Al₈₅Ni₉Ta₆, a refractory Al –rich ternary alloy glass and its crystallization kinetics

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Abstract. There are no reported Al-rich alloys that are both easy glass formers upon melt-spinning processing without RE additions and have a crystallization temperature sufficiently high to ensure long metastable life times at room temperature. A representative of a new family of ternary Al-based glasses is described here that contains Ni and Ta with total additive element concentration as low as 15 at % and its devitrification characteristics are reported. Using the melt-spinning technique under protective atmosphere, the alloy Al₈₅Ni₉Ta₆ easily forms a ductile glass, with the crystallization onset temperature Tx = 370 °C, enthalpy of transformation ΔH = 68 J/g and an activation energy of crystallization Ea = 266.83 kJ/mole, i.e., 2.76 eV.

1. Introduction

Al-based glassy alloys entered into the history of amorphous alloys by independent publications of Japanese and US groups [1-3] who reported the first ductile Al-based glasses with excellent mechanical properties.

Despite their practical importance, these Al-rich glasses are not conveniently prepared due to the large cooling rate necessary to prepare an amorphous state. The largest critical thickness obtained so far is 0.5 mm [Gd containing alloy]. On the other hand, for applications one needs bulk samples obtainable in this case only by consolidation of the amorphous flakes or powders prepared by rapid solidification techniques. This consolidation needs hot isostatic pressure or hot extrusion which should be carried out much below the crystallization temperature in order to prevent the devitrification during the compaction. Thus, it was of interest to search for compositions rich in Al with good glass-forming ability (GFA) and with relatively high Tx values. A study of promising ternary compositions was undertaken, comprising refractory elements like W and Ta. Such refractory Al-based amorphous alloys have been prepared so far in thin film-layers only, like Al₈₂W₁₈ to Al₆₂W₃₈ alloys with Tx ranging from 800 K to 920 K [4].

The guide followed in this research is discussed more fully in a separate paper [5] on the GFA of Al-based amorphous alloys prepared by melt-spinning. The 3 rules of “thumb” of Inoue are only partially fulfilled: i) the atomic mismatch condition in terms of Egami’s expression is not fulfilled in this case, obtaining λ = 0.05, which is smaller than the imposed limit of 0.1; ii) there is an appropriately large negative enthalpy of mixing as expressed for binary mixtures in ΔH versus radius ratio maps of GFA [6]; iii) there are more than two components.

2. Experimental

Alloy ingots were prepared by inductive melting, starting from pure elements in water cooled copper boat under Argon. About 10 grams of alloy quantities were rapidly solidified using the melt spinning method also under protecting Ar atmosphere. The peripheral speed of the casting wheel was 40 m/s.

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The resulting ribbons were studied by X-ray diffraction (XRD, using Co-K\(\alpha\) radiation on a Bruker ASM 200 diffractometer and differential scanning calorimeter (DSC, using a Perkin–Elmer DSC-4 unit).

3. Results and discussions

It seems that Ta is a good glass former element and can substitute the rare earth metals in the usual Al-RE-Ni compositions. Both Ta and Ni have a very limited solubility in Al (less than 0.04 at% of Ta and less than 0.01 at% for Ni. [7]), but both forms compounds Al\(_3\)Ta and Al\(_3\)Ni, respectively. Both XRD and DSC proved glass formation as documented here. The important low-q region (2.1<q<3.8) of a representative XRD pattern is shown in Figure 1. This pattern is characteristic for an amorphous structure. The first broad peak presented here is exceptionally wide, being consistent with the large range of interatomic distances expected to be present in the amorphous structure, in view of the large range of atomic sites of the components (\(r_{Al} = 1.43 \text{ Å}, \ r_{Ni} = 1.24 \text{ Å and } r_{Ta} = 1.45 \text{Å}\)).

![Figure 1. XRD patterns of amorphous Al\(_{85}\)Ni\(_9\)Ta\(_6\) and after annealing at 400 °C for 0.5 h.](image)

The first broad peak is centred at \(2\theta = 40^\circ\). The first broad peak maximum at \(2\theta = 40^\circ\) correspond to \(q_{\text{max}} = 4\pi\sin \theta / \lambda = 2.67 \text{ Å}^{-1}\). When converting this into a principal interatomic distance \(d\) by use of the Ehrenfest relation: \(q_{\text{max}} \cdot d = 7.7\), we get \(d = 2.8 \text{ Å}\), equal to the 12–coordinated elemental Al-Al distance which dominates the diffraction pattern. This coincidence between the distances in the amorphous and crystalline states may be fortuitous because the Ehrenfest constant in amorphous structure may range from 7.6 to 8.

The DSC scans taken at heating rates of 10, 20 and 40 K/min are shown in Figure 2. The higher resistance to crystallization of the Ta-containing glass compared to the RE-containing glasses is their most significant feature. The values of the onset glass transition temperature, \(T_g\), the onset of crystallization temperature, \(T_x\), and the crystallization peak temperature, \(T_p\), were determined directly from the DSC curves. The onset temperatures were determined as the intersections between linearly extrapolated curves below the transition with the steepest tangent of the rise in the heat flow signal. The supercooled liquid region \(\Delta T_x = T_x – T_g \sim 58 \text{ K}\) at heating rate of 40 K/min. The crystallization temperature \(T_x\) for Al\(_{85}\)Ni\(_9\)Ta\(_6\) is 370°C (for \(\beta = 20 \text{ K/min}\)), as compared to the low value of \(T_x \sim 300\) °C for Al\(_{85}\)RE\(_8\)Ni\(_5\)Co\(_2\) [8]. This strongly enhanced \(T_x\) indicates that the new alloy has sufficient long-term stability at room temperature, and thus fulfils a necessary condition for applications.
It is reasonable to assume that the higher Tx value of the new Al-based glass, as contrasted to those of earlier RE-containing Al-based glasses, is correlated with the stronger bonding in the new alloy. Stronger bonding is reflected in the microhardness data as well, measured by Vickers method using 10 gram load. The obtained value of 486 kg/mm$^2$ is about 1.5 times larger than the usual HV values for the Al-based amorphous alloys and permits to estimate the ultimate tensile stress value from the well known correlation $HV = 3 \sigma$ as $\sigma = 1620$ MPa, which is really a record number among the Al-based amorphous alloys [9].

Next we compare the crystallization temperature $Tx = 670$ K of the new glass to the melting temperature of the corresponding multiphase crystalline alloy ($Tm \sim 1130$ K). $Tx/Tm$ is about 0.6 to be compared to $Tx/Tm = 0.48$ for Al85Ce8Ni5Co2, which again shows the greater thermal stability for the new glass. It is worth mentioning that the typical $Tx/Tm$ values for metallic glasses lie between 0.44 and 0.68 [4].

The multiphase product of crystallization after a heat treatment at 400 °C for 30 minutes consists of fcc-Al and some binary (Al$_3$Ni and Al$_3$Ta) and ternary (AlNi$_2$Ta) intermetallic phases (see Fig. 1). The DSC trace from specimens annealed at 450 °C did not show any exothermic peak.

The enthalpy of amorphous to crystalline transformation was estimated by integrating the area corresponding to the exothermic transformation in Fig. 2. The obtained value, $\Delta H = 68$ J/g, is...
relatively low, compared to $\Delta H = 86$ J/g for Al85Ce8Ni5Co2 [8], suggesting that, in the present new glass, strong metal-metal binding and short-range order exists already in the amorphous state, causing only a small amount of enthalpy to be released upon crystallization. The apparent activation energy of the crystallization are estimated by the Kissinger method [10]. The peak temperature of the exothermic event taken at different heating rates $\beta$ is described in this model by

$$\frac{\beta}{T_p^2} = \left(\frac{Z}{E_a}\right) \exp\left(-\frac{E_a}{RT_p}\right),$$

where $Z$ is the frequency factor, $R$ is the gas constant and $E_a$ is the apparent activation energy. Plotting $\ln(\beta/T_p^2)$ as a function of $1/T_p$; a good linear behaviour between 10 and 40 K/min is obtained, which yields an activation energy of crystallization $E_a = 266.83$ kJ/mole = 2.76eV. This may be compared to $E_a = 270,15$ kJ/mole = 2.8eV of Al85Ce8Ni5Co2.

As to the mechanical properties, the new Al-glass has fair bend ductility at room temperature, permitting a 180° bend test over a bend radius of 1 mm, although not over a razor blade edge. But it is not tough enough, showing fracture after re-bending. In order to avoid the residual stresses after grinding, the new Ta-containing amorphous ribbon was cryogenically chopped into amorphous flakes and consolidated by hot pressing at ~330°C, below the crystallization temperature in order to prevent devitrification during the compaction. A fully amorphous disk was obtained having the density of 90% only of the theoretical value. Further experiments are in course by electric discharge compaction to enhance the density.

Conclusions
Results on a new Al-based metallic glass were presented with nominal composition of Al85Ta6Ni9, exhibiting a high crystallization onset temperature of about 643 K and a wide supercooled liquid region of about 58 K. The crystallization occurs through 3 overlapping processes. The Vickers microhardness $HV_{0.01} = 486$ is one of the biggest among the known Al-based glasses, permitting to estimate a record value of the tensile strength which makes this new glass a perspective material for preparing bulk samples by different powder consolidation techniques.

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