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Crystallization kinetics of $Cu_{33}Zr_{67}$ amorphous alloy during continuous cooling annealing

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ABSTRACT

A temperature-time program, i.e., continuous cooling annealing (CCA), was studied for the crystallization of amorphous alloy. The CCA crystallization behavior of $Cu_{33}Zr_{67}$ amorphous alloy was investigated by differential scanning calorimetry. Kinetic analysis indicates that commonly used methods (e.g., the Kissinger plot) become invalid. The general kinetic theory was applied for describing the CCA crystallization kinetics, and two kinetic recipes were proposed for the determination of kinetic parameters. By applying them to the measured data, reasonable parameter values were obtained. Accordingly, the CCA crystallization mechanisms of $Cu_{33}Zr_{67}$ amorphous alloy were determined as approximately continuous nucleation and 3-dimentional interface-controlled growth.

1. Introduction

Recent studies have shown the importance of controlled crystallization of amorphous alloy as its mechanical and physical properties are improved with annealing treatments [1–4]. To exploit this tool to its full extent, much effort has been spent on the studying of crystallization kinetics of amorphous alloy during annealing [5–12]. With proper kinetic analysis, the kinetic parameters reflecting crystallization mechanisms can be extracted from the experimental data measured by differential scanning calorimetry (DSC) [10,13].

The theory for describing crystallization kinetics was built on the basis of the Kolmogorov-Johnson-Mehl-Avrami (KJMA) equations [5–9]. And some efficient kinetic recipes were proposed, e.g., the Kissinger plot [14], the Friedman plot [15], the Avrami plot, the Ozawa plot [16] and the Starink-Zahra plot [17]. All these models and recipes have been wildly used to analysis isothermal annealing (IA) or continuous heating annealing (CHA) data. However, it has been ignored for a long time that the amorphous alloy with wide supercooled liquid region may be subjected to an interesting temperature (T)-time (t) program, i.e., cooling from a temperature above glass transition temperature, T_g, in which crystallization may occur.

Compared with a huger number of literatures focusing on the IA and CHA kinetics, the crystallization behavior during continuous cooling annealing (CCA) is largely unknown. Therefore, the CCA crystallization behavior of $Cu_{33}Zr_{67}$ amorphous alloy was investigated experimentally, and then the crystallization mechanisms were analyzed in this work.

2. Experimental methods

A master alloy with a nominal composition of $Cu_{33}Zr_{67}$ was first produced by melting the bulk high-purity Zr (99.9 wt%) and Cu (99.999 wt%) in an electric arc furnace under a protective argon atmosphere. Then, the amorphous ribbon was prepared from the master alloy by melt spinning.

The crystallization behavior of the $Cu_{33}Zr_{67}$ amorphous ribbon was investigated by DSC runs (Perkin Elmer DSC 8500). The *T-t* program adopts a cooling process, i.e., each specimen was heated from room temperature up to different initial temperatures, T_i=674–678 K (T_g=635 K) with a rapid heating rate (Φ=300 K min^{-1}) in order to prevent crystallization during the primary heating stage, and then it was cooled form T_i with a fixed cooling rate (Φ=–40 K min^{-1}), immediately. Per sample, two identical DSC runs were performed successively under flowing pure nitrogen. The second run with the specimen in its crystalline state, served as an in situ recording of the baseline.

Structure of specimen was investigated by X-ray diffraction (XRD, Panalytical X'pert PRO) and transmission electron microscopy (TEM, JEM-3010, JEOL). Specimen for TEM studies was

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perforated by chemical jet thinning using a 35% nitric acid in ethanol at 243 K.

3. Results and discussion

3.1. Structural analysis

The XRD pattern of as-annealed alloy (cooling from T_i=678 K) is shown in Fig. 1a. It indicates that the production of CCA crystallization is composed only of $CuZr_2$ phase, which is in accordance with the IA/CHA crystallization [18,19]. Bright-field TEM image of as-annealed $Cu_{33}Zr_{67}$ alloy (cooling from T_i=678 K) is shown in Fig. 1b. The approximately equiaxed grains with uniform size approximately 0.5 μm can be observed. This is an evidence that the crystallization kinetics obeys the basic assumption of the KJMA equations, i.e., isotropic growth of randomly distributed nuclei. In addition, the homogeneous phase was indexed as $CuZr_2$ phase by

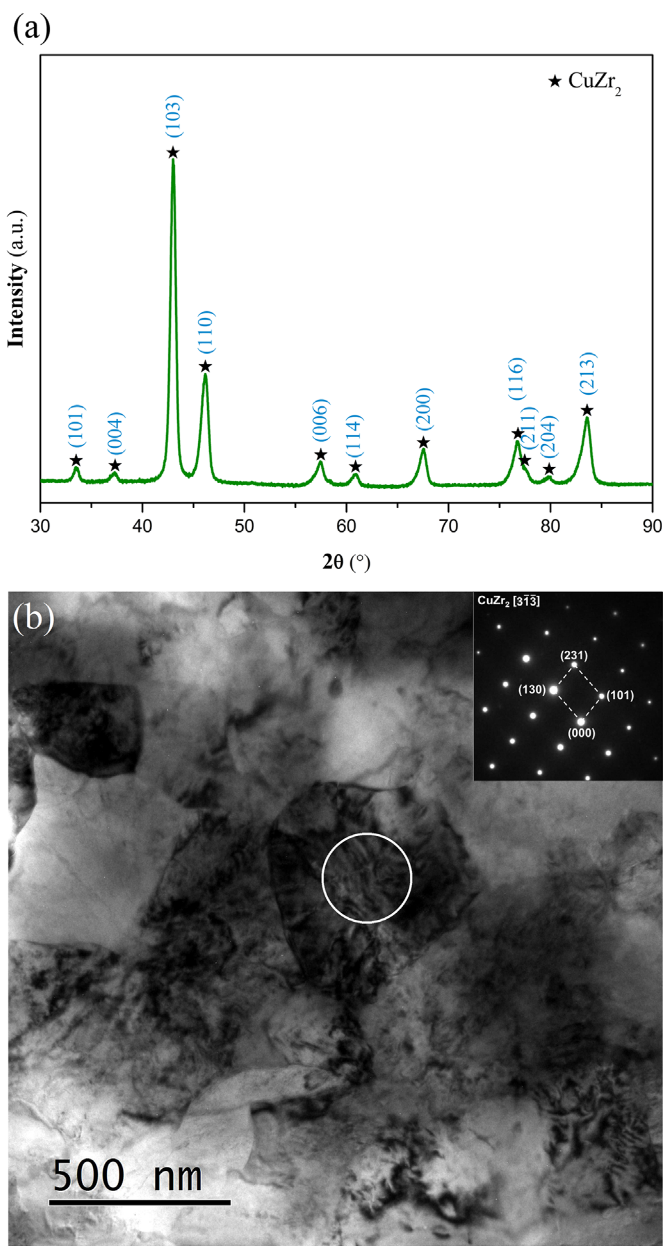

Fig. 1. (a) XRD pattern (Co Ka radiation) and (b) bright-field TEM image of the $Cu_{33}Zr_{67}$ amorphous alloy after CCA under T_i=678 K and $\Phi = -40$ Kmin^{-1}.

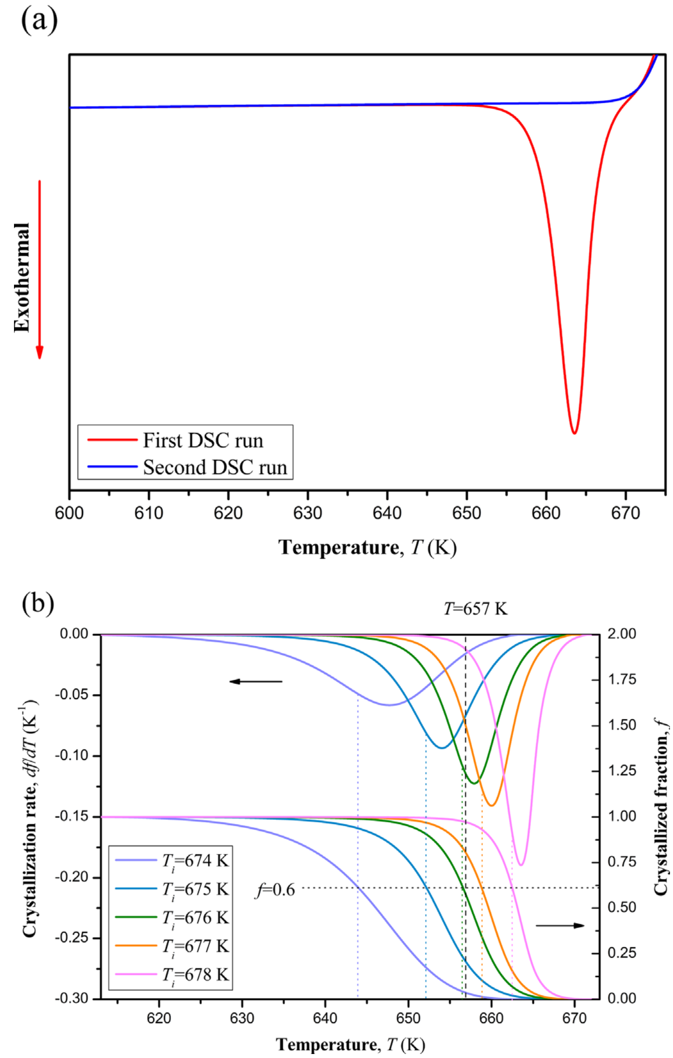

Fig. 2. (a) Two successive DSC scans of $Cu_{33}Zr_{67}$ amorphous alloy during CCA under T_i=678 K and $\Phi = -40$ K min^{-1}; and (b) evolutions of df/dT and f with T obtained from the baseline-corrected DSC scans under different initial temperatures.

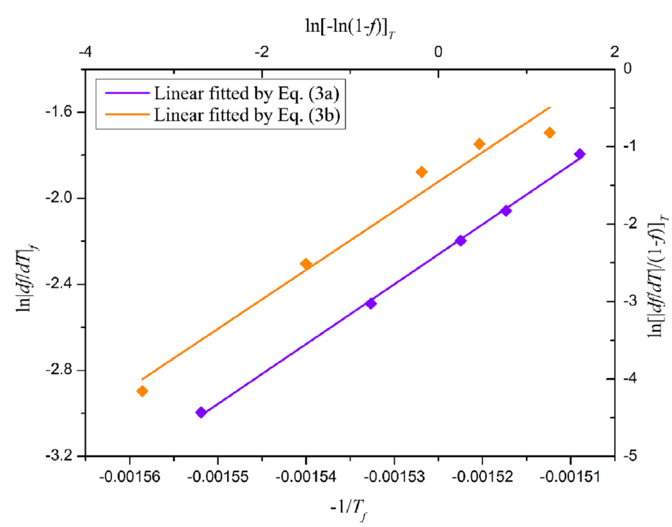

Fig. 3. Determination of Q and n for the CCA crystallization of $Cu_{33}Zr_{67}$ amorphous alloy.