CRYSTAL GROWTH DURING CRYSTALLIZATION OF AMORPHOUS ALLOYS

K. LU and J.T. WANG

Institute of Metal Research, Academia Sinica, Shenyang, People's Rep. of China

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Crystallization process of a Ni–P glass was investigated by use of an in situ TEM observation. Crystal growth was found to proceed in two exponential processes: single atoms jumping from amorphous matrix to crystal, and ordered clusters shearing and depositing to crystal front. Crystal growth velocities at two different temperatures were measured and it was found that the crystal growth velocity is not only related to the anneal temperature, but also to anneal time and microstructure of the amorphous sample. Ordered clusters existing in the amorphous matrix accelerate the crystal growth at lower temperature and slow the growth down at higher temperature. Based on the new micromechanism, a new expression of crystal growth velocity was deduced, which contains two exponential terms of $U_{AI}$ and $U_{CD}$. Experimental results of crystal growth during crystallization of amorphous alloys could be explained satisfactorily by this expression.

I. Introduction

Crystallization of amorphous alloys has been studied for many years and the atomic diffusion mechanism has been commonly accepted to interpret the crystallization process. Crystallization kinetics, based on such a micromechanism that activated atoms diffuse from amorphous state to crystal front, has been established. The crystal growth velocity expression deduced from the classical phase transformation theory is regarded valid for the polymorphous and eutectic crystallization processes [1,2]:

$$U = a_0 \nu_0 \exp \left( - \frac{\Delta E}{RT} \right) \left[ 1 - \exp \left( - \frac{\Delta F_v}{RT} \right) \right], \quad (1)$$

where $a_0$ and $\nu_0$ are the atomic diameter and atomic jump frequency, $\Delta F_v$ is the molar free energy difference between two phases and $\Delta E$ is the activation energy for an atom to leave the amorphous matrix and attach itself to the growing crystal. Since the crystallization of amorphous alloys is always studied at large undercooling, $\Delta F_v \gg RT$, and then:

$$U = a_0 \nu_0 \exp \left( - \frac{\Delta E}{RT} \right). \quad (2)$$

This Arrhenius dependence of growth velocity on temperature has been "confirmed" experimentally by many researchers [2–4], although both the activation energy $\Delta E$ and the pre-exponential are inconsistent with the growth mechanism involving activated jumps of single atoms across the amorphous interface [2]. Moreover, the atom diffusion coefficients estimated from crystal growth during crystallization of amorphous alloys are much larger than the directly measured results [5].

The autocatalytic acceleration of crystal growth during crystallization processes of amorphous alloys [6] and amorphous semiconductors [7] is also apparently contrary to the atomic diffusion mechanism.

Nunogaki et al. [8] have measured the crystal growth velocities during crystallization of an amorphous Fe–B alloy at different temperatures in fine time scales. The growth velocity of bct Fe$_3$B crystal [9] gradually decreased with anneal time at higher temperatures (634–654 K), while the growth of the crystal was accelerated rather than slowed down at lower temperature (594 K). They contributed these results, which cannot be explained by the atomic diffusion mechanism, to the change in amorphous matrix (to be referred to as relaxation; actually it is the increase of ordered...
clusters, which would be discussed in the next section) during crystallization process.

A new crystallization micromechanism was supposed according to the internal structures of crystallization products and an in situ TEM (transmission electron microscope) observation of the crystallization process [10]. The crystallization process of an amorphous alloy occurs not only by single atom diffusion, but also by the ordered clusters (in the amorphous matrix) shearing and depositing to the crystal front as well. In this paper, an in situ TEM observation of the latter process was presented and the crystal growth velocity was thoroughly studied by means of a video camera. The crystal growth velocity was found to be closely related to the anneal temperature, anneal time and amorphous matrix structures. A new expression of crystal growth velocity was established based on the new crystallization micromechanism, an it was used to give satisfactory explanations to many experimental results.

2. Experimental procedures

Amorphous Ni$_{80}$P$_{20}$ (at%) ribbon about 2.2 mm wide and 20 μm thick was prepared by melt-spinning technique using a single roller rapidly quenching equipment. Amorphous state was examined by X-ray diffraction, electron diffraction, and thermal analysis.

Thin foils for TEM observation were prepared by electro-polishing using an alcoholic solution of 10% perchloric acid at −40°C. A JEOL-100CX scanning transmission electron microscope (STEM) and an EM-SHH specimen heating holder were used to observe the crystallization processes when the amorphous foils were heated inside the TEM. Temperature measurement was made by a Pt/Pt–13%Rh thermocouple, and a Sony video camera was used to record the processes.

3. Results and discussion

3.1. Crystal growth process

An in situ TEM observation of the crystallization process was made to a partially crystallized Ni–P amorphous foil which was pre-annealed for 5 min at 600 K (in a DSC-II, Perkin Elmer). A crystal front (which was formed during pre-anneal treatment) was chosen to be in the observation area, where new crystal might be formed. The sample was heated to 620 K, holding the temperature (which was measured by a thermocouple inside the EM-SHH specimen heating holder; perhaps the actual temperature in the observation area which was radiated by electron beams might be higher than the indicated value). With anneal time increasing, at the crystal front a new crystal was formed and it gradually grew into the amorphous matrix in an elliptical shape (as shown in the inset of fig. 1).

The movement of the new crystal front was very slow at the initial stage (at a velocity of about 1.0 Å/s), and gradually increased as shown in fig. 1. “Steps” (abrupt increases in the crystal size) are clearly visible during the crystal growth, which can be seen in fig. 1. And the “steps” increased both in frequency and attitude with the anneal time until the crystal grew almost totally in the “steps” manner, with an average velocity of about 13.0 Å/s.

Dynamic TEM observation of the crystal growth process revealed the fact that the abrupt growth (“steps” in fig. 1) was caused by ordered clusters shearing (changing their orientations) and depositing to the crystal front. This process was

![Fig. 1. The crystal size increases with anneal time during crystallization of Ni–P glass (in situ annealing) at 620 K. The inset shows shapes of the newly formed crystal at different times. Solid line represents theoretical calculation results using eq. (6) with the parameters listed in table 1.](image-url)
shown in fig. 2, in which a group of ordered clusters in front of the growing crystal was indicated (fig. 2a). The crystal front moved downwards, touched the clusters (fig. 2b), and passed through them (fig. 2c). Although the contrasts of the clusters were slightly changed, the configuration of the clusters group remained unchanged.

This could be reasonably explained as directly depositing (and shearing, for details see ref. [10]) of the clusters onto the crystal front. If the clusters were transformed into parts of the crystal in form of atoms (inside the clusters) diffusing to the crystal one by one, the configuration of the newly formed crystalline part would be certainly different from that of the original clusters.

So we may suggest that the crystal growth process is composed of two exponential processes: single atoms jumping (or diffusing) and ordered clusters shearing and depositing, as schematically illustrated in fig. 3. These two processes can be used to give a satisfactory explanation to fig. 1. In the initial stage, the atom jumping process dominated the crystal growth which was in a slow, continuously growing manner, as there were not yet enough clusters. With the anneal treatment proceeding, ordered clusters within the amorphous matrix grew. Larger and more clusters were formed and they were touched by the growing crystal. At this temperature the growth velocity of the clusters depositing was greater than that of the atoms jumping, and the average growth velocity would be increased by more clusters depositing. When there were so many ordered clusters in the amorphous matrix that crystal growth was dominated by the clusters depositing, the crystal growth velocity tended to be a constant of about 13.0 A/s.

3.2. Crystal growth velocity

The crystal growth velocities during in situ crystallization of amorphous Ni–P alloy were measured at two different anneal temperatures, 620 and 680 K, respectively. Due to electron beam radiation, there were more ordered clusters formed in the observation area than outside, as shown in fig. 4. The crystal growth velocity changed dramatically in and out of this area, which can be

Fig. 2. Dynamic in situ TEM observation of movement of a growing crystal front which was outlined. A group of ordered clusters indicated by the arrow was unchanged in its configuration when it was in front of (a), on the front of (b), and in (c) the crystal.

Fig. 3. Schematic diagram illustrating the two processes of the crystallization: single atoms jumping from amorphous state to the crystalline state (AJ), and ordered clusters shearing and depositing on the crystal front (CD), in one dimension.
According to the new micromechanism for crystallization process that crystals growth proceeds by single-atom jumping (AJ) process and ordered-cluster shearing and depositing (CD) process, the crystall growth velocity, as a function of anneal temperature \( T \) and anneal time \( t \), should involve the two exponential contribution growth velocities \( U_{AJ} \) and \( U_{CD} \):

\[
U(T, t) = (1 - \alpha) U_{AJ}(T) + \alpha U_{CD}(T),
\]

where \( \alpha \) is a parameter describing the occurrence of the CD process: when a CD process occurs, \( \alpha = 1 \), and no CD process (AJ process only), \( \alpha = 0 \). The value of \( \alpha \) is not only dependent on the anneal temperature and anneal time, but also on the microstructures of the as-quenched amorphous alloys.

The AJ process causes crystal growing in a velocity \( U_{AJ} \), which is actually the growth velocity in eq. (2):

\[
U_{AJ}(T) = U_0 \exp\left(-\frac{E_{AJ}}{RT}\right),
\]

where \( U_0 \) is a velocity constant, equals \( a_0 v_0 \), and \( E_{AJ} \) is the activation energy for atomic jumping to the crystal front.

The CD process is an activated process, too. It causes crystal growth in a velocity \( U_{CD} \), which is

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Fig. 4. A TEM photograph of the Ni–P amorphous foil irradiated by electron beams (observation area (A)) and the outside region (B).

Fig. 5. Relationship between the growing crystal size, \( R \) (which was shown in the insets of the figures), and anneal time at 620 K (a) and 680 K (b), respectively. These results were measured by using a video camera. Insets show the crystals (shadow) growing in a different amorphous matrix.
related to both clusters sizes ($S$) and shearing and depositing time ($\delta$), and can be written as:

$$U_{CD} = (S/\delta) \exp(-E_{CD}/RT), \quad (5)$$

where $E_{CD}$ is the activation energy for the clusters shearing and depositing, as discussed in detail elsewhere [2]. Experimental observation showed that the time used to shearing and depositing a cluster is approximately proportional to the cluster's size, i.e. $S/\delta$ equals to a constant, $C$. So $U_{CD}$ can be expressed as:

$$U_{CD} = C \exp(-E_{CD}/RT), \quad (5')$$

and the crystal growth velocity can be written as the following expression:

$$U(T, t) = (1 - \alpha)U_0 \exp\left(-\frac{E_{AJ g}}{RT}\right) + \alpha C \exp\left(-\frac{E_{CD}}{RT}\right). \quad (6)$$

The anneal time, anneal temperature and initial states dependent parameter $\alpha$ has significant effects on the crystal growth velocity. Assuming that the initial states of the crystal-like clusters are periodically distributed with an initial size of $s_0$, and interval spacing $d_0$, we have successfully modelled the experimental results of the crystal growth velocity at 620 K using eq. (6), as shown in fig. 1. In the calculation, the growth velocity of the ordered clusters was taken as $3.6 \times 10^{-12}$ m/s at 620 K, which was measured experimentally, and the values of the other parameters used are listed in table 1.

Actually, the temperature and time dependence of crystal growth velocity is controlled by the ratio of $U_{AJ}$ to $U_{CD}$:

$$\frac{U_{AJ}}{U_{CD}} = \frac{U_0}{C} \exp\left(-\frac{E_{AJ g} - E_{CD}}{RT}\right). \quad (7)$$

As $E_{AJ g} > E_{CD}$ [11], an increase in temperature will cause the contribution of the weight of the AJ process to increase and the CD process to decrease. So there exists a critical temperature, $T_c$, such that $U_{AJ}(T_c) = U_{CD}(T_c)$:

$$T_c = \frac{E_{AJ g} - E_{CD}}{R \ln(U_0/C)}. \quad (8)$$

When $T > T_c$, $U_{AJ} > U_{CD}$, an increase of the ordered clusters in front of the growing crystal (i.e. an increase of the CD process) would reduce the crystal growth velocity, and when $T < T_c$, $U_{AJ} < U_{CD}$, an increase of the CD process would accelerate the crystal growth. This tendency can be used to interpret our experimental results (fig. 5) as well as Nunogaki et al. [8]. By use of the parameters listed in table 1, the value of $T_c$ was estimated to be 728 K. According to our experimental results, the value of the critical temperature should be in the region of 620–680 K. The difference between theoretical and experimental value of $T_c$ might be attributed to errors in values

![Figure 6](image-url)
that the crystal growth proceeds in two processes: single atoms jumping from amorphous matrix to crystal front, and ordered clusters shearing and depositing onto the growing crystal.

(2) According to the new micromechanism for crystallization process, a new expression of crystal growth velocity was established:

\[ U(T, t) = (1 - \alpha)U_0 \exp\left( -\frac{E_{\text{AJ}}}{RT} \right) + \alpha C \exp\left( -\frac{E_{\text{CD}}}{RT} \right) \]

The crystal growth velocity is not only related to anneal temperature, but also to the anneal time and microstructure of the amorphous sample. The new equation of growth velocity could give a satisfactory interpretation to the experimental results.

(3) There is a critical temperature, \( T_c \), at which \( U_{\text{AJ}} = U_{\text{CD}} \). When \( T > T_c \), increase of ordered clusters would reduce the crystal growth velocity, and when \( T < T_c \), accelerate the crystal growth. This deduction from the new expression of crystal growth velocity was proved to be valid by our experiments and literature works.

**References**

planes spacing of these two phases are very closed, as listed in: F. Vafaei-Makhsoos, E.L. Thomas and L.E. Toth, Met. Trans. 9A (1978) 1449.

[9] We think it is the eutectic crystallization products of Fe₃B and fcc Fe, which were always thought as Fe₃B crystal from the electron diffraction, as the values of diffraction
