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Non-isothermal and isothermal crystallization kinetics and their effect on microstructure of sintered and crystallized TiNbZrTaSi bulk alloys

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ABSTRACT

Non-isothermal and isothermal crystallization kinetics of mechanically alloyed $Ti_{65}Nb_{23.33}Zr_5Ta_{1.67}Si_5$ metallic glass (MG) powder and their effect on microstructure and mechanical property of spark-plasma-sintered and crystallized bulk counterparts were investigated by using Johnson–Mehl–Avrami–Kolmogorov equation. Results show the MG powder has two distinct crystallization steps, which precipitates bcc β-Ti and hexagonal $(Ti, Zr)_2Si$ phases successively. The larger apparent activation energy of the second crystallization step than that for the first one indicates the easier occurrence of precipitation for bcc β-Ti phase. Comparative analysis of crystallization kinetics indicates that regardless of non-isothermal and isothermal crystallization types, the first crystallization step is dominated by diffusion-controlled three- and two-dimensional growth of nuclei for the early and late crystallization stage, respectively, while the second one is governed by diffusion-controlled three-dimensional growth of nuclei in the whole crystallization process. Both nucleation rates of these two steps increase firstly and then reduce in the early and late crystallization stage, respectively. The processing technologies combined with crystallization kinetics decide different grain sizes and yield strengths for the sintered and crystallized bulk alloys. The results obtained provide a new insight into tailoring microstructure and mechanical property of bulk alloys by designing and optimizing processing technologies based on crystallization kinetics.

1. Introduction

Generally, high strength is accompanied by relatively low ductility and high elastic modulus in metallic materials. To obtain the good combination of high strength and large ductility as well as low elastic modulus at room temperature has become one of the main research goals in the design of new materials, for example biomedical metallic materials. It has been well accepted that metallic materials with fine grains have excellent comprehensive properties. In this viewpoint, a series of strategies have been used to develop biomedical metallic materials with nanostructure and ultrafine grains [1–4]. One noticeable way of obtaining fine grains is sintering and crystallizing metallic glass (MG) powder by powder metallurgy reported in our previous work [5–11], or crystallizing melt-solidified bulk metallic glasses (BMGs) by annealing treatment [12]. So, the research on the crystallization kinetics and crystallization mechanism of each phase is helpful to control the phase precipitation and grain size during the crystallization process [13–18]. In both cases, fine-grained metallic materials can be achieved by two processing technologies, directly continuous heating to target temperature T ($T_m - 100\ K \geq T \geq T_x + 200\ K$), which is far above the onset crystallization temperature T_x and lower than the melting temperature T_m of MG, then holding for several minutes (≤10 min) [17,18], or isothermal annealing at a given temperature, which is in the middle of the supercooled liquid (SCL) region below T_x of MG, then holding for a long time (≥60 min) [15]. Correspondingly, crystallization kinetics of the two processing technologies are connected with non-isothermal and isothermal conditions. Spontaneously, comparative study of non-isothermal and isothermal crystallization kinetics and their effect on microstructure and mechanical property of achieved fine-grained metallic materials become a significant academic question, which would provide an important guidance to select an optimized processing technology for desired microstructure and mechanical property.

Theoretically, the crystallization kinetics can be characterized by the Johnson–Mehl–Avrami–Kolmogorov (JMAK) equation which bases on four assumptions as follows [19]: (a) isothermal crystallization condition, (b) homogenous nucleation or heterogeneous nucleation at randomly dispersed particles of the second phase, (c) growth rate of new phases is only controlled by temperature and is independent of time, and (d) low anisotropy of growing crystals. So the JMAK equation is usually utilized to analyze crystallization kinetics in isothermal conditions [15,16,19,20]. Henderson et al. [14,21,22] have verified that the JMAK equation can also be extended to non-isothermal condition if the entire nucleation process occurs during the early crystallization process and becomes negligible afterward. Based on this consideration, the JMAK equation has been successfully used under non-isothermal condition to discuss the crystallization kinetics and crystallization mechanism [16–18,23–26]. Unfortunately, to our best knowledge, little research

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[19] has been focused on the topic of similarity and difference in non-isothermal and isothermal crystallization kinetics for a given constituted MG up to date.

In our previous work, it was found that minor alloying substitution element [16] or minor varying content in the same alloying element [17,18,27] could cause different nuclei growth mechanisms for mechanically alloyed MG powders under non-isothermal condition, which finally resulted in different microstructures and mechanical properties of sintered and crystallized bulk alloys. Also, based on non-isothermal crystallization kinetics [18] and classical theory of nucleation and growth [28], we have revealed the effect of heating rate on microstructures and mechanical properties of sintered and crystallized bulk alloys. However, based on crystallization kinetics theory for a given constituted MG, the systematic study about intrinsic relationship between the non-isothermal and isothermal crystallization mechanisms and the microstructure and mechanical property of sintered and crystallized bulk alloys have never been reported so far.

In the present work, the JMAK equation was applied to comparatively investigate both non-isothermal and isothermal crystallization kinetics for mechanically alloyed $Ti_{65}Nb_{23.33}Zr_5Ta_{1.67}Si_5$ MG powder. The TiNbZrTaSi alloy system was selected as research object because its constituent elements are of good biocompatibility. The validity of the JMAK theory is verified by the similarity in the crystallization mechanisms under both non-isothermal and isothermal conditions. Besides, the effect of both non-isothermal and isothermal crystallization kinetics on microstructure and mechanical property of achieved fine-grained bulk alloys has been elucidated. The results obtained are helpful for tailoring microstructure and mechanical property of fine-grained bulk alloys by designing and optimizing processing technologies based on crystallization kinetics.

2. Experimental procedure

$Ti_{65}Nb_{23.33}Zr_5Ta_{1.67}Si_5$ MG powder was prepared by mechanically alloying the mixtures of respective elemental powders with purities above 99.9 wt.% and particle sizes below 48 μm. The mechanical alloying process was conducted in a QM-2SP20-CL high-energy planetary ball milling system with stainless steel vial and balls. The ball-to-powder weight ratio is 10:1. The balls with diameters of 15, 10 and 6 mm (with a weight ratio of 1:3:1) were used. The vial and the lid were sealed using an O-ring with a circular cross section. High-energy ball milling was performed at a rotation speed of 4.1 s^{-1} under a high purified argon gas atmosphere (99.999%, 0.5 MPa). The milling process was stopped every 5 h to cool the vial to room temperature. Then a small amount of powder was taken out from the vial through the use of argon-filled glove-box for characterization analysis until the volume fraction of MG phase maximized. The non-isothermal and isothermal crystallization mechanisms of the as-prepared MG powder were investigated by differential scanning calorimetry (DSC; NETSCH STA449C, Germany) under a high-purity argon atmosphere. Non-isothermal heating process was performed at different heating rates ranging from 10 K/min to 40 K/min. The onset crystallization temperature T_x was defined as the intersection of the tangents to the DSC trace above and below the initial change in the baseline slope. Isothermal DSC measurement was carried out by heating to different temperatures ranging from 770 K to 780 K (below T_{x1} ~ 820 K, Fig. 2b) and 928 K to 943 K (below T_{x2} ~ 973 K, Fig. 2b), respectively, at a heating rate of 20 K/min and holding for 20 min.

Subsequently, the as-prepared MG powder was spark-plasma-sintered under the protection of argon gas atmosphere by a Dr. Sintering SPS-825 system (Sumitomo Coal Mining Co. Ltd., Tokyo, Japan). In order to analyze the effect of the non-isothermal and isothermal crystallization kinetics for the as-prepared MG powder on microstructure and mechanical property of the achieved fine-grained bulk alloys, the sintering parameters were set up according to the non-isothermal and isothermal DSC process parameters (Figs. 1, 3 and 9). All the sintered and crystallized bulk samples, marked as S_{P1}, S_{P2} and S_{P3} corresponding to different sintering process parameters (Fig. 1), were achieved by final heating to 1233 K far above the T_x and holding for 5 min at 50 MPa. The heating rate of 20 K/min was used. The selection of the S_{P1}, S_{P2} and S_{P3} is to comparatively investigate the non-isothermal and isothermal crystallization kinetics. In two isothermal crystallization steps, annealing temperatures of 780 K (40 K below T_{x1} ~ 820 K, Fig. 2b) and 943 K (30 K below T_{x2} ~ 973 K, Fig. 2b) and annealing time of 20 min were selected to guarantee proper isothermal condition.

X-ray diffraction (XRD) (D/MAX-2500/PC; Rigaku Corp., Tokyo, Japan) with Cu K_α radiation ($\lambda = 1.5418$ Å), a Philips XL-30 FEG scanning electron microscopy (SEM) (Amsterdam, The Netherlands) combined with quantitative image analysis using ImageJ software and a Tecnai G2 F30 field emission gun transmission electron microscopy (TEM) (FEI, Eindhoven, The Netherlands) were used to examine the phase constituents and microstructures of the as-prepared MG powder and the sintered and crystallized bulk alloys, respectively. Compressive tests were conducted by a MTS Test Star 810 testing system at a strain rate of 5×10^{-4} s^{-1}. The compressive specimens of $\phi 3 \times 6$ mm were used and a small strain gauge was used to calibrate and measure the strain during loading.

3. Crystallization kinetic models

Employing the DSC experiments, the apparent activation energy E, the local values of activation energy $E(x)$ and the local Avrami exponents $n(x)$ can be calculated [24,29]. It is suggested that the T_x is related to the nucleation process, and the crystallization peak temperature T_p is associated with the growth process [30]. Therefore, it may presume that the E_x and E_p could stand for the activation energy of nucleation and growth of crystals. E can be used to describe the difficulty of the crystallization steps and it can be obtained by Kissinger equation given by [31]:

$$\ln\left(\frac{T^2}{\beta}\right) = \frac{E}{RT} + \text{const.} \tag{1}$$

where β is the heating rate; R is the ideal gas constant; T represents the characteristic temperatures at a certain heating rate β, such as T_x and T_p, respectively. E denotes the apparent activation energy, namely, E_x and E_p, corresponding to the ones at aforementioned characteristic temperatures, respectively. Ln (T^2/β) versus $1/T$ exhibits a linear relationship whose slope indicates the value of E/R.

Otherwise, E can also be calculated by Ozawa equation, which is given by [32]:

$$\ln\beta = -\frac{E}{RT} + \text{const.} \tag{2}$$

where the slope of the plot of ln β versus $1/T$ reflects the value of $-E/R$.

In addition, the Augis–Bennett equation is also introduced to evaluate the apparent activation energy E. The Augis–Bennett equation can be written as follows [33]:

$$\ln\left(\frac{T}{\beta}\right) = \frac{E}{RT} + \text{const.} \tag{3}$$

Here, the equation displays a linear relationship between ln (T/β) and $1/T$ with a slope of the value E/R.

E is somehow an average value of the activation energy of crystallization, while $E(x)$ corresponds to the appropriate values of activation energy in a wide range of crystallized volume fraction. It can be evaluated from the following Kissinger–Akahira–Sunose (KAS) model [14]:

$$\ln\left[\frac{T^2(x)}{\beta}\right] = \frac{E(x)}{RT(x)} + \text{const.} \tag{4}$$