Effect of melt temperature on primary crystallization and thermal stability of Al$_{86}$Ni$_6$Y$_{4.5}$Co$_2$La$_{1.5}$ metallic glass

Zhizhi Wang$^{1,2,3}$, Xingyu Zhang$^{1}$, Lin Liu$^1$, Qin Zhao$^1$ and Shoujun Liu$^1$

$^1$ College of Mechanical Engineering, Changzhou University, Changzhou 213164, People’s Republic of China
$^2$ Changzhou High Technology Research Key Laboratory of Mold Advanced Manufacturing, Changzhou University, Changzhou 213164, People’s Republic of China
$^3$ Author to whom any correspondence should be addressed.
E-mail: 673668731@qq.com

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Abstract

In this paper, the correlations between the melt temperature of Al$_{86}$Ni$_6$Y$_{4.5}$Co$_2$La$_{1.5}$ alloy and its crystallization behavior were studied. The results of differential scanning calorimetry (DSC) showed that the primary crystallization of Al$_{86}$Ni$_6$Y$_{4.5}$Co$_2$La$_{1.5}$ alloy was greatly affected by the melt temperature: compared with the amorphous ribbons prepared at 1373 K and 1673K, the primary crystallization of the ribbons prepared at 1523 K was significantly advanced; The calculation of the activation energy indicated that the amorphous ribbon prepared at 1523 K has a lower energy barrier to be overcome during the first crystallization stage, which means that its thermal stability is worse, and fcc-Al is more likely to be precipitated; Abnormal melt structural changes were observed by electrical resistivity (ER), and liquid-liquid structure transition (LLST) occurred after 1402 K, which can be proved by the results of x-ray diffraction (XRD); Compared with the amorphous ribbons prepared at 1523 K and 1673K, the one prepared at 1373 K were more likely to precipitate intermetallic compounds during crystallization, which may be related to the disappearance of some atomic clusters caused by the increase of melt temperature.

1. Introduction

With the rapid development of aerospace, the demand for materials that have high strength and low density is becoming more and more urgent. Amorphous alloys are a new class of advanced materials with a variety of applications and superior properties [1–3], and Al-based metallic glasses (MGs) are very attractive in the aerospace field due to its elevated corrosion resistance, high wear resistance, high strength, and relatively low density [4]. What is more, fcc-Al are formed during crystallization of the amorphous matrix [5–7], numerous studies have shown that precipitation of the aluminum nanocrystals significantly enhances the mechanical strength of the materials, for example, Kan et al [8, 9] have obtained the composite materials of an Al–Ni–Y–Co–La amorphous alloy with an ultrahigh strength of 1.34 Gpa. For this reason, many investigations have focused on studying the crystallization process of amorphous Al-based alloys.

MGs are typically produced by rapid quenching from the melt and retain melt structures of the maximum extent [10], so the original liquid state plays an important role in the crystallization behavior of MGs. Numerical evidence has been accumulated for the existence of liquid-liquid structure changes induced by temperature [11–14], and endeavors have been ceaselessly made to investigate the influence of liquid states on the thermal stability, glass-forming ability (GFA), and crystallization behavior of MGs, for instance, Juan Mu et al [15] eliminated the high-melting-temperature phases and enhance the thermal stability of Al$_{85.3}$Ni$_{9.3}$La$_{5.3}$ metallic glass by melt treatment. Although many research studies have been carried out on this topic, liquid metallic alloys can still be a complicated object.

In the present work, the Al$_{86}$Ni$_6$Y$_{4.5}$Co$_2$La$_{1.5}$ amorphous alloy (crystallized type is primary crystal crystallization) was chosen as the object of this study for its excellent GFA, fcc-Al will be precipitated during its...
first crystallization stage [7, 16–18]. Three melt temperatures were chosen to prepare the amorphous samples, the effect of melt temperature on its crystallization behavior and thermal stability was investigated by DSC, XRD. In order to detect whether the melt structure has changed, the variations on electrical creativity as a function of temperature for the Al_{86}Ni_{6}Y_{4.5}Co_{2}La_{1.5} melt were investigated by continuous heating.

2. Experimental

The Al_{86}Ni_{6}Y_{4.5}Co_{2}La_{1.5} alloy ingots were prepared by arc melting the mixtures of pure Al, Ni, Y, Co, and La (99.99%) metals (in atomic percentage) under a Ti-gettered argon atmosphere in a water-cooled copper crucible. The ingots were remelted five times to prevent compositional inhomogeneity and then were divided into two pieces. In order to observe LLST, one of them was broken and placed in a porcelain boat for ER measurement, the ER against temperature was measured using the D.C. four-probe method [11] under vacuum of about 10^2 Pa, tungsten wire with a diameter of 1 mm was chosen as the electrode, cover the tungsten wires with graphite rod to prevent it from reacting with the alloy. Temperature was measured by K-type thermocouple, PF66M current source providing the constant current (500 mA) and the continuous heating process of the alloy was conducted in the resistance furnace (GSL-1500X KeJin), the rate of heating is set as 10 K min⁻¹, a PC is used to record the experimental data at constant time intervals (400 ms) during continuous heating.

The other ingot pieces were used to prepare amorphous ribbons using a single roller melt-spinning apparatus with a copper-wheel surface velocity of 40 ms⁻¹, three quenching temperatures were chosen to prepare amorphous ribbon with 30-40 μm thickness, which was 1373, 1523 and 1673 K. The melt temperature is controlled by adjusting the magnitude of the induction current, which is measured with a high-precision infrared thermometer. When the melt temperature reaches 1373, 1523 and 1673 K, insulation for one minute and then cool the alloy melt rapidly to form the amorphous ribbon.

Thermal analysis was performed using a Perkin-Elmer Pyres Diamond differential scanning calorimeter, the heating rate of the experiment was 20,40, 80 K min⁻¹. The structure of the annealed ribbons was examined by XRD (D/MAX2500, Rigaku Corporation, Tokyo, Japan) to identify the crystallization phase. The whole process of heating was protected by pure argon (> 5 N).

3. Results and discussion

Figure 1 shows the x-ray diffraction patterns of the amorphous ribbons prepared at three different melt temperatures (1373, 1523 and 1673 K). All these curves consist only of one large broad peak (2θ ≈ 38°), and no diffraction peaks corresponding to crystalline phases can be seen, indicating that all tissues of the sample are in the amorphous state.

In order to determine the effect of melt temperature changes on amorphous crystallization behavior, DSC was performed on the Al_{86}Ni_{6}Y_{4.5}Co_{2}La_{1.5} amorphous ribbons with respect to three different heating rates, the experimental results are shown in figure 2.
For Al₈₆Ni₆Y₄.₅Co₂La₁.₅ amorphous, its main precipitated products are fcc-Al in the first stage of crystallization, and some intermetallic compounds will be gradually precipitated during the second stage of crystallization. Apparently, the values of Tₓ are almost identical to the samples prepared at 1373 K and 1673 K. While for the sample prepared at 1523 K, the Tₓ is significantly lower, and the results suggest that the first crystallization stage of the amorphous ribbon prepared at 1523 K was advanced, which means worse thermal stability and GFA of the amorphous alloy. Tₓ₂ of these ribbons has no obvious gap, so it can be temporarily considered that melt temperature has a little effect on the second crystallization stage of Al₈₆Ni₆Y₄.₅Co₂La₁.₅ amorphous ribbons.

From the figure above, the crystallization onset temperature Tₓₒ, and the peak temperature Tₓ₁, Tₓ₂ can be found, so these data were summarized in the table 1 for clear observation, together with the calculated Tₓₓ.

### Table 1. The characteristic temperatures Tₓₒ, Tₓ₁, Tₓ₂, Tₓ₁, and Tₓ₂ determined by DSC, together with the calculated Tₓₓ.

| MT/K   | Rate K/min | Tₓₒ/K | Tₓ₁/K | Tₓ₂/K | Tₓ₁/K | Tₓ₂/K | Tₓ₁/K | Tₓ₂/K | Tₓₒ/K | Tₓ₁/K | Tₓ₂/K | Tₓₒ/K | Tₓ₁/K | Tₓ₂/K | Tₓₒ/K | Tₓ₁/K | Tₓ₂/K | Tₓₒ/K | Tₓ₁/K | Tₓ₂/K |
|--------|------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1373 K | 20         | 509   | 520   | 529   | 617   | 619   | 1175  | 0.433 |
|        | 40         | 513   | 524   | 535   | 623   | 626   | 1175  | 0.436 |
|        | 80         | 516   | 529   | 543   | 630   | 634   | 1175  | 0.439 |
| 1523 K | 20         | 475   | 500   | 509   | 620   | 621   | 1175  | 0.404 |
|        | 40         | 479   | 504   | 514   | 625   | 626   | 1175  | 0.407 |
|        | 80         | 482   | 509   | 520   | 630   | 634   | 1175  | 0.410 |
| 1673 K | 20         | 503   | 519   | 528   | 616   | 618   | 1175  | 0.428 |
|        | 40         | 508   | 523   | 533   | 622   | 624   | 1175  | 0.433 |
|        | 80         | 514   | 528   | 539   | 628   | 632   | 1175  | 0.438 |

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From the figure above, the crystallization onset temperature Tₓₒ, and the peak temperature Tₓ₁, Tₓ₂ can be found, so these data were summarized in the table 1 for clear observation, together with the calculated Tₓₓ = Tₓₒ/Tₓ₁.

The changes in characteristic temperature mean the variations in crystallization behavior, the widely accepted Kissinger method was then used to assess the thermal stability of the powder based on the DSC results of the heating rate of 20, 40, 80 K min⁻¹. Its expression is as follows:
\[
\begin{align*}
\ln \left( \frac{T^2}{Q} \right) &= \frac{\Delta E}{RT} + \ln \frac{\Delta E}{Rv_0},
\end{align*}
\]

Q: the rate of heating
R: gas constant
\(\Delta E\): apparent activation energies

Take \(1/T\) as the abscissa, \(\ln(T^2/Q)\) as the ordinate, then the apparent activation energies can be calculated by a slope. The results of the calculation are shown in table 2.

As can be seen from the data in table 2, \(E_{x1}\) of the sample prepared at 1523 K is lower than the other samples prepared at 1373 and 1673 K, indicating that the energy barrier of first crystallization stage needed to be overcome is low, and fcc-Al is easier to nucleate, which means the worse thermal stability of the alloy. On the contrary, \(E_{x2}, E_{p2}\) of the sample prepared at 1523 K is the highest, indicating that the process of second crystallization stage can be harder, the nucleation and growth of brittle intermetallic compounds will become more difficult.

In order to prove that the liquid-liquid structure transition induced by temperature happened, ER measurement of aluminum alloy was carried out, figure 3 shows the \(\rho(T)/\rho(300 \text{ K})\)-\(T\) curve of the \(\text{Al}_{86}\text{Ni}_{6}\text{Y}_{4.5}\text{Co}_{2}\text{La}_{1.5}\) liquid at a heating rate of 10 K min\(^{-1}\), where \(\rho(T)\) and \(\rho(300 \text{ K})\) represent the resistivity at the temperature of \(T\) and 300 K, respectively, and a solidus and a liquidus temperature of 915 K and 1175 K can be observed from figure 3. It also can be seen that the resistivity has become very unstable since 1402 K, the unusual variation on \(\rho(T)/\rho(300 \text{ K})\)-\(T\) curve might suggest an LLST during the heating process.

According to the figure above, it can be seen that the melt was undergoing structural transformation at the temperature of 1523 K, which led to a decrease of \(E_{x1}\). Based on previous studies, the change of crystallization behavior is often caused by the oxygen content in melt or the destruction of atomic clusters by temperature, but in this paper, the amorphous ribbon is prepared by pre-pumping high vacuum and induction heating under hydrogen protection conditions, and the aluminum oxide film will also protect the alloy from further oxidation, so the influence of the oxygen content in the melt can be excluded for the two reasons above.

Generally, it is difficult to determine the existence of nanoscale compositional clusters in the multi-component alloys directly; however, these clusters could be inferred from the microstructure evolution of the amorphous ribbon sample during annealing. Therefore, the ribbons were annealed at different temperatures and times to confirm the effect of melt temperature on its structure, the results of XRD are shown in figure 4.

**Table 2.** The apparent activation energy calculated according to the Kissinger method.

| \(T_q/\text{K}\) | \(E_{x1} (\text{KJ/mol}^{-1})\) | \(E_{p1} (\text{KJ/mol}^{-1})\) | \(E_{x2} (\text{KJ/mol}^{-1})\) | \(E_{p2} (\text{KJ/mol}^{-1})\) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1373 K          | 342.6           | 226.5           | 332             | 291.2           |
| 1523 K          | 316             | 269             | 438             | 332             |
| 1673 K          | 340.6           | 288             | 362             | 309             |
The atomic-level structure of Al-based amorphous can be generally described as the solute-centered clusters [19, 20], and the direct growth of the clusters inherited from the melt during the rapid cooling is the main factor of the formation of intermetallic compounds. The main clusters in the melt of this experiment are Al–Ni, Al–Co, and Al–Y [21], according to the phase diagram of binary alloys, the melting points of these intermetallic compounds are close to the temperature of LLST. Based on the results of the XRD that materials annealed at 753 K (far higher than \( T_{p2} \)), it can be inferred that melt temperature has no effect on the type of final crystallized product of Al\(_{86}\)Ni\(_6\)Y\(_{4.5}\)Co\(_2\)La\(_{1.5}\), but it has a significant effect on the crystallization behavior of amorphous at different crystallization stages, ribbons prepared at 1523 K and 1673 K are less susceptible to precipitate brittle intermetallic compounds when annealing at 603 K (between \( T_{p1} \) and \( T_{p2} \)), which implies that the atomic clusters of Al-Co, Al-Ni and Al-Y remain in the melt below 1402 K, and then with the melt temperature increasing, parts of atomic clusters are broken down gradually, which makes the second crystallization harder to occur. Moreover, the destruction of the atomic cluster leads to an increase of free Al atoms, so the diffusion capacity of the Al atoms is enhanced, which suggests that the amorphous phase is more likely to precipitate fcc-Al during the heating process, and the results are consistent with the previous calculation of activation energy.

But the strange thing is that \( E_{\text{at}} \) appears to increase when the melt temperature rises to 1673 K according to the result of activation energy. On the one hand, more clusters will be broken down by the excessive melt temperature, the increase of free Al atom will decline its diffusion ability, and fcc-Al will be more difficult to form and grow up due to the enrichment of atoms around it like Ni, Y, Co, and excessive atomic concentration around fcc-Al will also lead to the precipitation of metastable phase more easily. On the other hand, excessive solute atomic concentration can cause it to be dissolved in Al, although the solid solubility of Ni, Y, Co in Al is low (0.023%, 0.01%, 0.01%, respectively) [22, 23], it also can cause the increase of \( E_{\text{at}} \), so the \( E_{\text{at}} \) of ribbons prepared at 1673 K is higher than that prepared at 1523 K.

4. Conclusions

(1) Means of ER were used to examine the structure change of the Al\(_{86}\)Ni\(_6\)Y\(_{4.5}\)Co\(_2\)La\(_{1.5}\) liquid, the liquid-liquid structure transition (LLST) exists when the melt temperature reaches 1402 K, which presented as fluctuations on the curve of \( \rho(T)/\rho(300\text{ K}) \)-T.
(2) Solute-centered clusters can be destroyed by high melt temperatures. When the amorphous sample is prepared under the temperature experienced LLST, fcc-Al appearing in the primary crystallization stage is more likely to precipitate during the annealing process, which means worse thermal stability, but the nucleation and growth of intermetallic compounds can also be harder, therefore, the amorphous prepared at this melting temperature are more suitable for the preparation of amorphous nanocrystalline composites.

(3) Excessive melt temperature (1673 K) will lead to the destruction of a large number of atomic clusters, the increase of the concentration of Al atom and the solid solution of solute atom in Al will cause the precipitation of fcc-Al to be difficult again, and metastable intermetallic compounds can be precipitated more easily. Therefore, melt temperature plays an important role in primary crystallization and thermal stability.

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ORCID iDs

Zhizhi Wang https://orcid.org/0000-0001-7850-1532
Lin Liu https://orcid.org/0000-0002-7728-0317

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