A micromechanism for crystallization of amorphous alloys
II. Bulk crystallization process

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Bulk crystallization products of amorphous Ni-P alloy were studied by X-ray diffraction and transmission electron microscopy (TEM). The crystallization products contain two crystalline phases: body centered tetragonal (bet) Ni₅P and face centered cubic (fcc) Ni austenite. The orientation relationship between the two phases is $\langle 111 \rangle_{\text{bet}} / / \langle 110 \rangle_{\text{fcc}}$. High resolution electron microscopy (HREM) technique was used to get a detailed observation of the crystal structure. It was found that both the Ni₅P and the Ni phase were discontinuous rather than continuous. Very small crystals initially formed in crystallization were found to be composed of even smaller crystalline particles of the two phases. The morphologies and structures of the crystallization products, as well as the crystal formation process were interpreted using a new crystallization micromechanism proposed by the authors in a previous publication.

1. Introduction

In the first part of this work [1], a new universal micromechanism was proposed for the crystallization of amorphous alloys. As structures and morphologies of the crystallization products were closely related to the transformation mechanism, we will study the three-dimensional (3D) bulk crystallization products to enhance our understanding of the mechanism.

For amorphous TM₈₀M₂₀ (at%) alloys, eutectic crystallization is frequently preferred to occur on annealing [2,3]. Such a eutectic crystallization, i.e. simultaneous decomposition of the amorphous phase into two crystalline phases, has been intensively studied in several systems [4-9].

Microstructural aspects of the eutectic crystallization has been well illustrated by the much studied glass (Fe, Ni)₆₀(P, B)₂₀ (METGLAS 2826) [3]. Crystallization occurs by the apparently homogeneous nucleation and growth within the amorphous matrix of two-phase barrel-shaped crystals (as in fig. 1) which grow unchanged until they impinge. The crystal was described as containing two finely spaced crystalline phases: a continuous metastable body centered tetragonal compound (Fe, Ni)$_₃$(P, B) which is isomorphous with Ni₅P; and rods of Fe-Ni austenite which
2. Experimental procedures

The Ni$_{50}$P$_{50}$ (at%) amorphous alloy samples used in this part came from the same ribbon as used in Part I. Anneal treatment to crystallize the amorphous sample was performed in a differential scanning calorimeter (DSC-II, Perkin-Elmer). The thin foils used for TEM observation were prepared by electro-polishing using an alcoholic solution of 10% perchloric acid at a temperature of $-40^\circ$C.

The TEM used in this work is a JEOL-100CX scanning transmission electron microscope (STEM) with an accelerating voltage of 100 kV. X-ray diffraction experiments were performed on a Rigaku X-ray diffractometer ($D_{\text{max}} =$ 8 Å, 12 kW) using Cu K$\alpha$ radiation. The high resolution electron microscopy experiment was carried out using a JEOL-200CX electron microscope with an accelerating voltage of 200 kV.

3. Experimental results and discussion

3.1. Bulk crystallization products

The as-quenched amorphous Ni–P samples were annealed isothermally at 570 K in the DSC before, being thinned, and were examined by TEM. Crystals were found in the samples annealed for more than 80 min at 570 K.

Fig. 2 shows an X-ray diffraction spectrum of a partially crystallized Ni–P sample annealed at 570 K for 120 min. As indicated in the spectrum, the diffraction peaks can be indexed with two crystalline phases: a body centered tetragonal (bct) Ni$_3$P compound and a face centered cubic (fcc) Ni austenite. The lattice parameters of the phases were listed in table 1. It is clear from fig. 2 that the diffraction peak separations of these two phases can be identified.

Fig. 3a shows the crystals formed in the Ni–P glass partially crystallized. Randomly distributed barrel-shaped crystals were formed in the sample. The internal structure and corresponding selected area electron diffraction (SAED) pattern of the crystal were shown in figs. 3b and 3c, respectively. The crystalline phases seem to be finely spaced.

Fig. 1. Schematic diagram to show the internal structure of the crystal formed during eutectic crystallization of amorphous alloys. The rods are TM austenite; the matrix is the TM$_3$M compound (from ref. [7]).
plates and/or rods parallel to the crystal growth direction. The SAED pattern seems apparently a regular single phase diffraction pattern except some extraordinary strong diffraction spots in the pattern.

From the X-ray diffraction result we know that the crystallization products contain two phases of bct Ni₃P and fcc Ni austenite. As the values of the diffraction plane spacings of these two phases are very close, the diffraction spots of fcc Ni and bct Ni₃P may be overlapping in the electron diffraction pattern, which have a poorer resolution than the X-ray diffraction pattern. So the SAED pattern in fig. 3c can be indexed by using bct Ni₃P and fcc Ni. Fig. 4a shows our indexing of the pattern which contains a [110] austenite section and a [111] tetragonal section. The orientation relationship between the two phases obtained from this pattern is:

\[
\langle 111 \rangle \text{ bct} \parallel \langle 110 \rangle \text{ fcc}
\]

Coincidentally, the SAED pattern in fig. 3c is just the same as that of Watanabe and Scott obtained in Fe–Ni–P–B glass (fig. 11b in ref. [5]). The lattice parameters of (Fe, Ni)₅(P, B) are slightly different from those of Ni₃P, and the lattice parameters of (Fe, Ni) austenite from those of Ni austenite (see table 1). Watanabe and Scott [5] indexed the pattern (as shown in fig. 4b, called WS indexing) and concluded that there were two orientations of the austenite phase, i.e. a [110] and a [111] section together with a [110] tetragonal section. The orientation relationship they deduced was \( \langle 110 \rangle \text{ bct} \parallel \langle 110 \rangle \text{ fcc} \), which is different from ours in orientation of the bct phase.

Detailed analysis of WS indexing revealed that they have made a mistake in indexing the orientation of bct phase. It can be easily found that the WS indexing could not produce the diffraction spots at the middle points between [112] bct spots and the origin (but they do exist, as indicated in fig. 4b), while our indexing can.

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Table 1

Values of lattice parameters for TMₓM compounds and TM austenite phases formed in crystallization of amorphous alloys

<table>
<thead>
<tr>
<th>Alloys (at%)</th>
<th>TMₓM type</th>
<th>TM austenite type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₉₀P₂₀</td>
<td>Ni₁₃P/bct</td>
<td>Ni austenite/fcc</td>
</tr>
<tr>
<td></td>
<td>( a = 0.895 \text{ nm} )</td>
<td>( a = 0.3524 \text{ nm} )</td>
</tr>
<tr>
<td></td>
<td>( c = 0.439 \text{ nm} )</td>
<td></td>
</tr>
<tr>
<td>Fe₈₀Ni₂₀P₄₄B₂</td>
<td>(Fe, Ni)₃(P, B)/bct</td>
<td>(Fe, Ni) austenite/fcc</td>
</tr>
<tr>
<td></td>
<td>( a = 0.885 \text{ nm} )</td>
<td>( a = 0.3570 \text{ nm}^{(a)} )</td>
</tr>
<tr>
<td></td>
<td>( c = 0.440 \text{ nm}^{(b)} )</td>
<td></td>
</tr>
</tbody>
</table>

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(a) Data from X-ray diffraction experiment in ref. [5].
(b) \( \pm 0.005 \text{ nm} \) for values of \( a \) and \( c \).
(c) \( \pm 0.002 \text{ nm} \) for value of \( a \).
3.2. Crystal growth process

Fig. 5 shows a HREM image of the internal crystal structure along the [001] zone of the Ni$_3$P phase. As indicated in the figure, the Ni$_3$P phase with tetragonal lattices and the fcc Ni phase are segregated from each other, and both are discontinuous rather than continuous as described in ref. [7] (see fig. 1). The Ni austenite phase is in the

Fig. 4. (a) Indexing of the SAED pattern in fig. 3c; (b) Watanabe and Scott's indexing of the pattern, which is an exact copy from fig. 11 in ref. [5]. The twinned reciprocal lattices are shown in dashed lines in both figures.

Fig. 3. TEM bright field image of the partially crystallized amorphous Ni–P alloy (a); internal structure of the crystal (b); corresponding SAED pattern (c).
form of discontinuous elongated particles about 5 nm wide and 5–20 nm long in the crystal growth direction. The length/width ratios of the particles range from 1:1 to 4:1. The Ni₃P hct phase is in the form of blocks separated by Ni particles and Ni-rich regions (for details, see ref. [13]). From the HREM image it is clear that the orientations of the Ni₃P blocks differ slightly from each other.

Such a morphology of crystallization products is quite far from what the classical atomic diffusion mechanism can explain. During the eutectic crystallization of a melt, according to the atomic diffusion mechanism, atoms move by long-range diffusion at the amorphous/crystalline interfaces or in the amorphous matrix ahead of the crystal, redistributing the solutes to form the two crystalline phases. The crystal tends to form a lamella structure consisting of two competitively growing, continuous, fine-spaced phases, as illustrated in fig. 6a. The interphase spacing is closely related to the undercooling, which affects the atomic diffusion rates. For eutectic crystallization in an amorphous alloy, things are different. Atomic diffusion is rather difficult during crystallization of amorphous alloys due to the large undercoolings. The experimentally measured atomic diffusion coefficients are 2–4 orders of magnitude smaller than the calculated values from the classical mechanism [14,15].

In the Part I of this work, a new crystallization micromechanism was developed based on the experimental results of 2D crystallization in the Ni–P glass. It is supposed that the crystallization contains two processes: (i) formation and growth of the precursory ordered clusters, and (ii) crystal nucleation and growth which involve atoms jumping and precursory clusters shearing deposition. According to the new mechanism, when a crystal grows in a totally disordered region, atoms in the disordered state jump to the crystal front; when the crystal front touches a precursory ordered cluster, the cluster would prefer to shear and deposit onto the crystal front [16].

On annealing the Ni–P glassy sample, formation and growth of the precursory ordered clusters must have taken place due to thermal activation. Two kinds of coordination clusters of Ni–Ni and Ni P types would be formed in the amorphous matrix. When a crystal is growing, the crystal front is composed of two separated crystalline phases: hct Ni₃P and fcc Ni austenite. From a structure point of view, Ni–P coordination clusters have the same structure unit as that of the Ni₃P phase and Ni–Ni clusters as that of the Ni austenite [13]. If the crystal front of Ni phase touches a Ni–Ni cluster, the cluster will be sheared and deposited onto the crystal front which passes the cluster and continues growing; if the Ni crystal front touches a Ni–P cluster, the Ni front stops growing and a new crystal of Ni₃P phase begins. For a Ni₃P crystal front, if a Ni–P cluster is touched, it will deposit to the crystal front which goes on growing; if a Ni–Ni cluster is touched, the crystal front of Ni₃P will stop and a Ni phase starts. Combination of the atom jumping process and the Ni–Ni and Ni–P cluster shearing deposition process would result in discontinuously growing crystallization products of Ni and Ni₃P phases. Fig. 6b schematically shows the crystal growth process in the new mechanism.

Growing crystals accompanied by ordered clusters in and in front of the growing crystals were clearly identified in a partially crystallized bulk Ni–P glass annealed for 180 min at 565 K, as
shown in fig. 7. As schematically shown in fig. 7b, an amorphous region was left between two crystals. From the dark field images (figs. 7d–7f), it is evident that ordered clusters or even microcrystalline particles (bright spots) can be found in the crystals as well as in the amorphous region. The distribution of the clusters with certain orientations in the amorphous region is random, while that in the crystals is specific. It can be reasonably considered that the clusters in the crystals might come directly from the shearing deposition of the clusters in the amorphous matrix. This experimental evidence strongly supports the validity of the new mechanism for the bulk crystallization process in amorphous alloys.

The interphase spacings, which are actually the widths of the Ni and Ni₃P phases, should be closely related to the quantity and sizes of the ordered clusters in the amorphous matrix. Detailed measurement of the interphase spacings and investigation on the relationship among the spacing, clusters, and anneal temperature are in progress.

Fig. 7. Amorphous region left between two crystals during bulk crystallization of the Ni–P glass annealed at 565 K for 180 min; (b) is a schematic diagram, (c) a bright field image and (d)–(f) are dark field images corresponding to different diffraction spots indicated in the SAED pattern (a).

Fig. 8. TEM bright field image of the small crystals initially formed in the Ni–P glass annealed at 570 K.
### 3.3. Formation of crystals

Fig. 8 shows two typical small crystals initially formed in the crystallization process of the Ni–P glass, which are about 40 and 70 nm across. It can be seen that the irregularly shaped crystals are apparently composed of even smaller crystalline particles, 5–10 nm in diameter. The different contrast of these particles indicated their different diffraction orientations or different crystalline phases.

Crystals larger than 200 nm across were found to become regular elliptical or spherical crystals, as shown in fig. 9a. One of its corresponding electron microdiffraction patterns is shown in fig. 9b. The crystal was also found to consist of fine crystalline particles. The amorphous/crystalline interface was indistinct and it seems that the crystal front extends to a distance of about 10 nm into the amorphous matrix, which is similar to the results reported in the literature [17].

The X-ray diffraction spectrum of the amorphous Ni–P sample with a very small amount of crystallization showed that two crystalline phases were formed: the Ni$_3$P phase and Ni austenite. From the microdiffraction pattern in fig. 9b, which is the same as the SAED pattern in fig. 3c, it can be deduced that the small crystals initially formed during crystallization also contain two crystalline phases of bet Ni$_3$P and fcc Ni austenite, and that their orientation relationship is the same as that in the large crystals.

Formation of the small crystals cannot be fully understood by means of the classical atomic diffusion. An attempt was made to give an interpretation of the crystal formation process by using the new crystallization mechanism.

As mentioned in section 3.2, there are two kinds of ordered clusters existing in the amorphous Ni–P alloy: Ni–P and Ni–Ni coordination clusters. On annealing, some of these clusters would be able to grow in the form of active atoms (in disordered state) adhering to the cluster surface. With the clusters growing, atoms in the neighboring disordered regions become fewer and fewer until all the disordered atoms are exhausted when the growing clusters touch. Hence, in a region where the ordered clusters are densely distributed in the as-quenched state, combination of the growing clusters would be preferred to occur to form a crystal. Because of the random distribution of ordered clusters, the shapes of the early formed crystals might be irregular, as schematically illustrated in figs. 10a and 10b. The crystal combined of several grown clusters would grow by getting more atoms as well as clusters to it. To minimize the free energy of the system, the crystal grows to a shape with minimum surface/volume ratio, a spherical or elliptical crystal, as in fig. 10c. The surface of the crystal is not smooth because of

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![Fig. 9](image_url)

**Fig. 9.** (a) TEM bright field image of a crystal (a) and its corresponding microdiffraction pattern (b).
the clusters adhering to the surface. The crystal front came into the amorphous matrix about 10 nm deep (as in fig. 9a), which is in the neighborhood of the cluster sizes. With the crystal growing, more and more disordered regions would be exhausted and then more latent heat would be released radially through the crystalline/amorphous interfaces. The disordered atoms and the clusters in front of the crystal would transfer themselves to energetic favorite positions in the growing crystal front, which would result in formation of large barrel-shaped crystals.

4. Concluding remarks

Structural investigation of the bulk crystallization products in the amorphous Ni–P alloy shows that the eutectic crystallization process in amorphous alloys is quite different from that in melts. The morphological and structural character of the crystallization products as well as the crystal formation and growth process, which are difficult to be understood by means of the classical atomic diffusion mechanism, can be reasonably interpreted by using the newly developed crystallization mechanism. Dark field TEM images of a partially crystallized Ni–P glass sample provided evidence supporting the new mechanism. Nevertheless, much more work should be done before establishment of a solid crystallization mechanism in amorphous alloys.

References