Composition Rules from Electron Concentration and Atomic Size Factors in Zr-Al-Cu-Ni Bulk Metallic Glasses*1

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In this paper, we will discuss and apply the formation rules for bulk metallic glasses, originated from quasicrystals composition rules, by combining two most common factors, atomic size factor and electron concentration (e/a) factor. According to literature survey, to our experience on quasicrystal formation, and to our own experimental verification, we propose two criteria, based on atomic size and electron concentration e/a respectively. The first criterion is quantified as the Rav-constant criterion, Rav being the average atomic radius, and the second one the e/a-constant criterion. In a given alloy system the optimum BMGs and their crystalline counterparts tend to share the same Rav and e/a values. These criteria have been applied to determine the ideal BMGs in Zr-Al-Cu-Ni system.

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1. Introduction

Bulk metallic glasses (BMGs) have been found in many Zr-based multi-component alloy systems1) in the past two decades, and much efforts2–4) have been devoted to the fundamental reasons for such large glass-forming abilities (GFAs). Recently, Shindo et al.5,6) introduced an empirical method to estimate the critical BMG forming compositions for several known BMG-forming systems such as La-Ni-Al, Cu-Zr-Ti and Zr-Ni-Al. They applied these criteria in predicting the glass formation ranges of transition metal-transition metal binary systems.7) The large negative values of the Cowley’s order parameter, and hence the ease of atomic clustering in the alloy melts at the composition with a large GFA, have been associated with an icosahedron-like short range ordered atomic cluster. Such a thermodynamic consideration, eventually originating from basic microscopic mechanisms, imposes both a strict atomic size condition to form an icosahedral atomic configuration as well as an electronic constraint as involved in the Miedema’s method. In the electronic structure model of metallic glasses proposed by Nagel and Tauc,8) a metallic glass is treated as a free electron gas and its formation and stability is related to the conduction electron concentration per atom, e/a. Later, Häussler9) further termed the optimum metallic glasses “ideal amorphous state”. Mizutani and Massalski10) attempted to combine the contributions of electronic and atomic size effects as the two main parameters to assess the glass forming ability.

It is known that stable quasicrystals satisfy an e/a-constant rule, i.e. they and their crystalline counterparts share a nearly constant e/a ratio.11) This has led us to the establishment of ternary quasicrystal composition rules.12) Ternary quasicrystalline compositions are located near the crossing points of the e/a-constant line and another straight line linking a binary quasicrystal composition and the third element, termed specific e/a-variant line. These two criteria can precisely determine the composition of any ternary quasicrystalline phase. In this paper we attempt to extend the rules originated from quasicrystals to the BMG forming systems. We introduce two criteria, one is based on e/a and the other on the average atomic size Rav. We will then verify them by examining a series of new BMG compositions in the Zr-Al-Ni-Cu system.

2. The e/a-constant Rule in Ternary Quasicrystalline Systems

Stable quasicrystals have been found in many ternary Al-based alloy systems. For example, in Al-Cu-Fe, there exists a stable ternary icosahedral quasicrystal with composition close to Al62.5Cu24.5Fe12.5.13) Figure 1 is the phase diagram at room temperature as reported in reference.13) Taking the valence contributions from Al, Cu, and Fe respectively as Na½ = 3, NCu½ = 1, and NFe½ = –2, the Al62.5Cu25Fe12.5 quasicrystalline phase has e/a = 1.86 and the constant e/a = 1.86 line follows equation CFe = 0.23 – 0.4Cu. Notice that the Al62.5Cu25Fe12.5 quasicrystal and its approximants λ-Al13Fe4, φ-Al10Cu10Fe are all located near this line.11) Such a rule is universal in ternary quasicrystalline phase diagrams. We have applied this rule and other information derived from phase diagrams to determine the exact composition zone of the Al-Ni-Fe decagonal quasicrystal.12)

3. The e/a and Atomic Size Rules in the BMGs-related Phases

In the Zr-Al-Ni-Cu alloys system, the BMG with the highest glass forming ability known so far is the Inoue alloy Zr65Al17.5Ni10Cu17.5 with the highest ΔTs of 127K.14) During

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an investigation of the microstructure of an as-cast Zr_{65}Al_{17.5}Ni_{10}Cu_{17.5} ingot, we found five crystalline phases in coexistence with the glassy phase.\(^{15}\) What is remarkable about these phases, as we have noted, is that they share nearly constant e/a ratios. This is strikingly similar to the e/a-constant phenomenon in quasicrystalline systems.\(^{11}\) Thereof we obtain the first criterion for the BMG formation: a BMG all have specific in a given alloy system. In a binary system, the e/a-constant compositions correspond to a straight composition line, or the specific e/a ratio determines the composition of the best glass forming composition.\(^{39}\) In a ternary system, the e/a-constant compositions correspond to a straight composition line, or the e/a-constant line, and in a quaternary system, to an e/a-constant plane. The known amorphous phases in the Zr-Al-Ni-Cu systems, and the crystalline phases in Zr-Al-Ni-Cu system all have e/a ratios close to 1.4, as shown in Table 1.

We further notice that these amorphous and crystalline phases are not distributed randomly on the e/a-constant plane in the quaternary phase diagram, as shown in Fig. 2. Their compositions are located close to a specific straight line on the e/a-constant plane. This special composition distribution reflects the influence from factors other than the electron concentration. It is known that atomic size is an important factor in forming amorphous structures. By analogy to the calculation of the average electron number per atom, e/a, we introduce the concept of average atomic size \(R_{av}\) as the second criterion to judge the glass forming compositions. \(R_{av}\) is defined as the summary of multiplications of atomic fraction \(C_i\) and Goldschmidt atomic radius \(R_i\) of each element

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R_{av} = \sum C_i R_i
\]

We then calculated the \(R_{av}\) values for the phases mentioned above. As shown in Table 1, the constant \(R_{av}\) phenomenon is obvious; all the compositions have \(R_{av}\) close to 0.15 nm. The specific composition line, near which all the phases are located, is the intersection of two planes, one being the e/a-constant and the other the \(R_{av}\)-constant.

We take the e/a and \(R_{av}\) values of the Inoue alloy Zr_{65}Al_{17.5}Ni_{10}Cu_{17.5} and plotted the two planes in the quaternary phase diagram in Fig. 2. All the compositions of known BMGs and quaternary phases in this system are

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\begin{array}{llll}
\text{Phases} & \text{Structure and origin} & e/a & R_{av} (\text{nm}) \\
\hline
\text{Zr}_{65}\text{Al}_{17.5}\text{Ni}_{10}\text{Cu}_{17.5} & \text{BMG} & 1.38 & 0.1496 \\
h\text{p}\text{-Zr}_{65}\text{Al}_{11.7}\text{Ni}_{11.0}\text{Cu}_{11.7} & \text{Hexagonal Al}_{1.5}\text{Ni}_{5.0} \text{type, observed in as-cast Zr}_{65}\text{Al}_{11}\text{Ni}_{10}\text{Cu}_{17.5} & 1.45 & 0.1502 \\
o\text{p}\text{-Zr}_{65}\text{Al}_{11.7}\text{Ni}_{11.0}\text{Cu}_{11.7} & \text{Orthorhombic, superstructure of hP, observed in as-cast Zr}_{65}\text{Al}_{11}\text{Ni}_{10}\text{Cu}_{17.5} & 1.45 & 0.1502 \\
t\text{I}\text{-Zr}_{66.7}\text{Al}_{13.7}\text{Ni}_{8.4}\text{Cu}_{22.9} & \text{Tetragonal Cu}_{2}\text{Zr}_{2} \text{type, observed in as-cast Zr}_{65}\text{Al}_{11}\text{Ni}_{10}\text{Cu}_{17.5} & 1.28 & 0.1487 \\
\text{fCc}\text{-Zr}_{67.5}\text{Al}_{17.5}\text{Ni}_{15.5}\text{Cu}_{11.8} & \text{Fcc Zr}_{2}\text{Ni} \text{phase with NiTi}_{2} \text{structure} & 1.29 & 0.1499 \\
\text{QC}\text{-Zr}_{65.5}\text{Al}_{13.1}\text{Ni}_{11}\text{Cu}_{11.8} & \text{Icosahedral quasicrystal} & 1.39 & 0.1509 \\
\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{20} & \text{BMG} & 1.50 & 0.1496 \\
\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{35} & \text{BMG} & 1.43 & 0.1479 \\
\text{Zr}_{65}\text{Al}_{10}\text{Ni}_{35} & \text{BMG} & 1.35 & 0.1487 \\
\text{Zr}_{65}\text{Al}_{10}\text{Cu}_{27.5} & \text{BMG} & 1.48 & 0.1499 \\
\text{Zr}_{65}\text{Al}_{10}\text{Cu}_{30} & \text{BMG} & 1.50 & 0.1487 \\
\text{Zr}_{65}\text{Al}_{10}\text{Cu}_{4} & \text{BMG} & 1.63 & 0.1533 \\
\end{array}
\]
located near this specific intersection line with $e/a = 1.4$ and $R_g = 0.1496$ nm. By doing so we establish two quantitative criteria for the formation of BMGs in the Zr-based alloy systems.

4. Optimization of the Glass-Forming Compositions in the Zr-Al-Ni-Cu System

Six Zr-Al-Ni-Cu alloys, Zr$_{65.5}$Al$_{14.5}$Ni$_{6.5}$Cu$_{22.4}$, Zr$_{65.3}$Al$_{5}$Ni$_{6.5}$Cu$_{23}$, Zr$_{65.5}$Al$_{5}$Ni$_{5.2}$Cu$_{30}$, Zr$_{65.8}$Al$_{7.5}$Ni$_{10}$Cu$_{17.5}$, Zr$_{65.6}$Al$_{8.3}$Ni$_{11.4}$Cu$_{15.5}$, Zr$_{66.5}$Al$_{2}$Ni$_{11.3}$Cu$_{13.1}$, Zr$_{63.8}$Al$_{14.2}$Ni$_{17.2}$Cu$_{7.6}$, were designed which satisfy constant $e/a = 1.4$ and constant $R_g = 0.1496$ nm. These alloys were suction cast into $d_3$ mm cylindrical bars. According to XRD, all the as-cast samples are amorphous.

DSC and DTA measurements were carried out to determine the thermal stability and glass forming ability of these alloys. The temperature data derived from the DSC and DTA curves are shown in Table 2.

We see from Table 2 that the supercooled liquid region $\Delta T_g$ values are all quite large, close to 100 K, the largest being 105 K for sample #2. This means that we have found a series of the $e/a$-constant and the $R_g$-constant BMGs with large supercooled liquid regions, and the well-known Inoue alloy is only one of a series of good BMGs. In order to assess the relative thermal stability among the six samples, we compare the glass transition temperature $T_g$ and the crystallization temperature $T_x$. The higher the transition temperature, the higher the thermal stability of the metallic glass. The stability of the BMGs increases from sample #1 to #6, and the best of them is #6, instead of the Inoue alloy (#3). The glass forming ability is denoted by $T_{eg}$, reduced glass transition temperature, either expressed as $T_g/T_m$ or $T_g/T_1$, $T_m$ and $T_1$ are respectively the melting temperature and the liquidus temperature. The highest $T_{eg}$, and then the best glass forming composition is found in the vicinity of the composition #6, Zr$_{63.8}$Al$_{14.2}$Ni$_{17.2}$Cu$_{7.6}$.

5. Conclusions

We have shown by examples of a series of Zr-Al-Cu-Ni alloys that the electron concentration $e/a$ and average atomic size $R_g$ factors are useful criteria to judge the BMG forming composition zone. For the well-known Inoue alloy, the specific $e/a$ ratio is close to 1.4 and $R_g$ close to 0.1496 nm. The samples satisfying these $e/a$ and $R_g$ values are in glassy state after suction casting in a copper mould. They all have large supercooled liquid regions $\Delta T_g$ (about 100 K) and reduced glass transition temperatures $T_g$ (about 0.6), as well as high glass transition and crystallization temperatures. The best glass forming composition in this series of alloys is Zr$_{63.8}$Al$_{14.2}$Ni$_{17.2}$Cu$_{7.6}$, sample #6), instead of the Inoue alloy Zr$_{65.5}$Al$_{14.5}$Ni$_{10}$Cu$_{17.5}$. This new BMG has $T_{eg} = T_g/T_m = 0.61$, $\Delta T_g = 87$ K, $T_g = 671$ K, $T_x = 758$ K according to the thermal analysis results.

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