Revisiting Al-Ni-Zr bulk metallic glasses using the ‘cluster-resonance’ model

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Six series of alloys, namely, Ni$_3$Zr$_x$Al$_{x}$, Ni$_3$Zr$_x$Al$_{x}$, Ni$_3$Zr$_x$Al$_{x}$, Ni$_3$Zr$_x$Al$_{x}$, Ni$_3$Zr$_x$Al$_{x}$ and Ni$_3$Zr$_x$Al$_{x}$, ($x=1, 1.5, 2, 3$) were designed in this work and the bulk metallic glass (BMG) formation of these compositions was investigated by copper mold suction casting. A centimeter-scale BMG sample was obtained for the Ni$_4$Zr$_9$Al$_2$ (Al$_{13.3}$Ni$_{26.7}$Zr$_{60}$ in atomic percent) composition. The thermal glass parameters for this BMG were determined to be $\Delta T_x = 68$ K, $T_{rg} = 0.579$, and $\gamma_m = 0.689$. Using the ‘cluster-resonance’ model for glass formation an optimal BMG composition was determined using the cluster formula $[\text{Ni}_3\text{Zr}_9\text{Al}_2\text{Ni}_1]$. 

bulk metallic glass, glass-forming ability, Al-Ni-Zr, cluster formula

To date, a large variety of bulk metallic glasses (BMGs) have been discovered [1], and Zr-based BMGs are among the most promising structural materials. This is because they exhibit a combination of high strength, toughness and anti-corrosion properties [1,2]. Many multi-component Zr-based BMG systems exist such as Al-Cu-Ni-Zr [3], Be-Cu-Ni-Ti-Zr [4], Al-Cu-Ni-Nb(Ti)-Zr [5,6] and Ag-Al-Cu-Zr [7]. These complex alloys are based on the basic ternary systems of Al-TM-Zr (TM = Ni, Co, Cu) together with specific alloying substitutes [5,7,8]. A rationalization of the glass-forming abilities (GFAs) of Al-TM-Zr alloys is desirable to quantify complex BMG compositions. Disagreements exist with regard to experimental accounts of the GFA for fundamental ternary systems [9–11]. This study is devoted to a reexamination of the GFAs of Al-Ni-Zr alloys.

We first use the ‘cluster-plus-glue-atom’ model [12,13] for BMG composition design. This model presents a semi-phenomenological treatment of a BMG structure. An atomic cluster of specific topology, chemical composition and glue structure were used to establish the statistical composition of a BMG system. An ideal BMG assumes universal cluster formulae such as $[\text{cluster}]_x(\text{glue atoms})_x$, with $x=1$ or 3 [13,14]. To determine the structural stability of the model structure we recently proposed a ‘cluster-resonance’ model by taking the coupling of long-range Friedel oscillations of valence electrons with the pair correlation function into consideration [15]. The composition design of Al-Ni-Zr BMG alloys is incorporated into the model that follows.

1 The ‘cluster-resonance’ model and composition design

According to Häussler et al. [16] the static atomic structure of an ideal amorphous state is in resonance with the long-range Friedel oscillations of valence electrons. The resonance results in spherical periodicity as shown by the peak (shell) oscillation with a certain period in the pair correlation function of an ideal amorphous state. The spherical periodicity gives an oscillation wavelength ($\lambda_{Fr}$) in the form of
\[ r_n = \left( 1 + \frac{1}{4} \right) \lambda_{r_n}, \]  
(1)

where \( r_n \) is the radius of the \( n \)th shell centered by any atom and

\[ \lambda_{r_n} = \frac{2\pi}{K_p}, \]  
(2)

where \( K_p \) is the wave vector of the reciprocal space. The resonance condition for an ideal amorphous state yields a matching relation \( K_p = 2k_F \) where \( k_F \) is the Fermi momentum. Therefore,

\[ k_p = \frac{K_p}{2} = \frac{\pi}{r_i} = \frac{1.25\pi}{r_i}, \]  
(3)

with which the effective electron concentration \((e/a)\) for an ideal amorphous state can be obtained:

\[ \frac{e}{a} = \frac{1.25\pi}{3} \times \frac{1}{\rho_a r_i}, \]  
(4)

where \( r_i \) is the radius of the nearest-neighbor shell of the cluster and \( \rho_a \) is the number of atoms per unit volume. The determination of the atomic cluster structure is, therefore, required for the composition design of Al-Ni-Zr BMGs.

Although not entirely convincing the existing experimental evidence discloses a local structure similarity between metallic glasses and their crystalline counterparts [17–19]. A strongly negative mixing enthalpy exists between Ni and Zr at a 1 : 1 atomic ratio. We considered Ni-Zr atomic clusters in the known crystalline phases of the Al-Ni-Zr system. Intermetallic phases of Al\(_3\)NiZr\(_6\) (InMg\(_2\) type), NiZr\(_2\) (Al\(_2\)Cu type) and metastable cF-NiZr\(_2\) (NiTi\(_2\) type) are known crystallization products of Zr-based Al-Ni-Zr BMGs [20,21]. In the different structures three Ni-centered clusters, namely, a CN11 Ni-Ni\(_2\)Zr\(_9\) capped trigonal prism (Figure 1(a)), a CN10 Ni-Ni\(_2\)Zr\(_8\) octahedral antiprism (Figure 1(b)) and a CN12 Ni-Ni\(_3\)Zr\(_9\) icosahedron (Figure 1(c)) have been identified. Here ‘-’ is used to distinguish the central atom (before -) from shell atoms (after -). A binary NiZr phase of BCr-type is also considered and it consists of an atomic cluster of a CN9 Ni-Ni\(_2\)Zr\(_7\) Archimedes octahedral antiprism (Figure 1(d)). Within the framework of the ‘cluster-plus-glue-atom’ model, atomic clusters that preserve the same topological configurations that are of a statistically averaged composition serve as the chair tilings of an ideal amorphous structure pattern.

In a ternary composition diagram, the ‘cluster-plus-glue-atom’ model is embodied by a cluster line, which links an atomic cluster composition to the glue atom [14]. Therefore, four cluster lines in the forms of Ni\(_3\)Zr\(_6\)-Al, Ni\(_3\)Zr\(_5\)-Al, Ni\(_2\)Zr\(_7\)-Al and Ni\(_2\)Zr\(_7\)-Al were established by linking the respective atomic clusters to the glue atom Al in the Al-Ni-Zr system. Another two composition lines, Ni\(_3\)Zr\(_6\)-Al and Ni\(_3\)Zr\(_6\)-Al, were also considered for comparison. An experimental investigation into GFAs was performed for the six series of alloys shown in Figure 2: Ni\(_3\)Zr\(_6\)Al\(_x\), Ni\(_3\)Zr\(_5\)Al\(_x\), Ni\(_3\)Zr\(_6\)Al\(_x\), Ni\(_3\)Zr\(_6\)Al\(_x\), Ni\(_3\)Zr\(_6\)Al\(_x\), and Ni\(_3\)Zr\(_10\)Al\(_x\) (\(x=1, 1.5, 2\) and 3).

### 2 Experimental

Ingots for the designed alloys along with a reference composed of Al\(_{15}\)Ni\(_{20}\)Zr\(_{60}\) were prepared by arc melting the mixtures of the elemental constituents under an argon atmosphere. The purities of Zr, Ni and Al are 99.99 wt.%. The ingots were remelted three times to ensure composition homogeneity. The overall weight loss was less than 0.1% after arc melting. Alloy rods of various diameters from 3 to 1.5 mm were cast using the centrifugal casting technique.

![Figure 1](image1.png) Schematics of the Ni-Zr clusters. (a) Ni\(_3\)Zr\(_6\), (b) Ni\(_3\)Zr\(_5\), (c) Ni\(_3\)Zr\(_6\) and (d) Ni\(_3\)Zr\(_6\). Dark circles represent Ni atoms and white circles represent Zr atoms.

![Figure 2](image2.png) Six composition lines in the Al-Ni-Zr ternary system with experimental compositions marked by the symbols △, ▽, ○, □, which indicate the compositions of the composition lines as \(x=1, 1.5, 2, 3\), respectively.
10 mm and 40 mm long were made by copper mold suction casting. A phase identification of the alloy rods were carried out using X-ray diffractometry (XRD, D8 Discover, Bruker AXS GmbH, Germany) with Cu-Kα radiation (λ=0.15406 nm). A TA-Q100 differential scanning calorimeter (DSC, TA-Q100, TA Instruments, USA) and a TA-Q600 SDT differential thermal analysis instrument (DTA, TA-Q600, TA Instruments) were employed to examine the glass transition temperature ($T_g$), the onset crystallization temperature ($T_x$), the onset melting temperature ($T_m$) and the liquidus temperature ($T_l$) of the BMG samples at a constant heating rate of 20 K/min. The mass densities of the glassy rods were measured using the Archimedes water immersion method.

3 Results and discussion

3.1 BMG formation

Figure 3(a) shows XRD results of the 3 mm diameter as-cast rods. All the rods except for Ni$_2$Zr$_6$Al$_3$ appear to be amorphous. The amorphous structure is retained in the 5 mm rod diameter samples of Ni$_2$Zr$_6$Al$_x$ (x=1, 1.5, 2, 3), Ni$_2$Zr$_8$Al$_x$ (x=2, 3), Ni$_2$Zr$_9$Al$_x$ (x=2, 3), Ni$_2$Zr$_{10}$Al$_x$ (x=2, 3) and Ni$_2$Zr$_{11}$Al$_x$ (x=2, 3) (Figure 3(b)). For the 8 mm diameter cases, the Ni$_2$Zr$_7$Al$_x$ (x=1.5, 2, 3), Ni$_2$Zr$_8$Al$_x$ (x=2, 3) and Ni$_2$Zr$_{10}$Al$_x$ (x=1.5, 2, 3) alloys are fully amorphous (Figure 3(c)). Ni$_2$Zr$_9$Al$_x$ (Al$_{13.3}$Ni$_{26.7}$Zr$_{60.0}$ at%) was found to have the best BMG-forming ability, which is associated with its critical diameter of up to 10 mm (Figure 3(d)). The other alloys, including Al$_{15}$Ni$_{20}$Zr$_{60}$, were partially crystallized under the slowest cooling rate. The quantized experimental GFA evidence is summarized in Figure 4. The critical BMG diameter decreases drastically from 8 to 3 mm with a decrease in Al content around Ni$_2$Zr$_7$Al$_3$. Li et al. [11] reported a critical diameter of 15 mm for Al$_{15}$Ni$_{20}$Zr$_{60}$ glass in a pour-casting experiment. Our casting experiment, however, indicates that its GFA is inferior to that of Ni$_2$Zr$_7$Al$_3$.

3.2 Thermal glass parameters

The thermal glass properties of the Al-Ni-Zr BMG samples were examined with 3-mm diameter samples and Ni$_2$Zr$_6$Al$_3$ (2 mm critical BMG diameter) was excluded. All the DSC

Figure 3 XRD diffraction patterns of the suction-cast rods with diameters of (a) 3 mm, (b) 5 mm, (c) 8 mm and (d) 10 mm. The alloy composition is denoted by a specific number series of “z-y-x”, e.g., “3-6-3” represents the Ni$_2$Zr$_6$Al$_3$ alloy.
and DTA curves are given in Figure 5 from which \( T_g, T_x, T_m \) and \( T_l \) were determined following common criteria. The GFA indicators, e.g., \( \Delta T_x (= T_x - T_g) \) [22], \( T_{gr} (= T_g / T_l) \) [23] and \( \gamma_m (= (2T_x - T_g) / T_l) \) [24] were calculated using the obtained experimental thermal glass data. The data are summarized in Table 1. The DSC curves are characterized by a distinct glass transition followed by crystallization exothermic peaks. The crystallization behavior evidently changes with composition as signaled by the different amounts of exothermic peaks. The DTA curves reveal multiple melting peaks while \( T_m \) is nearly the same for most of the Al-Ni-Zr alloys.

A special phenomenon as observed from the DSC curves is that some of BMG series like Ni₃Zr₆Al \( x \) (\( x = 1.5, 2 \)), Ni₃Zr₇Al \( x \) (\( x = 2, 3 \)), Ni₄Zr₉Al \( x \) (\( x = 2, 3 \)), Ni₅Zr₁₀Al \( x \) and Al₁₅Ni₂₅Zr₆₀ are quite weird, while others look normal. It has to noted that all the DSC curves were obtained under the same DSC experimental conditions. The unusual phenomena are confirmed by our repeated DSC experiments carefully, which imply that the irregular peaks are the intrinsic responses of the materials rather than from the instrument problem. We suppose that the weird DSC curves may be relevant to the thermal-conduct properties of the BMG alloys and will be the subject of our future research.

Figure 6 shows the composition dependence of the GFA indicators of these BMG alloys. The \( \Delta T_x \) and \( \gamma_m \) values peak in the vicinity of Ni₅Zr₁₀Al while \( T_{gr} \) has a maximum value at Ni₃Zr₉Al. The DTA melting behavior of Ni₃Zr₁₀Al indicates that it is near to a eutectic composition. The GFA indicator values are \( \Delta T_x = 68 \) K, \( T_{gr} = 0.579 \) and \( \gamma_m = 0.689 \) for Ni₃Zr₁₀Al and \( \Delta T_x = 68 \) K, \( T_{gr} = 0.568 \) and \( \gamma_m = 0.676 \) for Al₁₅Ni₂₅Zr₆₀, respectively.

### 3.3 \( e/a \) and cluster formulae

The Ni₅Zr₁₀Al \( (\text{Al}_{13.3}\text{Ni}_{26.7}\text{Zr}_{60}) \) alloy gave the best GFA in the casting experiment. However, the number ratio of the atomic cluster and the glue atoms does not satisfy the universal cluster formulae of \([\text{cluster}]_1(\text{glue atoms})_x\), with \( x = 1 \) or 3. The Ni₅Zr₁₀ cluster, therefore, cannot be viewed as a fundamental atomic cluster considering the model structure. The atomic cluster, to be feasible as a model structure, has to adhere to structural stability considerations. The cluster-resonance model was then employed to identify the model cluster from the four known clusters, namely, Ni₃Zr₉, Ni₅Zr₁₀, Ni₆Zr₁₀ and Ni₇Zr₁₀, with which the cluster formulae for the Al₁₃Ni₂₆Zr₆₀ BMG was eventually determined.

As shown in Section 2, the effective \( e/a \) value for an ideal amorphous structure can be determined from eq. (4) when \( r_1 \) and \( \rho_a \) are known. As for the Ni₅Zr₁₀ atomic cluster, \( r_{1-Ni5Zr10} = 0.29058 \) nm was obtained by averaging the distances between the first-neighbor shell atoms (Ni₅Zr₁₀) and the central atom Ni, which was abstracted from the structural
Table 1 Summary of the thermal properties of the ternary Al-Ni-Zr glassy alloys

| Designed compositions | Compositions (at.%) | $T_g$ (K) | $T_x$ (K) | $T_m$ (K) | $T_l$ (K) | $\Delta T_x$ (K) | $T_g/T_l$ | $\gamma_m$ |
|-----------------------|---------------------|----------|----------|----------|----------|-----------------|----------|----------|
| Ni_3Zr_9Al_1          | Al_12Ni_21Zr_11.4   | 638      | 676      | 1193     | 1223     | 38              | 0.522    | 0.584    |
| Ni_3Zr_9Al_1.5        | Al_12Ni_23Zr_10.4  | 659      | 704      | 1199     | 1263     | 45              | 0.522    | 0.593    |
| Ni_3Zr_9Al_2           | Al_11Ni_22Zr_10.7  | 673      | 716      | 1174     | 1307     | 43              | 0.515    | 0.581    |
| Ni_3Zr_9Al_3           | Al_10Ni_22Zr_20.7  | 712      | 751      | 1185     | 1319     | 39              | 0.540    | 0.599    |
| Ni_3Zr_9Al_2           | Al_11Ni_22Zr_10.7  | 669      | 691      | 1192     | 1233     | 42              | 0.526    | 0.594    |
| Ni_3Zr_9Al_3           | Al_10Ni_22Zr_20.7  | 690      | 731      | 1179     | 1316     | 41              | 0.524    | 0.587    |
| Ni_3Zr_9Al_1.5         | Al_9Ni_23Zr_11.4   | 727      | 765      | 1184     | 1319     | 38              | 0.542    | 0.598    |
| Ni_3Zr_9Al_2           | Al_10Ni_22Zr_10.7  | 663      | 710      | 1199     | 1236     | 47              | 0.536    | 0.612    |
| Ni_3Zr_9Al_3           | Al_9Ni_23Zr_20.7   | 682      | 729      | 1174     | 1283     | 47              | 0.532    | 0.605    |
| Ni_3Zr_9Al_1.5         | Al_8Ni_24Zr_11.4   | 703      | 758      | 1178     | 1266     | 55              | 0.555    | 0.642    |
| Ni_3Zr_9Al_2           | Al_10Ni_23Zr_10.7  | 745      | 784      | 1183     | 1342     | 39               | 0.557    | 0.615    |
| Ni_3Zr_9Al_3           | Al_9Ni_23Zr_20.7   | 680      | 721      | 1178     | 1220     | 41               | 0.557    | 0.625    |
| Ni_3Zr_9Al_1.5         | Al_9Ni_24Zr_11.4   | 702      | 770      | 1176     | 1263     | 68               | 0.556    | 0.663    |
| Ni_3Zr_9Al_2           | Al_10Ni_23Zr_10.7  | 721      | 789      | 1185     | 1289     | 68               | 0.559    | 0.665    |
| Ni_3Zr_9Al_3           | Al_9Ni_23Zr_20.7   | 772      | 813      | 1182     | 1338     | 41               | 0.578    | 0.639    |
| Ni_3Zr_9Al_1.5         | Al_8Ni_24Zr_11.4   | 673      | 706      | 1178     | 1244     | 33               | 0.541    | 0.594    |
| Ni_3Zr_9Al_2           | Al_9Ni_23Zr_20.7   | 691      | 739      | 1176     | 1239     | 48               | 0.558    | 0.635    |
| Ni_3Zr_9Al_3           | Al_9Ni_23Zr_20.7   | 707      | 775      | 1179     | 1222     | 68               | 0.579    | 0.689    |
| Ni_3Zr_9Al_1.5         | Al_8Ni_24Zr_11.4   | 742      | 804      | 1184     | 1336     | 62               | 0.550    | 0.642    |
| Ni_3Zr_9Al_2           | Al_9Ni_23Zr_20.7   | 702      | 743      | 1178     | 1219     | 41               | 0.576    | 0.643    |
| Ni_3Zr_9Al_3           | Al_9Ni_23Zr_20.7   | 720      | 780      | 1177     | 1280     | 60               | 0.563    | 0.656    |
| Ni_3Zr_9Al_1.5         | Al_8Ni_24Zr_11.4   | 748      | 800      | 1186     | 1252     | 52               | 0.597    | 0.681    |
| Ni_3Zr_9Al_2           | Al_9Ni_23Zr_20.7   | 659      | 710      | 1180     | 1348     | 51               | 0.493    | 0.570    |
| Ni_3Zr_9Al_3           | Al_9Ni_23Zr_20.7   | 710      | 778      | 1177     | 1251     | 68               | 0.568    | 0.676    |

The Z values of 15.0, 12.5, 14.3 and 11.8 that were obtained from the relationship correspond to atomic clusters of Ni_3Zr_9, Ni_3Zr_8, Ni_4Zr_9 and Ni_3Zr_7, respectively. By subtracting the atomic numbers of a cluster from Z the respective glue atom numbers are determined as 3, 1.5, 1.3 and 1.8 for the different model clusters. The Ni_3Zr_9 cluster was the only cluster that adequately satisfied the universal cluster formulae. The best BMG composition (Al_13.3Ni_26.7Zr_60) is described by the cluster formula [Ni_3Zr_9](Al_2Ni) in which two Al and one Ni are the glue atoms. It is worth mentioning that the Ni_3Zr_9 cluster is derived from one of its crystalline counterparts, the hP-Al_2NiZr_6 phase.

4 Conclusion

The GFAs of Al-Ni-Zr alloys were re-examined using the cluster-plus-glue-atom model. A centimeter scale BMG alloy of Ni_3Zr_9Al_1 = Al_13.3Ni_26.7Zr_60 was found in our mold casting experiment and it is associated with a cluster formula [Ni_3Zr_9](Al_2Ni) in which two Al and one Ni are the glue atoms. The Ni_3Zr_9 cluster is derived from one of its crystalline counterparts, the hP-Al_2NiZr_6 phase.
Figure 6 Composition dependence of (a) $\Delta T_x$, (b) $T_{rg}$ and (c) $\gamma_m$ for the Al-Ni-Zr glassy alloys. The blue star in each diagram represents the reference Al$_{15}$Ni$_{25}$Zr$_{60}$ and its $\Delta T_x$, $T_{rg}$ and $\gamma_m$ values are 68 K, 0.568 and 0.676, respectively.

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