}$ with $d_{\text{prot}}$ = 1.5 mm. In selecting the constituent elements, conventional glass-forming elements, such as, Ti, Zr, Hf, Ni, Cu, Pd, Ag, Pt, Au were considered as candidates, but Co, Fe and some other elements were excluded from the candidates because of the positive mixing enthalpy to Cu and Ni.$^{(13)}$ In a process of optimizing for obtaining a glassy phase, partial modification of the fractions of the constituent elements and minor addition of Al was considered to be the above inter-transition alloys.

A ribbon sample had a thickness of about 0.02 mm and width of 1.2 mm and a rod sample had a diameter up to 2 mm. Structural analysis of the samples was conducted using X-ray diffraction (XRD). The crystalline phases in XRD profiles were identified by referring to Pearson’s crystal data.$^{(12)}$ Here, the crystalline peaks were principally identified from possible crystalline phases with equi-atomicity from the constituent elements (Ti, Zr, Pd, Cu and Ni) of quinary Ti$_{20}$Zr$_{20}$Pd$_{20}$Cu$_{20}$Ni$_{20}$ alloy by referring to Pearson’s crystal data.$^{(12)}$ fcc for CuNiPd, bcc for TiZr, bct for with CuZr$_2$ structure for TiZrCu, fcc with MgZn$_2$ structure for TiZrNi and TiZrPd. The crystallographic data for these structures are summarized in Table 1. The formation and stability of the H-E alloys and H-E glassy alloys were analyzed with thermodynamic and physical parameters: mixing enthalpy ($\Delta H_{\text{mix}}$)$^{(13-15)}$ “Delta” parameter ($\Delta$)$^{(16)}$ and valence electron concentration (VEC).$^{(17)}$ The values of $\Delta H_{\text{mix}}$ were calculated by eq. (3) with the mixing enthalpy of an A-B binary system at the equi-atomic composition (A$_{50}$B$_{50}$) for a liquid phase ($\Delta H_{\text{L}}$) acquired from literature.$^{(15)}$ The multiplication factor of four and the product $c_i c_j$ on the right-side of eq. (3) means the assumption that $\Delta H_{\text{mix}}$ was calculated as quadratic formula with maximum or minimum at the composition of A$_{50}$B$_{50}$.

$$\Delta H_{\text{mix}} = 4 \sum_{i \neq j=1}^{N} \Delta H_{i,j} c_i c_j.$$  (3)

On the other hand, $\Delta$ was calculated by eqs. (4) and (5)$^{(16)}$

$$\delta = \sqrt{\sum_{i=1}^{N} c_i \left(1 - \frac{r_i}{\bar{r}} \right)^2} \times 100,$$  (4)

$$\bar{r} = \sum_{i=1}^{N} c_i r_i.$$  (5)

Here, $r_i$ is the atomic radius of the $i$-th constituent element and $\bar{r}$ is the average atomic radius of the alloy defined by eq. (5). The formulation of eq. (4) with multiplication factor of 100 is different from the original one without the factor, since $c_i$ in the present study is the faction of the constituent element ranging 0 to 1 and is not the percentage given in the original literature.$^{(16)}$ However, the authors confirmed that eq. (4) gives the same $\delta$ values of the alloys in the literature.$^{(16)}$ The values of VEC defined by eq. (6) were calculated with intrinsic VEC values of each constituent element, (VEC)$_i$, where (VEC)$_i$ = 3 (Al), 4 (Ti, Zr and Hf), 10 (Ni and Pd), 11 (Cu),$^{(17)}$

$$\text{VEC} = \sum_{i=1}^{N} c_i (\text{VEC})_i.$$  (6)

The (VEC) corresponds to the number of group (NoG) in the periodic table, which is NoG in the long-period form for the elements in the fourth or greater periods including transition metals and in the short-period form for the other elements including Al.

3. Results and Discussions

Figure 1 shows the XRD patterns of the (a) Ti$_{20}$Zr$_{20}$Hf$_{20}$Pd$_{20}$Cu$_{20}$Ni$_{20}$, (b) Ti$_{16.7}$Zr$_{16.7}$Hf$_{16.7}$Pd$_{16.7}$Cu$_{16.7}$Ni$_{16.7}$ and (c) Ti$_{20}$Zr$_{20}$Pd$_{20}$Cu$_{20}$Ni$_{20}$ alloys in a ribbon shape. The XRD
pattern for (c) Ti20Zr20Pd20Cu20Ni20 alloy does not exhibit distinct sharp peaks that corresponded to the presence of crystalline peaks, but only exhibits a halo peak with a primary broad peak at a scattering angle 2θ = 40.5 degrees. On the other hand, the XRD patterns for (a) Ti20Zr20Hf20Pd20Ni20 and (b) Ti16.7Zr16.7Hf16.7Pd16.7Cu16.7Ni16.7 alloys contain sharp peaks due to the reflections of crystals of hcp-TiZr, Laves phases and unknown phase. These XRD profiles for ribbon specimens indicate that the Ti20Zr20Pd20Cu20Ni20 alloy is formed in a single glassy phase, whereas the other two alloys are in a mixture structure of glassy and crystalline phases. Thus, the Ti20Zr20Pd20Cu20Ni20 alloy was selected as a candidate for HE-BMG in the subsequent experiments.

Figures 2(a) and 2(b) show the DSC scans measured at a heating rate of 0.67 K/s for the Ti20Zr20Pd20Cu20Ni20 alloy. The DSC trace in Fig. 2(a) exhibits distinct endothermic and subsequent exothermic reactions, suggesting the glass transition and crystallization occur during heating. Further analysis of the DSC trace with extrapolations of the scan gives a glass transition temperature (Tg) of 755 K, and an onset temperature for crystallization (Tx) of 806 K. Thus, it was found that the Ti20Zr20Pd20Cu20Ni20 H-E glassy alloy was obtained in a ribbon shape by melt-spinning. On the other hand, Fig. 2(b) exhibited a liquidus temperature (Ts) of 1404 K. Thus, glass-forming ability (GFA) parameters of the Ti20Zr20Pd20Cu20Ni20 H-E glassy alloy were evaluated as follows: The supercooled liquid range (ΔTs = Ts - Tg) is 51 K, and reduced glass transition temperature (Tg/Ts) is 0.538. These values are almost the same to those of the Ti20Zr20Hf20Cu20Ni20 HE-BMG reported by Ma et al. in 2002.4) with ΔTs = 53 K and Tg/Ts = 0.560 where Ti = 1176 K was evaluated by the present authors, since the authors in literature4) did not give Ti but used melting temperature (Tm) for evaluating GFA with Tg/Tm instead of Tg/Ts. The Ti20Zr20Pd20Cu20Ni20 H-E glassy alloy satisfies a necessary condition for obtaining high GFA leading to BMG in point that its ΔTs exceeds 50 K. Then, the authors examined BMG formation for the Ti20Zr20Pd20Cu20Ni20 alloy. Figure 3 shows the XRD profile of the Ti20Zr20Pd20Cu20Ni20 H-E alloy with a diameter of 1 mm where the pattern was taken from a vertical cross-section along the longitude direction of the specimen. One cannot rule out a possibility that the phases identified (hcp-TiZr, hcp-PdTiZr, hcp-NiTiZr, fcc-CuNiPd and bcc phase) can have solubility for the other elements from the ones described in the element symbols due to multi-principal alloying in the Ti20Zr20Pd20Cu20Ni20 H-E alloy.
summarized in Table 2, together with the data of Ti$_2$Zr$_2$Hf$_2$Cu$_2$Ni$_2$0$_2$ and Pd$_2$Pt$_2$Cu$_2$Ni$_2$P$_2$0$_6$ HE-BMGs for comparison.

With the aim to find a HE-BMG, the alloy compositions of the Ti$_2$Zr$_2$Pd$_2$Cu$_2$Ni$_2$0$_2$ were slightly modified in the following two cases. The first case is to fabricate a Ti$_2$Zr$_2$Pd$_2$Cu$_2$Ni$_2$0$_2$ alloy and the second one is to add Al to the Ti$_2$Zr$_2$Pd$_2$Cu$_2$Ni$_2$0$_2$ as well as Ti$_2$Zr$_2$Hf$_2$Cu$_2$Ni$_2$0$_2$ alloy. Figure 4 shows the XRD patterns of the Ti$_2$Zr$_2$Pd$_2$Cu$_2$Ni$_2$0$_2$ HE-BMGs.

Table 2 Glass transition temperature ($T_g$), crystallization temperature ($T_c$) and liquidus temperature ($T_l$) and critical diameter for the formation of bulk metallic glass ($d_{max}$), reduced glass transition temperature ($T_r/T_g$) and supercooled liquid range ($\Delta T_r$) of the Ti$_2$Zr$_2$Pd$_2$Cu$_2$Ni$_2$0$_2$ and Ti$_2$Zr$_2$Hf$_2$Cu$_2$Ni$_2$0$_2$ and Pd$_2$Pt$_2$Cu$_2$Ni$_2$P$_2$0$_6$ HE-BMGs.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$T_g$/K</th>
<th>$T_c$/K</th>
<th>$T_l$/K</th>
<th>$d_{max}$/mm</th>
<th>$T_r/T_g$</th>
<th>$\Delta T_r$/K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_2$Zr$_2$Pd$_2$Cu$_2$Ni$_2$0$_2$</td>
<td>755</td>
<td>806</td>
<td>1404</td>
<td>—</td>
<td>0.54</td>
<td>51</td>
<td>—</td>
</tr>
<tr>
<td>Ti$_2$Zr$_2$Hf$_2$Cu$_2$Ni$_2$0$_2$</td>
<td>658</td>
<td>711</td>
<td>1176</td>
<td>1.5</td>
<td>0.56</td>
<td>53</td>
<td>3)</td>
</tr>
<tr>
<td>Pd$_2$Pt$_2$Cu$_2$Ni$_2$P$_2$0$_6$</td>
<td>580</td>
<td>645</td>
<td>820</td>
<td>10</td>
<td>0.59</td>
<td>65</td>
<td>5)</td>
</tr>
</tbody>
</table>

Fig. 4 XRD patterns of the Ti$_2$Zr$_2$Pd$_2$Cu$_2$Ni$_2$0$_2$ alloy with 1 and 1.5 mm rod specimens.

Fig. 5 XRD patterns of the Al$_{0.5}$TiZrPdCuNi and Al$_{0.5}$TiZrHfCuNi alloys with shapes of ribbon and 1.5 mm diameter rod.
effectively changes the crystalline phases from polycrystalline including Laves phase to a bcc single phase in keeping with a bcc single phase is plotted apart from zone S as well as zone S’, indicating that the Al₀.₅TiZrPdCuNi H-E alloy has a considerably specific position among H-E alloys, when characterized by mixing enthalpy and atomic size effect.

In reality, the Al₀.₅TiZrPdCuNi H-E alloy has a large and negative \( \Delta H_{\text{mix}} = -46.7 \text{ kJ mol}^{-1} \) as shown in Table 3. According to Ref. 11, \( \Delta H_{\text{mix}} \) determines the number of stable intermediate phase (NoSIP). For \( \Delta H_{\text{mix}} \) in units of kJ mol\(^{-1}\) \( \text{NoSIP} = 0.2 \) for \( 5 > \Delta H_{\text{mix}} > 0 \), 0.6 for \( 0 > \Delta H_{\text{mix}} > -4 \), 1 for \(-4 > \Delta H_{\text{mix}} > -10 \), 2 for \(-10 > \Delta H_{\text{mix}} > -20 \), 2.8 for \(-20 > \Delta H_{\text{mix}} > -40 \), 3.8 for \(-40 > \Delta H_{\text{mix}} > -75 \) and 5 for \(-75 > \Delta H_{\text{mix}} \). Thus, the present case of \( \Delta H_{\text{mix}} = -46.7 \text{ kJ mol}^{-1} \) allows us to anticipate the evolution of further more than two intermediate phases.

However, the analysis revealed that the Al₀.₅TiZrPdCuNi H-E alloy with \( \Delta H_{\text{mix}} = -46.7 \text{ kJ mol}^{-1} \) is formed in a single bcc phase, indicating the peculiar \( \Delta H_{\text{mix}} \) of Al₀.₅TiZrPdCuNi H-E alloy. On the other hand, \( \delta = 8.8 \) for the Al₀.₅TiZrPdCuNi H-E alloy is considerably larger than the third criterion \( \delta < 4.6 \) for the conventional H-E alloys. Consequently, we conclude that the Al₀.₅TiZrPdCuNi H-E alloy found in the present study can be a new type of H-E alloy and it is worth searching for a H-E glassy alloy through a process of finding new H-E glassy alloys.

The item (4) mentioned above for the value of VEC was calculated to be 7.18 by eq. (6) for the Al₀.₅TiZrPdCuNi H-E alloy. The expected phase, according to the literature \(^{(39)}\) would be fcc + bcc phase from the criteria (4), but in reality the Al₀.₅TiZrPdCuNi H-E alloy is formed in a single bcc phase. The appearance of a single bcc phase in the Al₀.₅TiZrPdCuNi H-E alloy can be explained by neither VEC nor the crystallographic structures of the constituent elements where Al, Pd, Cu and Ni are fcc formers, and \( \alpha/\beta \)-Ti and \( \alpha/\beta \) -Zr are hcp/bcc formers at low- and high-temperature. A possible reason for the Al₀.₅TiZrPdCuNi alloy to exhibit a bcc single phase is that minor elements of Ti and Zr, which form in a bcc structure as a high-temperature phase, are included as a result of the allotropic transformation, which is explained by the following three factors: (i) the allotropic transformation of pure Ti and Zr elements and inclusion of Al as bcc formers, (ii) network formation due to percolation and (iii) atomic size effect of bcc formers.

First, we consider the solidification behavior of the Al₀.₅TiZrPdCuNi alloy with a schematically illustrated continuous-cooling transformation (C.C.T.) diagram shown in Fig. 7. A C-curve for a bcc phase is drawn at a high temperature range in Fig. 7. In part, this is due to allotropic transformation of pure Ti and Zr\(^{(20)}\) and is due to a widely-accepted fact that the bcc structure is often the high-temperature structure of a metal that has a close-packed

![Figure 6](image-url) Relationships between mixing enthalpy (\( \Delta H_{\text{mix}} \)) and Delta parameter (\( \delta \)) for S (solid solution), S’ (ordered solid solution), B₁ (BMG except for BMGs belonging to B₂), B₂ (Cu- and Mg-based BMGs) and C (intermediate phase).

Table 3 Mixing enthalpy (\( \Delta H_{\text{mix}} \)), Delta parameter (\( \delta \)), phases in the forms of ribbon and 1.5 mm rod specimens and reference of the H-E alloys.

<table>
<thead>
<tr>
<th>( \Delta H_{\text{mix}} )/kJ mol(^{-1})</th>
<th>( \delta )</th>
<th>Phase (Ribbon/(1.0)* 1.5 mm rod)</th>
<th>Ref.</th>
<th>Referential Fig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti₀.₅Zr₀.₅Pd₀.₅Cu₀.₅Ni₀.₅</td>
<td>10.3</td>
<td>Glass/Glass</td>
<td>3)</td>
<td>—</td>
</tr>
<tr>
<td>Al₀.₅ZrPdCuNi</td>
<td>8.8</td>
<td>Glass/bcc</td>
<td>—</td>
<td>Figs. 5(b)/(a)</td>
</tr>
<tr>
<td>Al₀.₅TiZrHfCuNi</td>
<td>9.9</td>
<td>Glass/(fcc + Laves)</td>
<td>—</td>
<td>Figs. 5(d)/(c)</td>
</tr>
</tbody>
</table>
structure at lower temperature.\textsuperscript{20} Thus, authors think that allotropic transformation of pure Ti and Zr could provide a symptom of the $\text{Al}_{0.5}\text{TiZrPdCuNi}$ alloy to be formed into a bcc phase. One such symptom would be provided as formulae of nucleation sites or embryos. In casting the alloy, when compared with critical site percolation concentration (eq. (7)), the alloy remains a bcc phase. One such symptom would be provided as formulae of nucleation sites or embryos. In casting the alloy, when compared with critical site percolation concentration (eq. (7)), the alloy remains a bcc phase.

Second, the authors focus on the fraction in composition of bcc formers ($f_{\text{bcc,comp}}$) in the $\text{Al}_{0.5}\text{TiZrPdCuNi}$ alloy. The $f_{\text{bcc,comp}} = 0.455$, which is from 0.182 for Ti and Zr and 0.091 for Al, is enough to form a network structure in an atomistic level due to percolation in the $\text{Al}_{0.5}\text{TiZrPdCuNi}$ alloy, when compared with critical site percolation concentrations ($p_{i}$) for possible 3-dimensional structures.\textsuperscript{21} $p_{i}$'s are 0.198 for fcc, 0.245 for bcc and 0.27 for dense random packing structure. It should be noted that all these $p_{i}$'s are smaller than $f_{\text{bcc,comp}} = 0.455$, indicating that bcc formers form a percolated network structure. Hence, it is possible that nucleation sites or embryos of a bcc phase formed by the presence of bcc formers at a high temperature could remain in the process (2) in Fig. 7 by cooperative motions of bcc formers inherent to percolated network formed in the alloy.

Third, the authors consider “a 45–55% rule”.\textsuperscript{22} The 45–55% rule claims that in an $\text{Al}_{x}\text{Co}_{y}\text{Zr}_{z}\text{Cu}_{w}\text{Fe}_{m}\text{Ni}_{n}$ H-E alloy a phase has a fcc structure for $f_{\text{fcc,comp}} \geq 45$ at% and a bcc structure for $f_{\text{bcc,comp}} \geq 55$ at%. Thus, the 45–55% rule does not explain the $\text{Al}_{0.5}\text{TiZrPdCuNi}$ alloy with $f_{\text{bcc,comp}} = 0.455$ for forming a bcc phase. However, this disagreement can be solved when focusing on the volume fraction of the space occupied by bcc formers ($f_{\text{bcc,space}}$). Assuming the atoms as spheres makes it possible to calculate $f_{\text{bcc,space}}$ with eq. (7).

\begin{equation}
 f_{\text{bcc,space}} = \sum_{i} \frac{c_{i}^{3}}{V_{i}} \cdot \frac{1}{\sum_{i} c_{i}^{3}},
 \end{equation}

Equation (7) yields $f_{\text{bcc,space}} = 0.573 > 0.55$ for the $\text{Al}_{0.5}\text{TiZrPdCuNi}$ alloy and $f_{\text{bcc,space}} = 0.53 < 0.55$ for the TiZrPd-CuNi alloy. These $f_{\text{bcc,space}}$'s explain that the $\text{Al}_{0.5}\text{TiZrPdCuNi}$ alloy is in favor to form a bcc phase according to the 45–55% rule modified. The agreement of the 45–55% rule takes place because of the larger atomic radii of bcc formers (Ti, Zr and Al) than those of fcc formers (Pd, Cu and Ni) in the $\text{Al}_{0.5}\text{TiZrPdCuNi}$ alloy where the values of atomic radii were shown in this Section. Hence, the authors herewith conclude that the simultaneous satisfactions of the factors (i)–(iii) can be possible reasons for the $\text{Al}_{0.5}\text{TiZrPdCuNi}$ alloy formed in a single bcc phase. Another possible reason is due to the addition of Al with $(\text{VEC})_{\text{Al}} = 3.17$, the small VEC value of 3 for Al plays a role to decrease the VEC values, leading to a tendency to form a bcc structure. The details of the effect of Al addition is unclear, but it was found that addition of Al was effective not only for the conventional H-E alloys, but also for the H-E glassy alloy, such as the $\text{Ti}_{20}\text{Zr}_{20}\text{Pd}_{20}\text{Cu}_{20}\text{Ni}_{20}$ alloy comprising glass-forming alloy elements of ETMs and LTMs.

4. Conclusions

Inter-transition alloys comprising Early-(E) and Late-(L) transition metals (ETM and LTM), respectively, were studied to obtain high-entropy (H-E) glassy alloys in accordance with equi-atomicity inherent to H-E alloys. Among the inter-transition alloys, it was found that the best glass-forming ability is obtained in a $\text{Ti}_{20}\text{Zr}_{20}\text{Hf}_{20}\text{Cu}_{20}\text{Ni}_{20}$ H-E BMG with a critical diameter of 1.5 mm, which was previously reported by Ma et al. in 2002. The $\text{Ti}_{20}\text{Zr}_{20}\text{Pd}_{20}\text{Cu}_{20}\text{Ni}_{20}$ alloy prepared by melt-spinning is formed in a glassy alloy as a H-E glassy alloy. The $\text{Ti}_{20}\text{Zr}_{20}\text{Pd}_{20}\text{Cu}_{20}\text{Ni}_{10}$ with 1 mm in diameter is not fully but mostly formed in a bulk metallic glass. It was found that an $\text{Al}_{0.5}\text{TiZrPdCuNi}$ alloy with 1.5 mm in diameter exhibits bcc single phase as a family of H-E alloys.

The analysis with mixing enthalpy $(\Delta H_{\text{mix}})$ and Delta parameter $(\delta)$ revealed that the $\text{Al}_{0.5}\text{TiZrPdCuNi}$ H-E alloy has $\Delta H_{\text{mix}} = -46.7$ kJ·mol$^{-1}$ and $\delta = 8.8$, which are larger and negative $\Delta F_{\text{mix}}$ and larger $\delta$ than those of the conventional H-E alloys. The significance of studying H-E glassy alloy was shown by finding the $\text{Al}_{0.5}\text{TiZrPdCuNi}$ H-E alloy through the process of developing H-E glassy alloy.

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REFERENCES