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Journal of Alloys and Compounds 434–435 (2007) 167–170

Journal of ALLOYS AND COMPOUNDS

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The best glass-forming compositions in Al–Co(or Ni)–Y ternary systems

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Available online 16 October 2006

Abstract

The present work aims at the investigation of the largest glass-forming abilities in the Al–Co(or Ni)–Y ternary systems. In the reduced isothermal sections of their ternary phase diagrams, the e/a-based composition line passes through three known phases, $Al_{50}Co(or\ Ni)_{50}$, $Al_{33}Co(or\ Ni)_{33}Y_{33}$ and α-Y. The atomic cluster-based criterion was incarnated into the $Co(or\ Ni)_3Y_7$–Al composition line. The crossing of the two composition lines gives the composition of $Al_{23}Co(or\ Ni)_{23}Y_{54}$. The critical diameters for a full glassy state are 4 mm and 3 mm for the Ni-bearing and Co-bearing alloys, respectively. Thermal analysis indicates that the compositions are not eutectic points. The characteristic thermodynamic parameters are $T_g = 645$ K, $T_x = 694$ K and $T_g/T_m = 0.64$ for $Al_{23}Ni_{23}Y_{54}$ and $T_g = 648$ K, $T_x = 681$ K and $T_g/T_m = 0.63$ for $Al_{23}Co_{23}Y_{54}$.

Keywords: Metallic glass; X-ray diffraction; Thermal analysis

1. Introduction

For a given metallic system, glass formation depends on several experimental parameters, such as composition, quenching rate, purity of constituents and fabrication methods. Bulk metallic glasses (BMGs) [1,2] are multi-component alloys emphasizing the crucial role of composition. Intense research efforts [2–4] have been focusing on the practical composition guidelines for the best glass-forming abilities (GFAs) as the traditional trial and error approach faces severe difficulties in these complex systems. With regard to GFA, Turnbull first pointed that glass formation should be the easiest at a eutectic composition [5]. Subsequently, the proposition was developed by Dubey and Ramachandrarao to show an asymmetry of GFA around the eutectic composition in most binary eutectic phase diagrams, GFA being larger on one side of the eutectic composition than on the other [6]. Recently, Wang et al. demonstrated that in the Cu–Zr system the largest GFA is located in the vicinity of the $Cu_{65}Zr_{35}$, which is neighboring the deepest eutectic $Cu_{61.8}Zr_{38.2}$ [3]. In ternary systems, for instance Ag–Cu–Sb, Dutkiewicz and Massalski found that glass-forming composition deviated from the eutectic composition [7]. The Al–Co(or Ni)–Zr systems in which Zr-based BMGs form, also exhibit a deviation from the deep eutectic guideline [8]. One finds that the eutectic composition does not always coincide with the largest GFA in a eutectic system. In the present work, we investigate two eutectic systems, Al–Co(or Ni)–Y. The empirical approach proposed in our previous work [2] was employed to locate the best glass-forming composition in the ternary systems.

The deepest eutectic reactions in the Ni–Y and Co–Y phase diagrams are, $Ni_{34.8}Y_{65.2\ (Liquid)} \Leftrightarrow NiY_3 + Ni_2Y_3$ and $Co_{37}Y_{63\ (Liquid)} \Leftrightarrow CoY_3 + Co_5Y_8$, respectively. Rapidly quenched glasses are available in the vicinity of the binary eutectic compositions [9]. In the empirical approach, two kinds of compositions lines are defined, namely the atomic cluster-based line and the e/a-based line. In the latter e/a is the average conduction electron to atom ratio, and for a given composition it is defined as: $e/a = \sum_i x_i (e/a)_i$, where x_i is the atomic fraction of the ith element and $(e/a)_i$ is the effective conduction electron number of the element. The side-capped trigonal prism (Fig. 1), $Co(or\ Ni)_3Y_7$, derived from the deepest eutectic-related topological close-packed crystalline phases, is taken as the glass-favored atomic cluster. The Al–$Co(or\ Ni)_3Y_7$ composition lines in the reduced isothermal sections of the Al–Co(or Ni)–Y phase diagram was constructed (Fig. 1). The e/a-based criterion is represented by the AlCo(or Ni)–Y compo-

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doi:10.1016/j.jallcom.2006.08.182

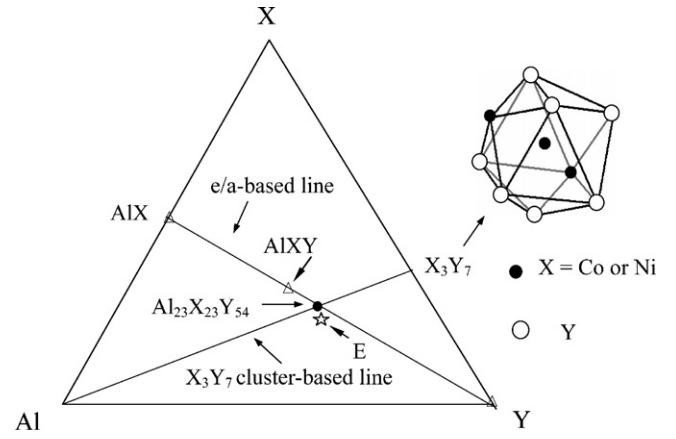

Fig. 1. The reduced isothermal section phase diagrams of Al–Co(or Ni)–Y. The e/a-based line and the atomic cluster-based line are constructed. The pinpoint of the composition lines gives the predicted compositions $Al_{23}Co(or\ Ni)_{23}Y_{54}$. The pentacle stands for the reported eutectic compositions $Al_{24}Co(or\ Ni)_{20}Y_{56}$.

sition line, passing through the known phases $Al_{50}Co(or\ Ni)_{50}$ (β-phase), $Al_{33}Co(or\ Ni)_{33}Y_{33}$ ($MgZn_2$ type Laves phases) and α-Y (Fig. 1). The intersection of the two composition lines gives the composition $Al_{23}Co(or\ Ni)_{23}Y_{54}$, which is close to the reported eutectic compositions $Al_{24}Co(or\ Ni)_{20}Y_{56}$ [10].

2. Experimental

Ingots with nominal compositions $Al_{23}Co(or\ Ni)_{23}Y_{54}$ and $Al_{24}Co(or\ Ni)_{20}Y_{56}$ were prepared by arc melting the mixture of the constituent elements under Ti-gettered argon atmosphere. The purities of metals are 99.999 wt.% for Al, 99.9 wt.% for Ni and Co and 99.5 wt.% for Y. Alloy rods with different diameters were prepared by means of copper mold casting. X-ray diffraction (Cu Kα irradiation, λ = 0.15406 nm) was carried out on the cross sections of these as-cast rods via standard θ–2θ scans. Thermal analysis was performed on a PE-7 differential scanning calorimeter (DSC) at a constant heating rate of 0.33 K/s. To examine the melting and solidification processes of these BMGs, samples were first heated to well above their liquidus temperatures and then cooled down to room temperature at a rate of 0.167 K/s in a high temperature DSC.

3. Results

Casting experiments revealed that the critical diameters for a fully glassy state are 4 mm and 3 mm for the $Al_{23}Ni_{23}Y_{54}$ and $Al_{23}Co_{23}Y_{54}$ compositions, respectively (Fig. 2). $Al_{24}Co_{20}Y_{56}$ and $Al_{24}Co_{20}Y_{56}$ alloy rods with 2 mm in diameter were prepared under an identical casting condition. The samples were found partially crystallized. The compositions $Al_{23}Co(or\ Ni)_{23}Y_{54}$ deviate only slightly from the reported eutectic point $Al_{24}Co(or\ Ni)_{20}Y_{56}$, but their difference in GFA is distinguished. This indicates that GFA is very compositional sensitive in the present system.

The DSC traces (Fig. 3) of the $Al_{23}Ni_{23}Y_{54}$ and $Al_{23}Co_{23}Y_{54}$ BMGs exhibit detectable glass transitions and wide undercooled liquid regions. For the $Al_{23}Ni_{23}Y_{54}$ BMG, the glass transition (T_g) occurred at 645 K and the onset crystallization temperature (T_x) is 694 K. Those for the $Al_{23}Co_{23}Y_{54}$ BMG are T_g = 648 K and T_x = 681 K. Fig. 4 shows the melting and solidification processes of these as-cast BMGs. The Ni-bearing BMG starts melting at T_m = 1007 K followed by a melting temperature span of

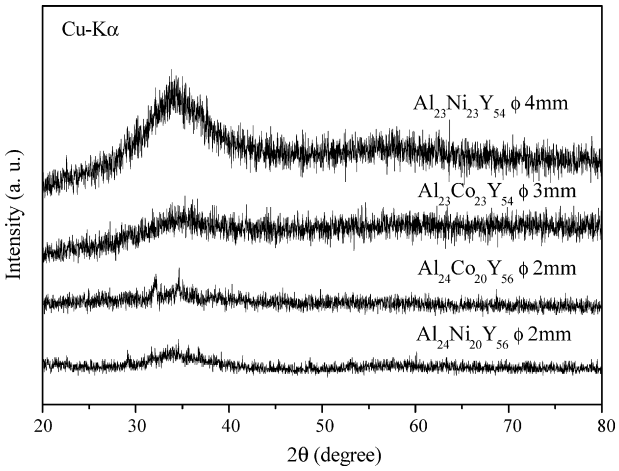

Fig. 2. XRD patterns obtained at the cross sections of these as-cast alloy rods with different diameters.

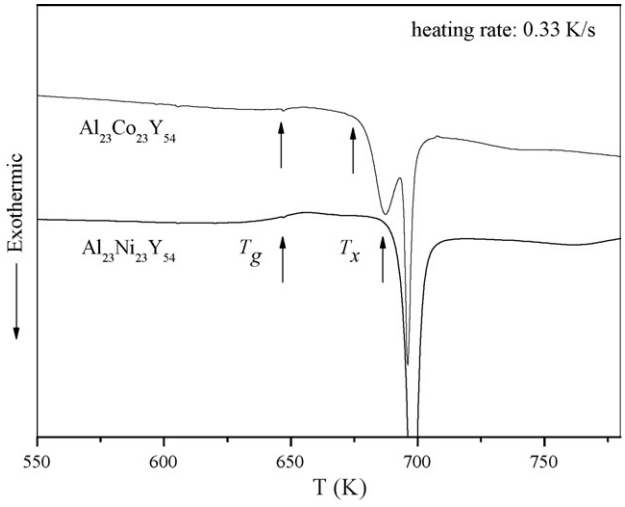

Fig. 3. DSC traces of the as-cast $Al_{23}Co(or\ Ni)_{23}Y_{54}$ BMGs at the constant heating rate of 0.33 K/s. The glass transition temperature (T_g), the onset temperature of crystallization (T_x) are indicated.

about 30 K. The solidification process exhibits multiple exothermic peaks (Fig. 4(a)). The $Al_{23}Co_{23}Y_{54}$ BMG exhibits similar melting and cooling behaviors (Fig. 4(b)). The two alloys are therefore off-eutectic compositions in the respective systems. GFA was then assessed by using the reduced glass transition temperature T_{rg} ($T_{rg} = T_g/T_m$) [11]. The calculated T_{rg} values are 0.64 and 0.63 for the Ni-bearing and Co-bearing BMGs, respectively. The assessment is in consistent with the critical diameter obtained by cooper mold casting.

4. Discussion

4.1. Glass-favored atomic cluster

Hume-Rothery and Anderson attributed the occurrence of eutectics at integer number atomic ratios to the specific atomic clusters in alloy liquids [12]. However, atomic clustering effect for the occurrence of eutectics and the formation of certain type of intermetallic phases is two-fold. As suggested by Sommer

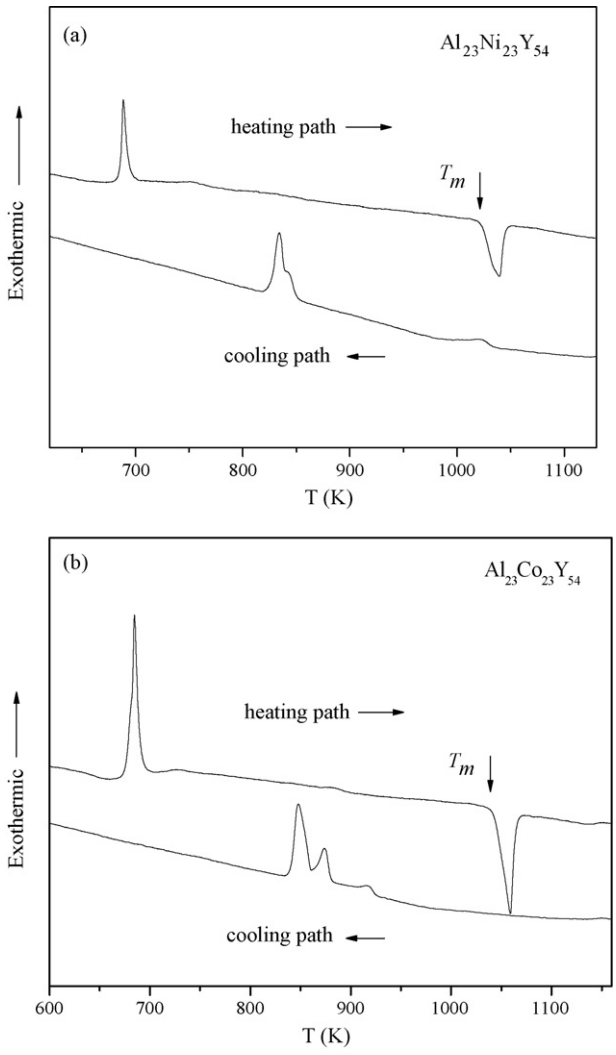

Fig. 4. High temperature DSC traces of (a) $Al_{23}Ni_{23}Y_{54}$ and (b) $Al_{23}Co_{23}Y_{54}$ BMGs. The heating and cooling rates are 0.167 K/s. The onset melting temperatures (T_m) are indicated.

[13,14], if the atomic cluster is incompatible with any periodic translation order, and has a composition that deviates significantly from that of the phase, the nucleation and growth of competing phases will be hindered. The clustering effect should be prominent in systems where constituents have large atomic size differences. Recently, Miracle and Senkov has made a comprehensive study on the local atomic packing of bulk metallic glasses, and it is found that, at a give size ratio, the maximum packing efficiency corresponds to specific coordination number (CN) of the solute (minority) atom [15].

Geometrically, large atomic size ratios allow the formation of topologically close-packed atomic polyhedra associated with high site symmetries. For purely close-packing reasons the local atomic packings in topologically close-packed crystalline phases and metallic glasses should be the same. In the present system, Y, Co and Ni atoms have Goldschimdt radii of 0.180 nm, 0.125 nm and 0.125 nm, respectively. The size ratio is about 0.70, corresponding to a CN 9 local packing in metallic glasses [15]. In the eutectic-related intermetallic phases, namely NiY_3, CoY_3, Ni_2Y_3 and Co_5Y_8, the small atom centered side-capped-trigonal-prism Co(or Ni)$_3$Y$_7$ (CN9) is the universal polyhedron. The atomic cluster has a composition different from those of the crystalline phases. It persists over a wide range of phase compositions, suggesting its considerable stability. Diffraction data of the $Ni_{33}Y_{67}$ metallic glass demonstrated the presence of atomic clustering [16]. Further, the partial pair correlation functions and the partial structure factors of the glass revealed a tendency to form unlike-atom pairs, the Ni–Y bond, in the atomic clusters [17–19]. Moreover, in the glass the distribution of bond angles formed by nearest-neighbor bonds around a central atom is similar to the trigonal prismatic order [17]. We thereby assume the existence of Co(or Ni)$_3$Y$_7$ atomic clusters in the binary eutectic liquids, and employ it to construct the atomic cluster criterion.

4.2. Alloying mechanism

Apart from the large atomic size ratio, the Co(or Ni)–Y systems are characterized by a large difference in the number of d electrons of Co (or Ni) and Y. The ultraviolet photon-emission spectrum of $Ni_{35}Y_{65}$ glass indicates that the electron density of states (DOS) has a split-band characteristic. The Ni-3d partial DOS is concentrated at the high binding energy and Y-4d is near the Fermi level (E_f) [20]. It is worthwhile noting that the electron DOS near E_f come primarily from the Y-4d subband. If alloying with a sp element Al, the sp-d hybridization would cause a bonding–antibonding split and result in a more declining pseudogap crossing the Fermi level. The mechanism is pronounced in the electronic structures of complex Hume-Rothery phases and quasicrystals in transition metal aluminides [21,22]. A strong sp-d coupling, associated with an ordered sublattice of transition metal atoms can lead to the formation of a pseudogap at E_f in most crystalline phases. Correspondingly, in completely disordered system the statistical distribution of transition metal atoms would destroy this pseudogap. The present unlike-atom pairs would present the so-called chemical short-range order in addition to the basic trigonal prismatic topological order. In this case the sp valence states would stabilize the metallic glass.

4.3. e/a factor

The structural stability of atomic cluster is dominated by the hybridization of the wave functions between nearest neighbor atoms in the cluster, which is essentially a short-range structural effect. Mizutani et al. have demonstrated that in alloys involving transition metals, the abovementioned hybridization effects coupled with the Fermi-surface–Brilluion-zone effect account for the structural stability [21]. The latter represents a long-range structure effect and is diffraction phenomena related. For metallic glasses the matching condition is denoted as $2k_f \approx K_p$, where $2k_f$ and K_p are the Fermi vector and the width of the spherical pseudo Brillouin zone, respectively. K_p, can be approximately calculated from $K_p = 4\pi \sin\theta_p/\lambda$, where θ_p is the diffraction angle of the strongest peak in the X-ray diffraction pattern. For a metallic glass, θ_p is derived from the principal diffused peak position. The above theoretical consideration can guide the assignment of effective conduction electron contribution of tran-

sition metals [23]. In the Al–Co(or Ni)–Y systems, β-Al_{50}Co(or $Ni)_{50}$ are known electron phases, stabilized by an e/a value of 1.5. The effective e/a values 3 and 0 are assigned to Al and Co (or Ni), respectively [22]. According to the 'constructive interference' theory proposed by Hafner [24], e/a also contributes to the structural stability of the Al_{33}Co(or $Ni)_{33}Y_{33}$ Laves phases. The strongest (2 0 1) diffraction peaks of the Laves phases are associated with K_p. Refereeing to the conduction band occupancy of elemental Y in Pettifor's band structure calculations [25], an effective e/a value of 1.5 was assigned for Y. These effective e/a values explain the matching conditions in the Laves phases and the α-Y ($k_{(1\,0\,1)}$) phase as well. As for the Y-based BMGs, their X-ray diffraction patterns show nearly the same $\theta_p \approx 17.5^\circ$, with which $K_p \approx 24.5\,nm^{-1}$ is obtained. The Fermi vector, k_f, is calculated by using the formula: $k_f = [3\pi^2(e/a)N_0\rho/M]^{1/3}$, where N_0, ρ and M are the Avogadro number, the mass density and the formula weight of the metallic glass, respectively. The mass densities of the Ni-bearing and Co-bearing BMGs were measured to be 5.08 g/cm^3 and 5.07 g/cm^3, respectively. The $2k_f$ values are calculated to be $25.2\,nm^{-1}$ and $25.2\,nm^{-1}$, being close to the K_p value. The effective e/a value explains the different matching conditions of these alloy phases, and is employed to construct another criterion to locate the BMG forming compositions.

5. Conclusions

The Co(or Ni)-centered side-capped-trigonal-prism Co(or $Ni)_3Y_7$ is a universal atomic polyhedron in the binary deepest eutectics related crystalline phases. It was adopted as a glass-favored atomic cluster to construct the Al–Co(or $Ni)_3Y_7$ composition line in the ternary system. The effective e/a value of 1.5 was suggested for the e/a-based composition line. In the reduced isothermal section of the Al–Co(or Ni)–Y ternary phase diagram, the crossing of the two composition lines gives the off-eutectic composition Al_{23}Co(or $Ni)_{23}Y_{54}$. In the systems BMG formation is very composition sensitive and the best glass-forming ability has been demonstrated in the vicinity of these off-eutectic compositions, glassy rods with the diameters up to 4 mm were made. Our latest investigation indicates that the empirical method is also applicable to the Sm (or Gd)–Al–Co(or Ni) ternary systems, which will be reported elsewhere.

Acknowledgements

This work was supported by the National Science Foundation of China (No. 50401020) and City University of Hong Kong Strategic Research Grant (No. 7001529).

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