Transactions of the Materials Research Society of Japan 28 [3] 747-750 (2003)

Orientation Control of Nanocrystals in an Amorphous Alloy by Ion Beam Irradiation

Takuya Kamikawa, Ryuichi Tarumi, Kazuki Takashima* and Yakichi Higo*
Graduate student, Tokyo Institute of Technology 4259 Nagatsuta-Cho, Midori-Ku, Yokohama 226-8503, Japan
e-mail: tkamikawa@ames.pi.titech.ac.jp, rtarumi@ames.pi.titech.ac.jp
*P&I Lab., Tokyo Institute of Technology
e-mail: takashik@pi.titech.ac.jp, yhigo@pi.titech.ac.jp

We have investigated the structural change of Ni-P amorphous alloy under the conventional ion beam irradiation with an ion source of Ar. Transmission electron microscopic observation for the irradiated area revealed the formation of nano-sized crystals (NCs) with a grain size of less than 10 nm in the amorphous matrix. The crystalline structure of NCs was determined to be a fcc by electron diffraction analysis. Furthermore, the formed NCs had a specific relationship with the ion beam direction, these are, a <110> and a {111} of NCs were parallel to the projected ion beam direction and the irradiated surface, respectively. These crystallographic features are exactly consistent with the results obtained by the focused ion beam irradiation for the amorphous alloy.
Key words: nanocrystal, Ni-P amorphous alloy, ion beam irradiation, crystalline orientation

1. INTRODUCTION

In the last decade, nano-sized crystals (NCs) have been intensively investigated. Many studies have been achieved to form NCs because NCs have a potential to improve mechanical, magnetic and catalytic properties of materials [1-3]. Up to now, several methods, deposition on substrates, recrystallization following severe plastic deformation, precipitation of a secondary phase, and crystallization from an amorphous state, have been proposed. Using such methods, however, it is difficult to obtain NCs with grain size less than 10 nm in diameter. Furthermore, it is difficult to control crystallographic orientation of NCs except for an epitaxial growth on a single crystal substrate [4].

Ion beam irradiation enables one to modify mechanical and electrical properties of materials by controlling their nano-sized structures. Several researchers have reported phase transformation from crystal into amorphous structure under ion beam irradiation [5]. Amorphous alloys are in a thermally metastable state so that crystallization may occur under suitable irradiation condition. In our previous study [6], we have succeeded to form crystallographically orientated NCs of nickel in a Ni-P amorphous alloy by means of focused ion beam (FIB) irradiation with an ion source of Ga. The formed NCs had a face centered cubic (fcc) structure with an average particle size of less than 10 nm. Furthermore, the irradiated plane normal and FIB direction were parallel to a <111> and a <110> of the formed NCs, respectively.

FIB device is generally used as microfabrication of materials, where the beam current and irradiation area are in the order of nA and μm^2, respectively. Thus, it is considered that it takes much time to irradiate an area in the order of mm^2 because the beam current of FIB is at most μA. On the contrary, the beam current of conventional ion beam irradiation is quite larger than that of FIB. Thus, conventional ion beam irradiation enables one to obtain NCs in the mm area within reasonable time. There are, however, several differences between the FIB irradiation and conventional ion beam irradiation including beam current, acceleration voltage, type of ion source and in terms of focusing ion beam. Because of these differences, it is uncertain whether formation of crystallographically orientated NCs occurs as a result of conventional ion beam irradiation for the Ni-P amorphous alloy. In this paper, we have investigated the structural change of a Ni-P amorphous alloy under conventional ion beam irradiation.

2. EXPERIMENTAL

In this study, a Ni-11.5 wt% P amorphous alloy prepared by electroless deposition on an Al-Mg alloy substrate was employed. The thickness of the amorphous alloy was 12 μm. The amorphous layer was separated from the Al-Mg alloy substrate by using a NaOH aqueous solution. The amorphous layer was mechanically cut into a circular disk with a diameter of 3 mm. For ion beam irradiation, we employed ion milling device TECHNOORG-LINDA. It plays a role in not only irradiation but also sputtering effect at the same time. Thus, thick specimens require much irradiation time to become thin enough for TEM observation. To shorten the irradiation time, we performed electro polishing in a HCl_4-CH_3COOH (9:1) mixed solution at 273 K to thin the specimens less than 1 μm. The disks were mechanically cut into semicircular disks. Then, ion beam irradiation was carried out. The ion milling was operated at 3 keV with an

ion source of Ar. The beam current was set to be a constant value of 2 mA. Irradiation time was controlled from 10 to 180 minutes. Since the beam current is relatively large compared with our previous FIB irradiation study, the temperature is considered to rise during the irradiation process. To eliminate the effect of the temperature, specimens were mounted on a cooling stage of the ion milling device. The stage was connected with a liquid N_2 cylinder to suppress the crystallization due to increase in temperature during irradiation. TEM observations were performed using a Philips CM200 operated at 200 keV. For selected area electron diffraction (SAED) analysis, an objective aperture with a diameter of 0.2 μm was used.

The geometrical relation between the ion beam and the specimen is schematically illustrated in Fig. 1. A (x-y-z) Cartesian coordinate system fixed to the specimens was employed. In this coordinate system, the y-axis and the z-axis were set parallel to the projected ion beam direction on a surface of the specimen and surface normal of the specimen, respectively. The incidence angle θ is defined as the angle between the ion beam and the tangent to the specimen surface, i.e. reducing θ means moving to grazing incidences. θ was set to less than 15 degrees.

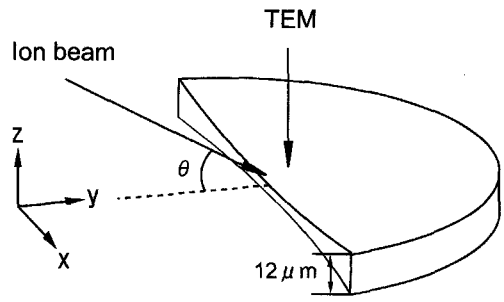

Figure 1 Schematic drawing of ion beam fabrication procedure. Y-axis and z-axis were set parallel to projected ion beam direction and surface normal of the specimen, respectively.

3. RESULTS AND DISCUSSION

Figure 2 (a) shows a selected area electron diffraction (SAED) pattern of the specimen irradiated for 150 minutes. Where, incident electron beam direction was set parallel to the z-axis. In the SAED pattern, six clear reflections were observed in addition to halo rings from the amorphous matrix. These reflections indicate the existence of crystallographically orientated crystals in the amorphous matrix. Figure 2 (b) shows a schematic drawing of the electron diffraction pattern. As shown in the figure, the obtained diffraction pattern corresponds to that of a <111> incident electron diffraction pattern of fcc crystal. Figure 2 (c) shows a dark field electron micrograph taken using a reflection in the SAED pattern. As shown in the micrograph, uniform distribution of large amount of NCs was confirmed throughout the irradiated plane and the size of NCs was less than 10 nm in diameter. Assuming that the formed NCs have a fcc structure and a <111> of NCs is parallel to the surface normal of the specimen, the projected ion beam direction becomes parallel to a fcc <110> within an accuracy of a few degrees. Based on those assumptions, a series of electron diffraction analyses was performed. As the results of the analyses, crystalline structure and orientation of the formed NCs were exactly consistent with above mentioned assumptions. Thus, it was confirmed that crystallographic orientation of the NCs corresponded to the ion beam direction. These are, irradiated plane // {111} and projected ion beam direction // <110>. These results were exactly consistent with those of our previous FIB study [6].

From the consistency of the results obtained from the ion beam and the FIB studies, it was revealed that the formation of orientated NCs occurred even though there are several differences in irradiation conditions such as beam current, acceleration voltage, type of ion source and in terms of focusing ion beam.

It is necessary to consider the reasons of the formation of orientated NCs under ion beam irradiation. An increase in temperature is considered to occur at local areas in specimens during ion beam irradiation [7]. At a chemical composition of the amorphous alloy, there are two thermodynamically equilibrium phases of Ni (fcc) and Ni_3P (bct) at a room temperature [8]. It should be noted here that precipitation of thermally stable phases was observed when the irradiation was performed without the cooling N_2. In this case, increase in temperature during irradiation may be too high to suppress the crystallization of stable phases. Where, the formed crystalline phases did not have specific orientations for the ion beam direction. Thus, crystallographic features of the NCs induced by ion beam irradiation are quite different from those of thermal diffusion and the formation of orientated NCs can not be explained only by an increase in temperature during irradiation.

None of crystallization was observed in specimens irradiated less than 20 minutes. One of the reasons for the non-formation of NCs is considered that increase in temperature of specimens is not high enough to form the NCs during the irradiation. Even though specimens were mounted on a cooling stage of ion milling device, temperature of the specimens increases with increasing of irradiation time. Thus, it is suggested that increase in temperature

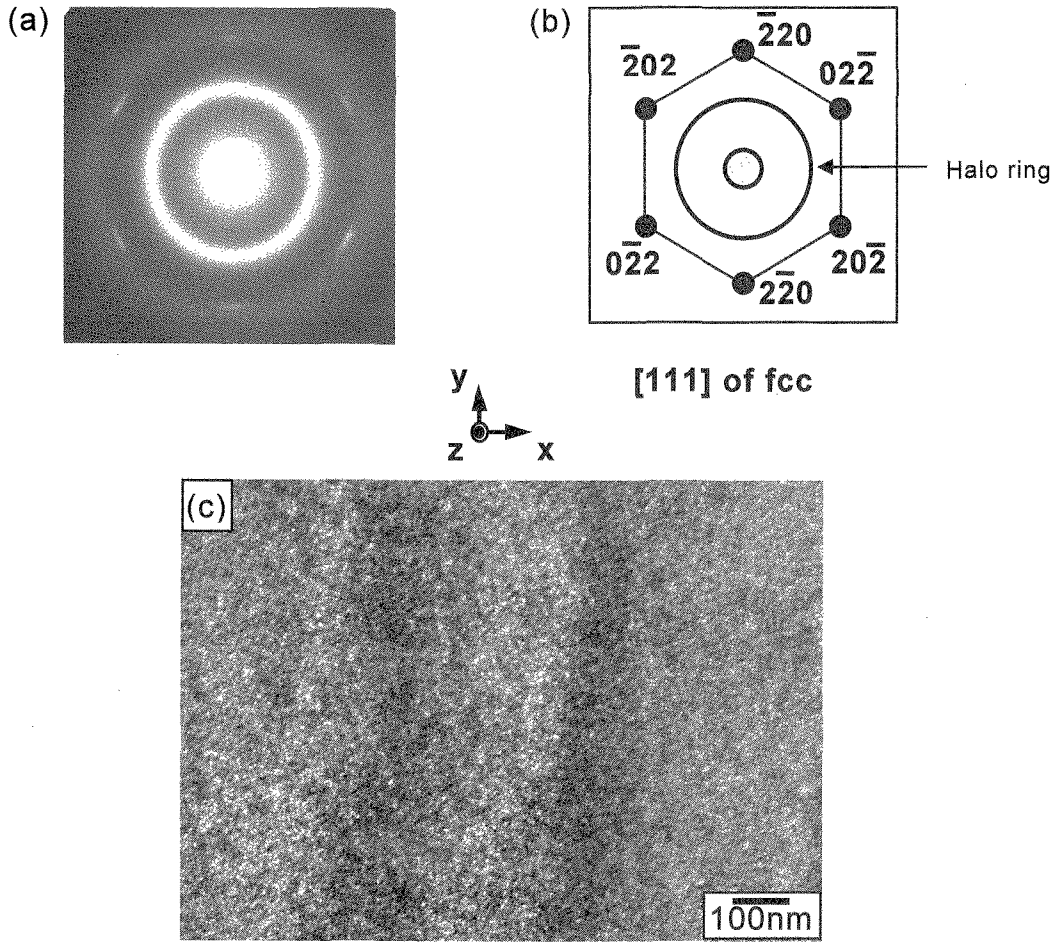

Figure 2 (a) A SAED pattern obtained from irradiated plane, (b) a schematic drawing of electron diffraction, and (c) a dark field electron micrograph taken using a reflection in (a)

contributes to the formation of the orientated NCs. It is reported that the structural change of a Ni-P amorphous alloy, which has the same composition of the present alloy, occurs due to increase in temperature [9]. Such structral change by increase in temperature may assist the formation of the orientated NCs.

It is known that the amorphous alloy has an isotropic structural property. Atoms in the matrix are considered to be displaced preferentially toward the incident ion beam direction due to the knock-on effect. Furthermore, a free surface of the specimen may affect the orientation of NCs because of image force. Although these effects, such as the incident angle and the surface effect may contribute to form the orientated NCs by both FIB irradiation and ion beam irradiation, the details have not been identified yet. Further investigations are required.

4.CONCLUSIONS

In the present study, we have investigated the structural changes of a Ni-P amorphous under ion beam irradiation using TEM. In the irradiated area, uniformly distributed NCs, with average grain size of less than 10 nm, were found in the amorphous matrix. A series of electron diffraction analyses revealed that the precipitated NCs in the irradiated plane were a fcc Ni, and the NCs and ion beam direction have the orientation relationships. These are, irradiated plane // $\{111\}_{fcc}$ and projected ion beam direction // $<110>_{fcc}$.

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(Received March 3, 2003; Accepted April 7, 2003)