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Formation of Orientated Nano-sized Crystals in an Amorphous Alloy under Focused Ion Beam Irradiation

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Temperature dependence on the formation and orientation of nano-sized crystals (NCs) in a Ni-P amorphous alloy, which induced by focused ion beam (FIB) irradiation, has been investigated using transmission electron microscope (TEM). The FIB irradiation temperatures were controlled from 140 to 250 K using a cooling holder of the FIB device. At irradiation temperatures from 170 to 250 K, formation of crystallographically orientated NCs was confirmed. While the particle number density of the formed NCs decreased with decreasing of irradiation temperature, structure, orientation and the grain size of the formed NCs were uchanged. On the contrary, no crystallization was confirmed throughout the irradiated area at an irradiation temperature of 140 K. Thermally crystallized phases obtained following the FIB irradiation at 140 K did not have specific orientation relationship with the FIB direction. The effect of FIB on the oriented formation of the NCs has been discussed.
Key words: Nanocrystals, Orientation control, Focused ion beam, Transmission electron microscopy

1. INTRODUCTION

Recently, nano-sized crystals (NCs) or nanocrystalline materials have been intensively investigated in many industrial fields because of their applications for the structural materials or magnetic recording devices. Up until now, numerous methods on the formation of NCs have been proposed such as recrystallization following the severe plastic deformation including equal channeling angular pressing method [1,2], deposition on a single crystal substrate [3-5], ion beam implantation for precipitation of secondary phase [6,7], chemical reaction in a colloid state [8,9] and crystallization from amorphous states [10]. Using these methods, however, it is difficult to control the crystallographic orientation of NCs with controlling their grain size within a diameter of 10 nm.

High energy particle beam irradiation, such as an ion or electron, is one of the suitable methods to control the structure of materials in the order of several nanometers. Up until now, many studies on the structural changes of crystalline materials under high energy ion/electron beam irradiation has been reported [11]. According to these studies, formation of point defect clusters, formation of dislocation loops and stacking fault tetrahedra, precipitation of secondary phase and phase transformations are reported. The most of ion/electron beam irradiation studies are performed for crystalline materials while little for amorphous alloys. It is well known that amorphous alloys are in a thermally meta-stable and non-equilibrium state so that phase transformation from amorphous into crystalline structure is considered to occur as a result of high energy ion/electron beam irradiation. The details structural changes of amorphous alloys as a result of ion/electron beam irradiation are, however, still uncertain yet.

In our previous study, we have found the formation of NCs, with their grain size of less than 10 nm in diameter, in a Ni-P amorphous alloy as a result of focused ion beam (FIB) irradiation [12]. Furthermore, the formed NCs had specific crystallographical and geometrical orientation relationships with the incident FIB direction [12]. This result suggests that the FIB irradiation for amorphous alloys has a possibility to be a new method to form and control the orientation of NCs in amorphous alloys. Mechanism of the oriented formation of NCs is, however, still uncertain yet.

Our interest here is the reason why the formed NCs have specific crystallographical and geometrical orientation relationships with the FIB direction. It has been reported that phase transformation from crystal into amorphous structure is strongly affected by the irradiation temperature [11]. Generally, thermal diffusion assists the nucleation and growth of crystals in amorphous alloys [10]. It is, therefore, considered that irradiation temperature is one of important factors on the oriented formation of the NCs. If thermal diffusion assists the nucleation and growth of NCs induced by the FIB irradiation, crystallographic features (structure, orientation, grain size and particle number density) of the formed NCs is considered to be affected from the irradiation temperature. To understand the mechanism on the oriented formation of NCs under the FIB irradiation, it is important to clarify the effect of irradiation temperature on the crystallographic features of the formed NCs. In this study, the effect of irradiation temperature on the crystallographic features of NCs has been investigated using low temperature FIB irradiation by means of transmission electron microscopy (TEM) observations.

2. EXPERIMENTAL PROCEDURE

The material used in this study was a Ni-11.5wt%P

amorphous alloy thin film. The amorphous alloy was prepared by electro-less deposition on an Al-Mg alloy substrate. Thickness of the amorphous layer is approximately 12 μm. The amorphous layer was separated from the Al-Mg alloy substrate using NaOH aqueous solution. The amorphous alloy was mechanically cut into semi-circular disks with their diameter of 3 mm. It was then, FIB micro-fabrications were carried out. Details of specimen preparation procedures are shown in our previous report [13]. Figure 1 shows a schematic drawing of the FIB micro-fabrication procedure. As shown in the figure, specimens were thinned by the FIB micro-fabrication to remain the center area to be their thickness of less than 100 nm. Because of the FIB micro-fabrication, irradiation damages are considered to be introduced in the hatched area. In this study, we term this area as an irradiated plane. To identify the geometrical relation between the specimen and the FIB direction, a x_1-x_2-x_3 Cartesian coordinate system was employed as shown in Fig. 1. The irradiated plane normal and the FIB direction were parallel to the x_3 and x_2 axes, respectively. After the FIB micro-fabrications, TEM observations for the irradiated planes were carried out. Note that the estimated dimensions of irradiated planes were 8 μm and 100 μm for the x_1 and x_2 direction, respectively.

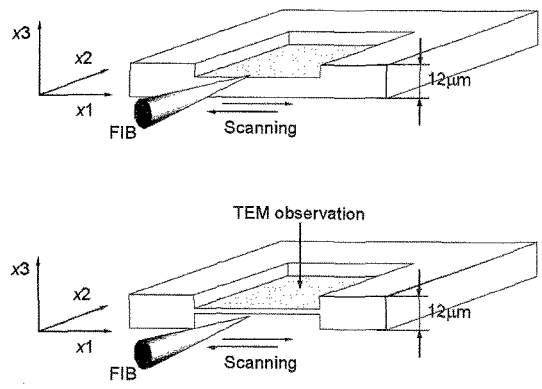

Figure 1. Schematic drawings for the FIB micro-fabrication procedure.

The FIB device used in this study was a HITACHI FB2000-A with a liquid metal ion source of Ga. The acceleration voltage was set to be 30 keV. The beam current was decreased from 3.53 to 0.08 nA with decreasing of thickness. The estimated dose rate at the final FIB micro-fabrication was approximately 6.2×10^{13} ions/cm^{2}s. The FIB device equipped a cooling stage which connected with a liquid N_2 cylinder. Using the cooling holder, temperature of a specimen can be controlled from room temperature to 140 K with an accuracy of 1 K. In this study, we set irradiation temperatures for 250, 170 and 140 K. The results obtained in this study were compared with our previous results obtained at an irradiation temperature of room temperature [12]. The TEM apparatus used in this study was a Philips CM200 equipped with a slow scan CCD camera.

3. EXPERIMENTAL RESULTS

3.1. FIB irradiation at 250 K

Figure 2 (a) shows a selected area electron diffraction (SAED) pattern obtained from an irradiated area which irradiated at a temperature of 250 K. In the SAED patterns, clear six reflections were observed in addition to halo rings from the amorphous matrix. This result indicates the existence of crystallographically orientated crystals in the amorphous matrix. A dark field electron micrograph taken using a reflection in Fig. 2 (a) is shown in Fig. 2 (b). In this micrograph, formation of NCs was clearly observed in the amorphous matrix. As shown in the micrograph, NCs were formed not uniformly but discretely. This feature was not confirmed at a temperature of room temperature. The average width of every bands consisted of the NCs was approximately 300 nm. This band was elongated to the x_2 direction. On the other hand, the size of crystals was approximately less than 10 nm in diameter. This size corresponds to the result obtained after the FIB irradiation at a room temperature [12].

From analysis of the SAED pattern (Fig. 2 (a)), it was revealed that the observed diffraction pattern corresponds to a <111> incident electron diffraction pattern from a f.c.c. structure of Ni. Furthermore, the x_2 axis direction was approximately parallel to a <110> within an accuracy of 2 degs. Thus, orientation of the formed NCs refer to the x_1-x_2-x_3 Cartesian coordinate system (defined in Fig. 1) can be expressed as follows.

$$x_3 \ plane \ // \ \{111\}_{f.c.c.} \qquad (1)$$
$$x_2 \ direction \ // \ <110>_{f.c.c.}$$

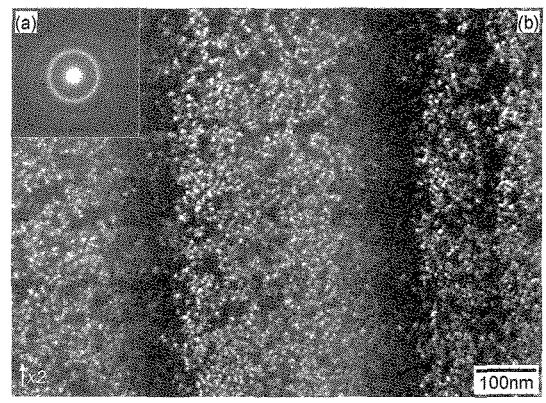

Figure 2. (a) a SAED pattern and (b) a dark field electron micrograph obtained after the FIB irradiation at a temperature of 250 K.

This crystallographical and geometrical orientation relationship between the formed NCs and the FIB direction correspond to our previous results which irradiated at room temperature [12].

3.2. FIB irradiation at 170 K

Figure 3 (a) and (b) show a SAED pattern and a dark field electron micrograph obtained after the FIB irradiation at a temperature of 200 K. As same as the previous SAED pattern (Fig. 2 (a)), clear six reflections correspond to a <111> incident electron diffraction

pattern of f.c.c.-Ni were observed in addition to halo rings from the amorphous matrix. Furthermore, a <110> direction was approximately parallel to the x_2 direction. These crystallographic features correspond to the previous results. In the dark field electron micrograph (Fig. 3 (b)), formation of NCs was confirmed. As shown in the dark field micrograph, the size of the formed NCs was approximately the same but the particle number density was clearly decreased. Since crystallization occurred discretely, it is difficult to quantitatively identify the volume fraction of the formed NCs in the amorphous matrix.

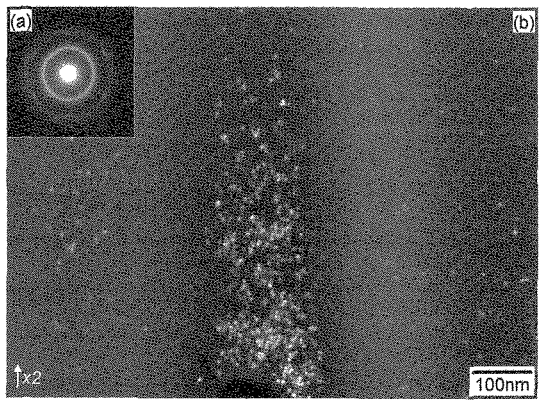

Figure 3. A SAED pattern and a dark field electron micrograph obtained after the FIB irradiation at a temperature of 170 K.

3.3. *In-situ* observation for crystallization

At an irradiation temperature of 140 K, crystallization was not confirmed throughout the irradiated planes. Even though crystallization was not occurred, we cannot neglect the irradiation damages. If irradiation damages are introduced as a result of the FIB irradiation at 140 K and if these irradiation damages affect as the nucleation site of the NCs, crystallographically orientated NCs which satisfy the relation of Eq. 1 are considered to be formed after the crystallization by thermal diffusion. This is important information to understand the mechanism on the oriented formation of NCs. To clarify the irradiation damage on the orientation of the formed NCs, *in-situ* observation of crystallization was carried out for the specimen in TEM.

The irradiated specimen was heat treated in the TEM at a temperature of 600 K and maintained to complete the crystallization. Figures 4 show (a) a SAED pattern and (b) a high resolution transmission electron micrograph (HRTEM) obtained after the crystallized area. Where, the incident electron beam direction was approximately parallel to the x_3 axis direction within an accuracy of 1 deg. From analysis of the SAED pattern, structure of the formed crystalline phase were determined to be b.c.t. of Ni_3P which is one of a thermally equilibrium phase. In the HRTEM, precipitation of NCs with their size of less than 10 nm in diameter was observed. According to the phase diagram, these fine particles are considered to be f.c.c. of Ni. Figures 4 (c) and (d) show a diffractgram and an enlargement of HRTEM enclosed by white lines in Fig. 4 (b). From analysis of the diffractgram and lattice image, it was revealed that the incident electron beam direction was $[011]_{b.c.t.}$ as shown in Fig. 4 (c). If the formed fine particles are f.c.c. of Ni, and if they satisfy the orientation relationships of Eq. (1), the $<111>_{f.c.c.}$ electron diffraction pattern should be appeared in the SAED pattern. In the SAED pattern, however, no such reflections were confirmed. We have also investigated the orientation of other crystals. However, no reflections correspond to a <111> incident diffraction pattern of f.c.c. crystal was confirmed.

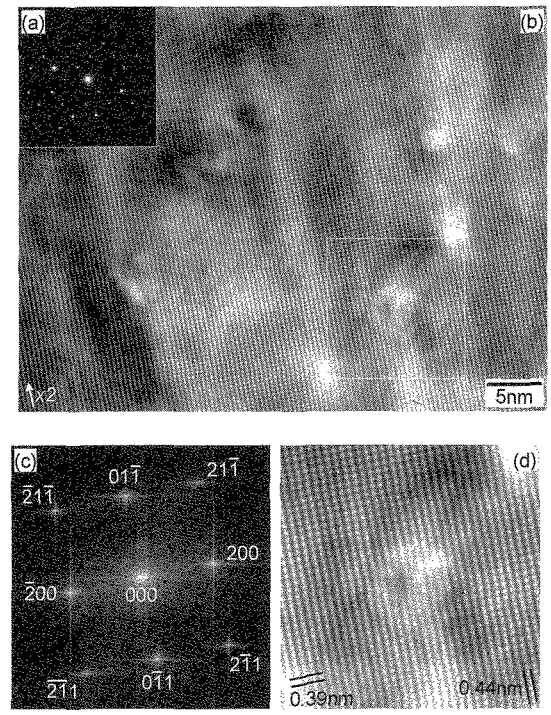

Figure 4. (a) a SAED pattern and (b) a HRTEM obtained after the complete crystallization. (c) and (d) show a diffractogram and an enlarged HRTEM obtained from the enclosed area by dotted lines in (b).

4. DISCUSSION

According to a previous work by Sui *et al.* [14] for a Ni-P amorphous alloy, thermally equilibrium phases of Ni (f.c.c.) and Ni_3P (b.c.t.) have following crystallographic orientation relationships.

$$\begin{aligned} &[001]_{b.c.t.} \,//\, [110]_{f.c.c.} \\ &(\bar{1}10)_{b.c.t.} \,//\, (\bar{1}\bar{1}\bar{1})_{f.c.c.} \\ &(150)_{b.c.t.} \,//\, (002)_{f.c.c.} \end{aligned} \tag{2}$$

Using these orientation relationships, the transformation matrix of Miller indices from b.c.t. crystal into f.c.c. crystal can be obtained as follows [14].

$$ {}_{b.c.t.}\boldsymbol{M}_{f.c.c.} = \begin{pmatrix} -5/18 & 1/18 & 4/7 \\ 5/18 & -1/18 & 4/7 \\ 1/18 & 7/18 & 0 \end{pmatrix} \tag{3}$$

As shown in Figs. 4, the zone axis of the formed crystal was exactly $[011]_{b.c.t.}$ Using the transformation matrix of ${}_{b.c.t.}\boldsymbol{M}_{f.c.c.}$, orientation of the f.c.c. crystal which

satisfies the ORs of Eq. (1) can be obtained as follows.

$$ {}_{b.c.t.}\boldsymbol{M}^{-1}_{f.c.c.}\,[011]^{T}_{b.c.t.} = [2.25, 2.25, 0.875]_{f.c.c.} \tag{4} $$

where T represents the transverse of matrix. As shown in the Eq. (4), the x_3 direction of the f.c.c. crystal, which satisfy the Eq. (1), becomes $[2.25, 2.25, 0.875]_{f.c.c.}$ The $[2.25, 2.25, 0.875]_{f.c.c.}$ direction is approximately 19.89 degs. away from the $[111]_{f.c.c.}$ It is, therefore, considered that the observed NCs in the HRTEM do not satisfy the orientation relationships of Eq. (1). These results suggest that irradiation damage introduced at 140 K does not affect as a nucleation site on the formation of crystallographically orientated NCs which satisfies the relation of Eq. (1). It is, therefore, considered that orientation of the formed NCs depend not on irradiation damage or initial structure of the material but on the dynamic crystallization process due to incident FIB.

4. CONCLUSIONS

Temperature dependence on the crystallographic features (structure, orientation, size and particle number density) of NCs induced by FIB irradiation has been investigated from TEM observations. The orientated formation of NCs has been confirmed at an irradiation temperature range from 170 to 250 K. The grain size of the formed NCs kept approximately constant while their density decreased with decreasing of irradiation temperature. At an irradiation temperature of 140 K, no crystallization was confirmed.

From the *in-situ* observation of crystallization after the irradiation at 140 K, formation of Ni_3P with a fine particle was confirmed. Based on the analysis of orientation relationship between the Ni and Ni_3P, it was revealed that the formed fine particle does not satisfy the relation of Eq. (1) if they have a f.c.c. structure. It is, therefore, considered that the FIB irradiation damage introduced at 140 K does not affect on the orientation of the NCs.

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