Journal of Alloys and Compounds 691 (2017) 436–441

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Non-isothermal crystallization behavior of U-based amorphous alloy

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ARTICLE INFO

Article history:
Received 23 July 2016
Received in revised form
23 August 2016
Accepted 25 August 2016
Available online 26 August 2016

Keywords:
Amorphous alloy
Uranium alloy
Crystallization
Percolation

ABSTRACT

The non-isothermal crystallization behavior of uranium-based amorphous alloy $U_{64}Co_{28.5}Al_{7.5}$ was investigated by using differential scanning calorimetry. Its kinetic fragility parameter, overall crystallization activation energy and Kauzmann temperature were determined to be 28, 234 kJ/mol and 580 K, respectively. The evolution of the crystallization activation energy with the volume fraction crystallized, which was established by both the Kissinger and Ozawa methods independently, suggests a typical three-staged process for the crystallization. As reflected by the change of the local Avrami exponent with the fraction crystallized, nucleation dominates the whole process that can be illustrated phenomenologically with the percolation model. This work is helpful for understanding the formation and thermal stability of U-based amorphous alloys, and also for the development of new materials of this kind.

1. Introduction

Amorphous alloys, belonging to a class of metastable materials, will transform into stable crystalline solids upon heating or staying at room temperature for a sufficiently long time [1–3]. This metastability strongly challenges their applications, because both structures and properties of this class of alloys will be changed by their crystallization [4–6]. Moreover, whether an alloy can possess a high glass-forming ability (GFA) in some cases depends on its crystallization behavior [7–10]. But the crystallization mechanism of amorphous alloys remains unclear at an atomic level. Hence, further attention needs to be paid on crystallization of such alloys.

As a small peculiar branch, U-based amorphous alloys that are strongly potential materials in nuclear-related industries have been scarcely studied after discovered. In particular, their crystallizing behavior has been never reported, possibly because valuable knowledge about this is hard to obtain by using the previous alloys with very weak GFA and thermo-stability [11–13]. Recently, U-rich alloys in U-Co-Al system with highly improved GFA and thermo-stability have been developed [14]. Most important, firstly observed clearly in their calorimetrical analysis is glass transition temperature (T_g) that is absent in early studies of U-based metallic glasses. This makes it possible to identify crystallization behavior of U-based amorphous materials.

In the present study, a typical U-Co-Al amorphous alloy with the composition $U_{64}Co_{28.5}Al_{7.5}$ was chosen for preliminary crystallization investigation by using differential scanning calorimetry (DSC). This method can be classified into the non-isothermal and the isothermal mode [15–20]. The former mode has been widely applied recently due to the advantage in detecting quite rapid phase transformation as well as a broader testing temperature range [21,22], although the latter is easier and often used. Considering probable quick formation and transformation of metastable uranium compound phases as well as complicated surface oxidation owing to 5f-electronic characteristic of uranium element [23,24], the non-isothermal mode is used here. After the crystallization measurement, some characteristic parameters were obtained, and the evolution of activation energy and local Avrami exponent with crystallized volume fraction was obtained by using the Kissinger and Ozawa methods. Finally, the crystallizing behavior was further illustrated phenomenologically in terms of the percolation model.

2. Experiment

For preparing $U_{64}Co_{28.5}Al_{7.5}$ alloy, the purities of the starting metals were 99.5 wt% for depleted uranium, 99.9 wt% for cobalt and 99.99 wt% for aluminum. The alloy was fabricated by arc-melting the metal mixtures in a water-cooling copper crucible in a Ti-gettered Ar atmosphere with a background vacuum level of about

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http://dx.doi.org/10.1016/j.jallcom.2016.08.252
0925-8388/

5×10^{-3} Pa. The ingot with about 5 g in mass was remelted four times to ensure compositional homogeneity. It was placed in a quartz tube to conduct liquid-quenching and the ribbon sample was made by using a single melt-spinner at a surface velocity of ~50 m/s.

The amorphous nature of the U-Co-Al ribbon was identified with an X-ray diffractometer (Cu-K_α radiation). The DSC test was carried out in the temperature range of 300 K–800 K, at the heating rates of 10, 20, 40, 80 and 160 K/min. To ensure the reliability of the experimental data, temperature and enthalpy calibration were performed with high purity of indium and zinc standard specimens before the practical examination. During testing, a fixed flow of nitrogen (200 ml/min) was maintained in order to provide a constant thermal blanket within the DSC cell, thus eliminating the thermal gradient and ensuring the validity of the applied calibration standard from sample to sample.

3. Results and discussions

3.1. Characteristic parameters

Fig. 1(a) shows the DSC curves of the $U_{64}Co_{28.5}Al_{7.5}$ ribbon at different heating rates. The characteristic parameters including T_g, the crystallization temperature (T_x) and peak temperature (T_p), and the crystallization enthalpy (ΔH_c) are listed in Table 1. It can be seen that when raising the heating rate, the values of T_g, T_x and T_p become larger and the glass transition feature becomes more prominent. This is characteristic of a kinetic process as found in ordinary metallic glass systems [15,20].

The overall activation energy (E_c) for the glass transition or crystallization of an amorphous alloy in a linear heating condition can be deduced by the classical Kissinger method [25], which

Table 1
Thermal parameters of $U_{64}Co_{28.5}Al_{7.5}$ amorphous alloy at different heating rates.

Heating rate (K/min)	T_g (K)	T_x (K)	T_p (K)	ΔH_c (J/g)
10	613	629	636	−19.2
20	616	638	646	−19.8
40	622	647	655	−19.7
80	629	658	666	−19.6
160	638	669	678	−19.3

expresses the dependence of T_g, T_x and T_p on the heating rate (θ) through the following equation:

$$\ln\left(\frac{T^2}{\theta}\right) = \frac{E_c}{RT} + \ln\left(\frac{E_c}{k_0 R}\right) \quad (1)$$

where T is the temperature, R the gas constant and k_0 the frequency factor that is usually adopted to estimate the probability of an atom being involved in the course of glass transition or crystallization. The different $\ln(T^2/\theta)$-$1000/T$ plots of $U_{64}Co_{28.5}Al_{7.5}$ alloy, which are an approximate line with the slope of E_c/R and the intercept of $\ln(E_c/(k_0R))$, are presented in Fig. 1(b). It can be determined that the activation energies, E_g, E_x and E_p are 338 kJ/mol, 234 kJ/mol and 228 kJ/mol, respectively. This E_g value is higher than those of $Pd_{40}Ni_{10}Cu_{30}P_{20}$ (228 kJ/mol) [26] and $Cu_{46}Zr_{45}Al_7Y_2$ bulk glasses (304 kJ/mol) [16], implying that the U-Co-Al alloy has a greater energy barrier for atomic rearrangement or diffusion in the undercooled liquid region. The k_0 value was 1.52×10^{27}/s at T_g, 3.38×10^{17}/s at T_x and 5.75×10^{16}/s at T_p. Compared with Co- [15], and Cu- [16], and Ti-based [17] amorphous alloys, the U-Co-Al alloy has a much smaller k_0, reflecting that atomic mobility in the alloy is more sluggish probably due to the large atomic size and weight of uranium element.

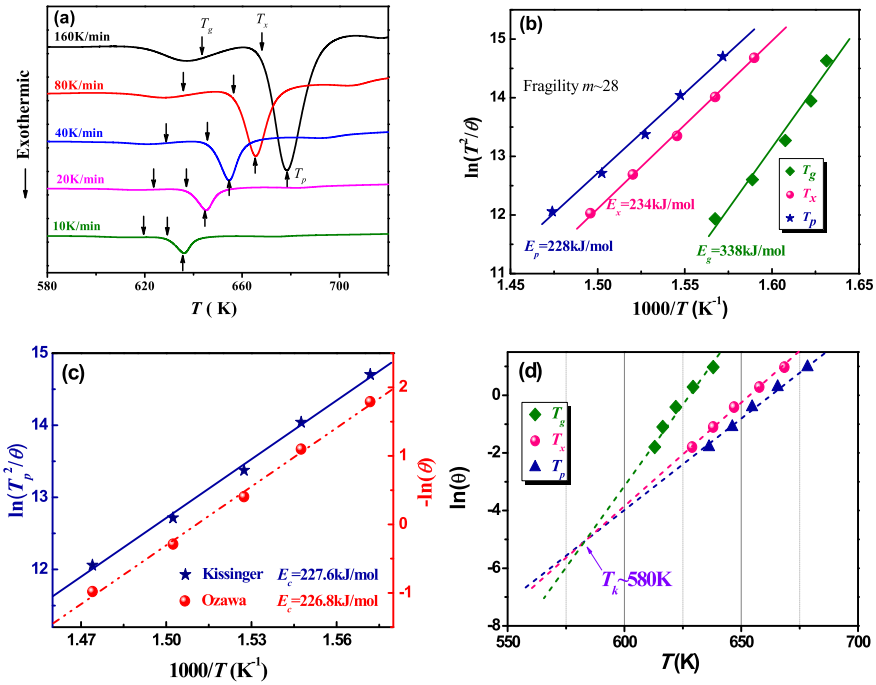

Fig. 1. Thermodynamic and kinetic characteristic parameters of $U_{64}Co_{28.5}Al_{7.5}$ amorphous alloy:(a) DSC curves at different heating rates, T_g denotes the glass transition temperature, T_x the onset crystallization temperature and T_p the peak crystallizaiton temperature; (b) Kissinger plots to calculate the activation energies relative to T_g, T_x and T_p, respectively, and the fragility parameter (m) can be deduced to be near 28; (c) Comparison of the Kissinger and Ozawa plots to calculate the activation energies relative to T_p; (d) Extrapolation of T_g, T_x and T_p at different heating rates to determine the Kauzmann temperature T_K (~580 K).