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Effects of P Content on Nanocrystalline Morphology Formed by FIB Irradiation in Ni-P Amorphous Alloy

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We studied the effects of phosphorus (P) on the Ni nanocrystalline morphology of Ni-P amorphous alloy thin films subjected to focused ion beam (FIB) irradiation. The P contents in the amorphous alloys varied from 14 to 20 at%. The nanocrystals induced by FIB irradiation of Ni-20.2, 15.6, and 14.0 at%P amorphous alloys had a face-centered-crystal (f.c.c.) structure and showed unique crystallographic orientation relationships to the geometry of the focused ion beam, with $\{111\}_{f.c.c.}$ parallel to the irradiated plane and $\langle 110 \rangle_{f.c.c.}$ parallel to the direction of the projected ion beam, respectively. The Ni nanocrystals formed by FIB irradiation precipitated in the same manner as aggregates, and the average size of the Ni nanocrystals increased as the P content decreased. These results indicate that the P content does not affect the crystallographic orientation relationships but does influence precipitation distribution of the Ni nanocrystals. [doi:10.2320/matertrans.MJ200754]

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1. Introduction

Over the past decade, many reports have been published concerning the fabrication of nano-sized crystals. Nanocrystalline materials are used in many scientific applications because of their excellent functional properties (physical, chemical, and mechanical), which are due to the relatively high densities of their interfaces as compared to those of conventional coarse-grained materials.^{1,2)} Nanocrystalline materials, therefore, are attractive for a variety of technological applications.

The structures of nanometer-size materials can be controlled by irradiating the materials with high-energy particles such as ions, electrons, and neutrons. Recent studies have reported several kinds of structural changes under high-energy particle irradiation: precipitation of implanted ions,³⁾ formation of dislocation loops,⁴⁾ and phase transformation from a crystalline structure to an amorphous structure⁵⁾ and *vice versa*.⁶⁾ Because amorphous alloys are in a state of thermodynamical non-equilibrium, ion beam irradiation causes a structural phase transformation from amorphous to crystalline. However, the details of this mechanism have yet to be clarified.

In previous reports, we described the formation of crystallographically oriented Ni nanocrystals 5~10 nm in size using focused ion beam (FIB) irradiation of a Ni-19.7 at%P amorphous alloy annealed at 473 K for 30 minutes prior to irradiation.^{7,8)} The Ni nanocrystals had orientation relationships to the geometry of the focused ion beam, with $\{111\}_{f.c.c.}$ parallel to the irradiated plane and $\langle 110 \rangle_{f.c.c.}$ parallel to the projected ion beam direction. Ni-19.7 at%P amorphous alloy pre-annealed at 473 K for 250 hours showed a fluctuation in the P concentration in the range of 11~17 at%. After pre-annealing, the Ni nanocrystals generated by the FIB irradiation showed a wide size distribution, indicating that the size of the Ni nanocrystals was influenced by the P content. The objective of this study is to clarify the effects of P content on the size, precipitation distribution, and

orientation relationships of Ni nanocrystals created by FIB irradiation of Ni-P amorphous alloys.

2. Experimental Procedure

2.1 Preparation and structure analysis of Ni-P amorphous alloys

A Cu substrate 0.3 mm in thickness was washed with acetone and rinsed in deionized water. Grease was removed by successively dipping the substrate in a 10 mass% solution of NaOH and a 10 mass% solution of HCl followed by rinsing in deionized water. The substrate was placed in an activator solution consisting of HCl (18%), PdCl₂ (0.04%), and ion-exchanged water (81.96%) at 303 K, then rinsed in deionized water. Ni-P amorphous alloy films were deposited on the Cu substrate by means of electroless plating. The electroless plating bath components and reaction conditions are listed in Table 1. The structures of the Ni-P films were examined by means of X-ray diffractometry using Cu-K_α radiation. X-ray energy dispersive spectroscopy (EDS) was used to analyze the Ni and P elements in the coatings.

2.2 FIB irradiation procedure

The Ni-P amorphous layers were separated from the Cu substrate by mechanical polishing and then mechanically cut into semi-circular disks 3 mm in diameter for TEM observation. Figure 1 is a schematic drawing of the FIB micro-fabrication procedure. As shown in the figure, micro-

Table 1 Bath components and operating conditions for Ni-P electroless plating.

	sample A	sample B	sample C
Nickel sulfate	20 g/L	40 g/L	20 g/L
Sodium hypophosphite	24 g/L	12 g/L	12 g/L
Lactic acid	27 g/L	27 g/L	27 g/L
Propionic acid	2 g/L	2 g/L	2 g/L
pH	5	6	6
P content	20.2%	15.6%	14.0%

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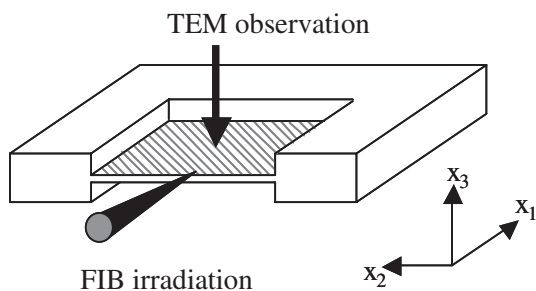


Fig. 1 Schematic drawing of the FIB irradiation process. The hatched region was irradiated until the thickness decreased to less than 100 nm. In the x_1 - x_2 - x_3 Cartesian coordinate system, the x_1 and x_3 axes are projections of the direction of FIB irradiation on the irradiated plane and the irradiated-plane normal, respectively.

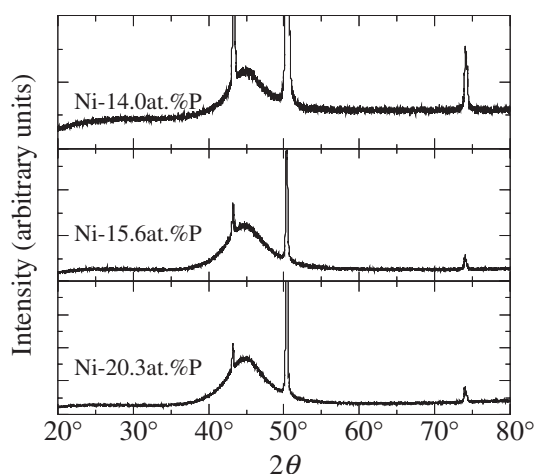


Fig. 2 XRD patterns of Ni-P coatings before FIB irradiation.

fabrications were performed from both sides (top and bottom sides) of each specimen. The FIB apparatus used in this study was a Hitachi FB2100 operated at 40 keV with a liquid-metal ion source of Ga^+ . The beam current was kept constant at 0.08 nA and the estimated dose-rate was 6.2×10^{13} ions/ $\text{cm}^2 \cdot \text{s}$. Structural changes in the irradiated area were investigated by means of TEM (Philips CM-200) at an acceleration voltage of 200 keV.

3. Results and Discussion

3.1 Characterization of Ni-P amorphous alloys

Figure 2 shows the XRD patterns of the Ni-P amorphous alloys produced by electroless plating. The group of sharp peaks in the spectra originates in the Cu substrate. The broad peak at around 45 degrees clearly shows that the Ni-P layers have an amorphous structure. EDS analysis showed P contents of 20.2, 15.6, and 14.0 at%, for samples A, B, and C, respectively.

3.2 Formation of oriented nanocrystals under FIB irradiation

Figure 3 shows selected area electron diffraction (SAED) patterns obtained from the irradiated plane in Fig. 1, and low-magnification dark-field images of the reflections in the SAED patterns for (a) Ni-20.2 at%P, (b) Ni-15.6 at%P and (c)

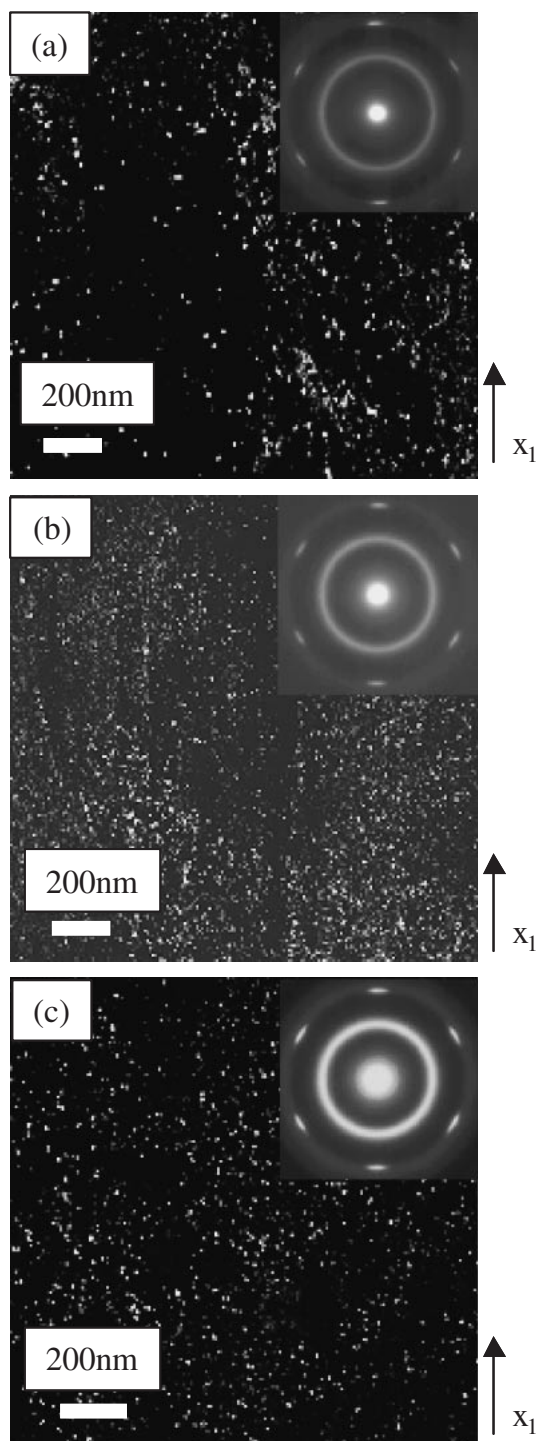


Fig. 3 Low-magnification dark-field micrographs of the irradiated plane and SAED pattern (a) Ni-20.2 at%P (b) Ni-15.6 at%P (c) Ni-14.0 at%P.

Ni-14.0 at%P amorphous alloy thin films. Six clear reflections and a halo ring from the amorphous matrix were observed in these SAED patterns of Ni-P films with different P contents, indicating the existence of crystallographically oriented crystals in the amorphous matrix. The observed SAED patterns correspond to the [111] incident diffraction pattern of $\text{Ni}_{\text{f.c.c.}}$, and the FIB direction (x_1 axis) corresponds to the [110] incident diffraction pattern of $\text{Ni}_{\text{f.c.c.}}$. Thus, the P content does not influence these crystallographic orientation relationships.

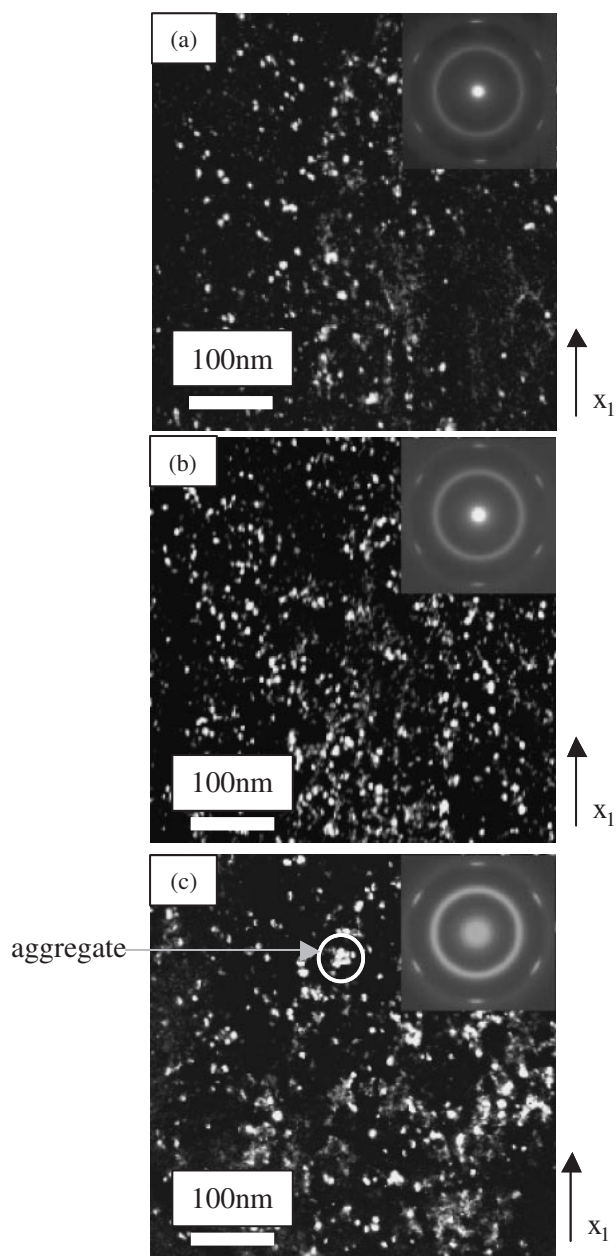


Fig. 4 High-magnification dark-field micrographs of the irradiated plane and SAED pattern (a) Ni-20.2 at%P (b) Ni-15.6 at%P (c) Ni-14.0 at%P.

As shown in the dark-field images, a large amount of uniformly distributed nanocrystals were observed throughout the irradiated plane. It is considered that the nanocrystals are precipitated near the both surfaces of Ni-P thin film. Tarumi reported that the nanocrystals of one side are distributed uniformly in the thickness direction approximately about 17 nm by the result of stereo-analysis.⁹⁾ These unique microstructures have not been identified by conventional heat treatment.¹⁰⁾ Therefore, the formation of oriented nanocrystals cannot be explained as simply an increase in temperature during irradiation. Under ion beam irradiation, the knock-on effect could preferentially displace the P or Ni atoms in the amorphous matrix in the direction of the incident ion beam.¹¹⁾ Here, the surface image force might affect to the preferential displacements of the P or Ni atoms under FIB irradiation.⁷⁾

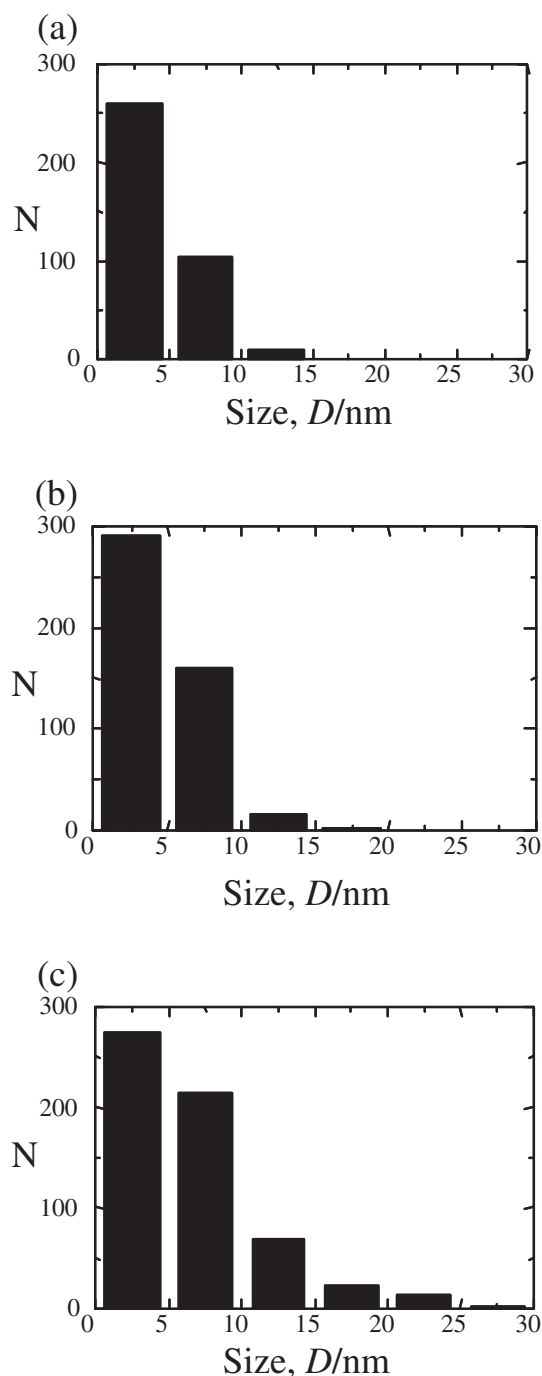


Fig. 5 Size histograms of the results of analyses of the high-magnification dark-field micrographs of the irradiated plane (a) Ni-20.2 at%P (b) Ni-15.6 at%P (c) Ni-14.0 at%P.

Figure 4 shows high-magnification dark-field micrographs of the irradiated area. Fig. 4(c) confirms the aggregation of nanocrystals. If we assume them to be one crystal, the crystal size histograms, obtained from analyses of a large number of pictures including those in Figure 4, are shown in the Fig. 5. As shown in Fig. 5, the grain sizes of the irradiation-induced nanocrystals for the three Ni-P amorphous alloys show wide distributions in the ranges of 1~15 nm, 1~20 nm, and 1~30 nm, respectively. All of the histograms show numerous nanocrystals less than 10 nm in size. These results show that the size distribution widened as the P content decreased. The

number densities of the nanocrystals in Ni-20.2 at%P, Ni-15.6 at%P, and Ni-14.0 at%P were $2156/\mu\text{m}^2$, $2180/\mu\text{m}^2$, $2050/\mu\text{m}^2$, respectively. In this study, aggregation of nanocrystals is treated as one crystal. Thus, the number densities remained almost constant as the P concentration changed. The average grain diameters for the Ni-20.2 at%P, Ni-15.6 at%P, and Ni-14.0 at%P amorphous alloys were 5.2 nm, 5.5 nm, and 8.2 nm, respectively, and the maximum grain diameters were 14 nm, 18 nm, and 28 nm, respectively. The average and maximum sizes of the Ni nanocrystals became larger as the P content decreased. This means that the P content affected the morphology of Ni nanocrystals formed by FIB irradiation of Ni-P amorphous alloys.

We investigated the reason for the changes in the average and maximum sizes of the Ni nanocrystals. Farber *et al.*, reported that when the P content was low, the electroless plating reaction transformed the structure from amorphous to nanocrystalline.¹²⁾ Irradiation-induced nanocrystallization could occur easily in a Ni-P amorphous alloy with a low P content. However, the number density of Ni nanocrystals formed by FIB irradiation did not depend on the P content because an aggregation of nanocrystals between 1 and 5 nm in size was considered to be one crystal in our study. In any sample, most of nanocrystals are less than 10 nm, but aggregations of nanocrystals can be larger. A nanocrystal formed by the collision of a Ga^+ ion would be less than 10 nm in size and the size would not be dependent on the P content. The size of a nanocrystal might depend on the energy of the irradiation ions. If we do not assume an aggregation of nanocrystals to be one crystal, it is considered that the number densities of nanocrystals increase as the P content decreased. In this study, the nanocrystals were formed by repeated FIB irradiation. Thus, nucleation around a nanocrystal can easily occur because the amorphous region around a nanocrystal formed by FIB irradiation has a complex stress-field caused by the change in the local P content, the contraction in the volume of the Ni nanocrystal, and the surface image force. Therefore, aggregates of nanocrystals could precipitate, and the observed average and maximum sizes of the Ni nanocrystals would consequently increase as the P content decreased.

4. Conclusions

We investigated the morphology of Ni nanocrystals

formed by FIB irradiation of Ni-P amorphous alloys with P contents ranging from 14 to 20 at%. The nanocrystals induced by FIB irradiation in Ni-20.2, 15.6, 14.0 at%P amorphous alloy had unique crystallographic orientation relationships: $\{111\}_{\text{f.c.c.}}$ was parallel to the irradiated plane and $\langle 110 \rangle_{\text{f.c.c.}}$ was parallel to the direction of the projected ion beam. The P content did not affect the crystallographic orientation relationships. The study confirmed that 1) FIB irradiation causes nanocrystals to aggregate, and 2) the average size of the Ni nanocrystals increases as the P content decreased.

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REFERENCES

- 1) K. Hono, K. Hiraga, Q. Wang and A. Inoue: *Acta Metall.* **40** (1992) 2137–2147.
- 2) A. M. Tonejc, N. Ramsak, A. Prodan, A. Tonejc, A. Khalladi, S. Surinach and M. D. Baro: *Nanostruct. Mater.* **12** (1999) 677–680.
- 3) C. W. Allen, R. C. Birtcher, S. E. Donnelly, K. Furuya, N. Ishikawa and M. Song: *Appl. Phys. Lett.* **74** (1999) 2611–2613.
- 4) E. Oliviero, M. F. Beaufort and J. F. Barbot: *J. Appl. Phys.* **89** (2001) 5332–5338.
- 5) S. Takeda and J. Yamasaki: *Phys. Rev. Lett.* **83** (1999) 320–323.
- 6) T. Nagase, Y. Umakoshi and N. Sumida: *Mater. Sci. Eng. A* **323** (2002) 218–225.
- 7) R. Tarumi, K. Takashima and Y. Higo: *Appl. Phys. Lett.* **81** (2002) 4610–4612.
- 8) R. Tarumi, K. Takashima and Y. Higo: *J. Appl. Phys.* **94** (2003) 6108–6115.
- 9) R. Tarumi: Dr. thesis, (Tokyo Institute of Technology, Japan, 2003) pp. 81.
- 10) S. Kobayashi and Y. Kashikura: *Mater. Sci. Eng. A* **358** (2003) 76–83.
- 11) F. Gao, D. J. Bacon, L. M. Howe and C. B. So: *J. Nucl. Mater.* **294** (2001) 288–298.
- 12) B. Farber, E. Cadel, A. Menand, G. Schmitz and R. Kirchheim: *Acta Mater.* **48** (2000) 789–796.