



Influence of the preparation cooling rate on crystallization kinetics of Fe₇₄Mo₆P₁₃C₇ amorphous alloys



Shuo Xiang^a, Qiang Li^{a,*}, Mingqing Zuo^a, Di Cao^b, Hongxiang Li^b, Yanfei Sun^a

^a School of Physics Science and Technology, Xinjiang University, Urumqi, Xinjiang 830046, People's Republic of China

^b State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, People's Republic of China

ARTICLE INFO

Keywords:

Preparation cooling rate
Apparent activation energy
Non-isothermal crystallization kinetics
Local Avrami exponent

ABSTRACT

Fe₇₄Mo₆P₁₃C₇ amorphous alloys have been prepared by three techniques with different preparation cooling rates, namely the melt-spinning, copper-mold casting, and J-quenching techniques. Differential scanning calorimetry (DSC) was used to investigate the thermal behavior and non-isothermal crystallization kinetics of the amorphous alloy samples. Through this, the effect of the preparation cooling rate on the amorphous alloy thermal parameters, apparent activation energy (E_{app}), and first crystallization event kinetics were investigated. The DSC tests show that there are no significant differences in the glass transition temperature (T_g) and the initial crystallization temperature (T_c) among the Fe₇₄Mo₆P₁₃C₇ amorphous alloy samples prepared by the different techniques, but the total crystallization heat increases with the preparation cooling rate. The E_{app} values corresponding to the first crystallization events of the three amorphous alloy samples are determined by the Kissinger and Ozawa methods, and the results show that E_{app} increases with a decreasing preparation cooling rate. This indicates that the amorphous alloy sample prepared at the lower cooling rate has a larger crystallization resistance, which may be ascribed to the lesser free volume. The non-isothermal kinetics analyses of the first crystallization events show that the local Avrami exponents (n) of the three amorphous alloy samples are < 1.5 during the initial stages, implying a crystallization mechanism based on the direct growth of pre-existing nuclei with a zero nucleation rate. This is then < 2.5 for the two bulk samples and in the range of 2.5–3.0 for the melt-spun ribbon sample in the intermediate crystallization stages. These values indicate the diffusion-controlled three-dimensional growth of small particles with decreasing ($n < 2.5$) and increasing ($n > 2.5$) nucleation rates. Meanwhile, the n values increase with the preparation cooling rate, indicating more short-range order in the amorphous alloy sample prepared at the lowest cooling rate.

1. Introduction

Amorphous alloys have structures characterized by their long-range disorder and short-range order, and are thermodynamically metastable. Due to their unique atomic arrangements, amorphous alloys exhibit outstanding features such as high mechanical strengths, excellent magnetic properties, and a good corrosion resistance [1,2], and so have attracted both scientific and technological interest.

The properties of a material depend on its internal structure, and the study of structure–property relationships is the core topic of materials research. However, due to the current lack of effective characterization techniques and atomic-level structural models for amorphous alloys, the influences of the microscopic states and atomic arrangements on amorphous alloy properties are still unresolved [3].

An amorphous alloy does not possess a defined atomic arrangement and there are multiple saddle points in its potential energy landscape

[4]. As a result, the atomic arrangement of an amorphous alloy correlates closely with its preparation history, especially the cooling rate during the preparation process. Therefore, comparing amorphous alloys prepared at different cooling rates provides us an opportunity to explore the relationship between the internal alloy structure and its properties.

An amorphous alloy is thermodynamically metastable and will spontaneously evolve to a more stable state upon heating by crystallization. Studying the crystallization behavior of amorphous alloys is very important from both scientific and technological points of view [5]. In our previous work [6], we performed a comparative study on the thermal behavior and non-isothermal crystallization kinetics of bulk and ribbon Fe₈₀P₁₃C₇ amorphous alloys, prepared by the J-quenching and melt-spinning techniques, respectively. The results indicated that the supercooled liquid states of the amorphous alloys were fully relaxed; this is related to the as-prepared states of the alloys. As a result,

* Corresponding author.

E-mail address: qli@xju.edu.cn (Q. Li).

the bulk and ribbon Fe₈₀P₁₃C₇ amorphous alloys exhibited different first crystallization event behaviors, likely resulting from the different atomic arrangements that are due to the different preparation cooling rates. However, the above work is not conclusive as only samples prepared at two cooling rates were compared. In the present work, we perform a similar comparative study of Fe₇₄Mo₆P₁₃C₇ amorphous alloys prepared by three techniques with different cooling rates, which are the J-quenching, copper-mold casting, and melt-spinning techniques. Through this study, the differences in the crystallization behavior of the amorphous alloys prepared by the different techniques can be investigated, and the influence of the preparation cooling rate on their atomic arrangements can be explored.

2. Experimental

Fe₇₄Mo₆P₁₃C₇ mother alloy ingots were prepared by torch-melting a mixture of Fe powder (99% mass% purity), Mo powder (99.9%), graphite powder (99.95%), and Fe₃P powder (99.5%) under a high-purity argon atmosphere. Subsequently, the mother alloy ingots were fluxed using a B₂O₃ and CaO fluxing agent (mass ratio of 3.5:1) at an elevated temperature for 4 h under a vacuum of ~50 Pa. After the flux treatment, the samples were cooled to room temperature and then were subjected to the different amorphous alloy preparation techniques. As a result, Fe₇₄Mo₆P₁₃C₇ cylindrical alloy rods with diameters of 1.0 mm and lengths of a few centimeters were prepared by J-quenching [7] and copper-mold casting, with corresponding cooling rates of about 800 K/s [8] and 4000 K/s [9], respectively. Additionally, a Fe₇₄Mo₆P₁₃C₇ ribbon with a thickness of ~25 μm was produced by the melt-spinning technique, and the corresponding preparation cooling rate was about 10⁴ K/s. The amorphous nature of the three samples was confirmed by X-ray diffraction (XRD; Bruker D8), and their thermal behaviors were investigated by differential scanning calorimetry (DSC; NETZSCH DSC 200F3) under an Ar atmosphere at various heating rates. For convenience, the Fe₇₄Mo₆P₁₃C₇ amorphous alloy samples prepared by J-quenching, copper-mold casting, and melt spinning are denoted as S1, S2, and S3, respectively.

3. Results and discussion

3.1. Thermal stabilities of S1, S2, and S3

The DSC thermal scans of S1, S2, and S3 measured at heating rates of 5, 10, 20, and 30 K/min are shown in Fig. 1, and the thermal properties determined from the DSC thermal scans are summarized in Table 1. For each of the three samples, T_g , T_x , and the temperature of the first crystallization peak (T_{p1}) shift significantly higher with an increasing heating rate, corresponding to the kinetic natures of the glass transition and crystallization of the amorphous alloys. For comparison, the DSC curves of the three samples at the heating rate of 20 K/min are overlaid in Fig. 1(d). The three samples exhibit similar crystallization behaviors, and all the T_g , T_x , and T_{p1} values of S1, S2, and S3 rise successively, indicating that these characteristic temperatures shift to slightly higher temperatures with increasing preparation cooling rates. Additionally, it is worth noting that the total enthalpy of crystallization ($\Sigma\Delta H_x$) of each sample is different, and the absolute $\Sigma\Delta H_x$ value increases in the order of S1, S2, and S3. The $\Sigma\Delta H_x$ parameter indicates the residual enthalpy or entropy of the amorphous alloy relative to the corresponding crystallized alloy. S1, S2, and S3 have the same compositions and energy states after complete crystallization so can be considered to be the same. Therefore, the internal energies of S1, S2, and S3 rise in turn, indicating that the slower preparation cooling rate leads to the more stable energy state.

3.2. Apparent activation energy of the first crystallization event of S1, S2, and S3

To describe the difficulty of the crystallization process, E_{app} of the first crystallization events were determined by the Kissinger [10] and Ozawa [11] methods. The Kissinger and Ozawa plots of S1, S2, and S3 corresponding to the peak temperature of the first crystallization event are shown in Fig. 2(a) and (b), respectively. The corresponding E_{app} values are determined to be 493, 483, and 435 kJ/mol by the Kissinger method, and 505, 495, and 448 kJ/mol by the Ozawa method for S1, S2, and S3, respectively. The apparent activation energies calculated from both methods are consistent and very close. This result shows that the E_{app} values of S1, S2, and S3 decrease successively. The apparent activation energy reflects resistance in the crystallization process. A smaller amount of free volume will be reserved in the amorphous alloy with the lower preparation cooling rate, and this will lead to a reduced atomic mobility and thus a larger apparent activation energy for crystallization.

3.3. Non-isothermal crystallization kinetics of the first crystallization processes of S1, S2, and S3

An exothermic peak in a DSC curve of an amorphous alloy corresponds to a crystallization process. The crystallized volume fraction x at time t (or temperature T in the case of a non-isothermal process) during crystallization can be taken as $A(t)/A_{total}$, where $A(t)$ is the area under the corresponding peak up to t and A_{total} is the total area of the peak. Before calculating x , the peak needs to be separated from any other peaks. It can be seen in Fig. 1 that there are partial superpositions of the peaks in the DSC curves of all three samples. Here, we use the Gaussian multi-peak fitting method to isolate the first peak. An example of the DSC curve of S1 (20 K/min) and the corresponding peaks isolated by the Gaussian multi-peak fitting is shown in Fig. 3.

Based on the above method, the crystallized volume fraction x as a function of T for the first crystallization peaks of S1, S2, and S3 (20 K/min) are plotted in Fig. 4. The slope of the x - T curve corresponds to the crystallization rate under a constant heating rate. The x - T curves of all the three samples obtained at 20 K/min show a typical 'S' shape, indicating that the crystallization rate first increases and then decreases, and is larger when x is in the range of ~20–80%. Fig. 4 also reveals that the induction time of the first crystallization event increases and the crystallization rate in the intermediate stage decreases with an increase of the preparation cooling rate. An amorphous alloy sample prepared at a slower cooling rate will contain more pre-existing nuclei of the primary crystallization phase, thus resulting in the longer induction time. On the other hand, a greater amount of free volume will be reserved in the amorphous alloy sample prepared at a higher cooling rate; this leads to a lower atomic diffusion resistance and thus enhances the crystallization rate. Furthermore, the apparent activation energy results also support the above proposal.

The first crystallization events of S1, S2, and S3 at the heating rate of 20 K/min were further investigated to determine the influence of the preparation cooling rate on the mechanism of crystallization. The local Avrami exponent n is calculated as a function of the crystallized volume fraction x based on the non-isothermal crystallization kinetics analysis proposed by Blázquez [12], as shown in Fig. 5. The exponent reflects the nucleation and growth mechanisms during crystallization, and can be expressed by the following formula [13]:

$$n = a + b \times c \quad (1)$$

Here, a is the nucleation index: $a = 0$ for a zero nucleation rate; $0 < a < 1$ for a nucleation rate decreasing with time; $a = 1$ for a constant nucleation rate; and $a > 1$ for a nucleation rate increasing with time. b is the dimensionality of the growth, where $b = 1, 2, \text{ or } 3$ correspond to a one-, two-, or three-dimensional particle growth, respectively. c is the growth index: $c = 1$ for interface-controlled growth

Download English Version:

<https://daneshyari.com/en/article/5441037>

Download Persian Version:

<https://daneshyari.com/article/5441037>

[Daneshyari.com](https://daneshyari.com)