Pressure–Composition Phase Diagram of Fe–Ni Alloy

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We investigated the structural phase transitions of Fe–Ni alloys under hydrostatic pressure conditions at 298 K by examining the X-ray diffraction patterns of polycrystalline samples with Ni contents of 5%–31.6%, and pressure–composition phase diagram was established for the pressure range of 0–15 GPa. The diagram comprised three structural phases: bcc, fcc, and hcp, and these all coexisted in 25% Ni at 11 GPa during compression and in 23% Ni at 7 GPa during decompression. During both processes, low- and high-pressure phases coexisted. During the pressure-induced structural transitions, significant hysteresis was also observed. The 27% Ni alloy showed the two-stage transition: bcc–fcc–hcp, and the fcc phase was quenched to ambient pressure. For the 5–23% Ni alloys, a bcc–hcp transition was observed at high pressure. As the Ni content increased, the transition pressure decreased, and the volume reduction of the bcc–hcp transition also decreased due to the increase in the atomic volume of the hcp phase. The transition pressure from fcc to hcp rapidly increased with the Ni content. Compression curves of 29.9% Ni and 31.6% Ni alloys exhibited an anomaly at 2.0 and 2.9 GPa, respectively, and the compression anomaly was attributed to the magnetic transition. [doi:10.2320/matertrans.MT-M2020047]

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1. Introduction

It is well known that three structural phases, bcc, fcc, and hcp, occur in the temperature–pressure phase diagram for the Fe-rich portion of the Fe–Ni alloy system.^{1–5)} One of these exhibits a martensitic transformation to other phases under certain temperature or pressure conditions. The bcc phase of a ferromagnet at ambient pressure transforms to hcp at high pressure.^{1–3)} The fcc phase with a Ni content close to the bcc–fcc martensitic transition line, which shows an Invar effect, transforms to bcc at low temperature.^{4,5)}

The Fe–Ni alloy is a base material like stainless steels, and information on its physical properties and phase stability at high pressure is fundamental to the developing high-performance alloys. Detailed studies on the bcc–hcp transition of pure iron have been reported^{6,7)} and the structural transition for Fe–Ni alloys under pressure has also been investigated from a geoscience viewpoint.^{8–10)} However, details of the stability of these three phases in the alloy system under given pressure–composition conditions remain unknown.

In this study, we report details of the phase transition for the Fe-rich portion of the Fe–Ni alloy system under hydrostatic pressure conditions, obtained by X-ray diffraction (XRD) experiments, and present the pressure–composition phase diagram. The phase transitions and phase diagram are also discussed based on structural data.

2. Experimental Procedure

The Ni contents of Fe–Ni alloys measured in the present study were 5, 5.3, 10, 15, 20, 23, 25, 27, 29.9, and 31.6 at% Ni. Each alloy was annealed at 1,000°C for 1 h and cold-rolled into a sheet after preparing a button ingot of each alloy by arc melting. The surface oxide layer of the sheet was

polished with an emery paper. The sheet was cut into squares $3 \times 3 \times 0.2 \text{ mm}^3$ in size, and which were solution-treated at 1,150°C for 3–60 h under vacuum before quenching in iced water. The sheet was then electropolished to a thickness of approximately 20 μm , using an electrolyte comprising 85% $\text{C}_2\text{H}_5\text{OH}$ and 15% HClO_4 by volume. The sheet was then cut into squares $100 \times 100 \times 20 \mu\text{m}^3$ in size, which were used as samples. Inductively coupled plasma optical emission spectroscopy was used for composition analysis.

Powder XRD experiments under ambient conditions showed that the 5–27% Ni alloys were bcc, but the bcc phase for 23–27% Ni contained traces of fcc. Alloys with 29.9% Ni and 31.6% Ni were fcc, but the alloy with 29.9% Ni contained a small % of bcc. The atomic volume of each bcc phase is shown in Fig. 1(a) as a function of the Ni content, compared with previous data by Zwell *et al.*¹¹⁾ These data were consistent within acceptable error margins.

A diamond anvil cell was used to generate high pressure. A methanol–ethanol–water (16:4:1) mixture was used as a pressure-transmitting medium. To confirm the hydrostaticity of the mixture, supercritical helium fluid was also used as the pressure medium in the experiment with 20% Ni alloy. The pressure was determined by using the ruby fluorescence method.¹²⁾

High-pressure XRD experiments were conducted at room temperature using an angular dispersion method with a monochromatic synchrotron radiation X-ray source ($E = 30 \text{ keV}$) on the BL10XU beamline at SPring-8.¹³⁾ The diffraction patterns were recorded on an image plate detector, and the 2θ -intensity patterns were obtained by integrating the recorded two-dimensional diffraction images.^{14,15)} The patterns were analyzed using the PDIndexer software.¹⁶⁾

Powder XRD data were collected up to about 15 GPa at room temperature, 298 K, increasing and decreasing in steps of $\sim 0.5 \text{ GPa}$. For fcc with Ni contents of 29.9% and 31.6%,

Fig. 1 The Ni composition dependence of (a) the atomic volume of the bcc phase under ambient conditions, together with previous data,¹¹⁾ (b) atomic volumes of the bcc, hcp, and fcc phases estimated at 10 GPa. Squares correspond to previous data for pure iron by Dewaele *et al.*⁷⁾

the pressure was increased in steps of ~ 2 GPa because the transition pressure to hcp exceeded 20 GPa. In the experiments in the high-pressure range for 29.9% and 31.6% Ni, pressure was estimated based on the equation of state of Pt.¹⁷⁾

3. Results and Discussion

Based on the present high-pressure powder XRD experiments, the bcc–hcp transition was observed up to 23% Ni; at 25% Ni, the bcc transformed to hcp via a coexistence phase between hcp and fcc, and a two-stage phase transition, bcc–fcc–hcp, was accounted for at 27% Ni. For 29.9 and 31.6% Ni, the fcc–hcp transition was observed in a range above 20 GPa. Details of these phase transitions are described below.

3.1 Pressure-induced phase transition

(1) bcc–hcp transition

Alloys with Ni contents reaching 23% showed the bcc–hcp transition. Figure 2 shows an example of the change in the diffraction pattern of 20% Ni as the pressure increased and decreased. In this experiment, helium was used as the pressure-transmitting medium. As the pressure increased from 11.2 to 11.4 GPa, the bcc phase started to transform to hcp, and bcc and hcp coexisted. The 100 and 101 diffraction peaks from the hcp phase appeared. Furthermore, when the pressure was increased from 13.6 to 14.4 GPa, the 200 and 211 diffraction peaks from the bcc phase disappeared, and the bcc completely transformed to hcp.

During decompression, the hcp phase began to transform to bcc when the pressure was reduced from 8.7 to 8.2 GPa, and it completely transformed to bcc at 4.6 GPa. Figure 3 shows the pressure change in the volume fraction of hcp estimated based on diffraction peak intensities. The evolution

Fig. 2 The change in the representative diffraction patterns for the Fe–20% Ni alloy as the pressure increased and decreased. In the experimental run, helium was used as the pressure-transmitting medium.

Fig. 3 The pressure evolution of the volume fraction of the hcp phase for the Fe–20% Ni alloy as the pressure increased and decreased.

of the bcc–hcp transition and its reverse transition during decompression can be seen. Since the pressure change in the volume fraction is rapid in the vicinity of the onset pressure of the transition, the estimation error for the onset transition pressure is smaller than that for the offset pressure.

The experimental results for Fe–20% Ni using a mixed alcohol medium showed good agreement with the results for the He pressure medium within error range. These transition behaviors were consistent with recent reports on pure iron,⁷⁾ although the transition pressures were different.

Additionally, for the 23% Ni alloy, fcc was observed during decompression. The transition from hcp to bcc and fcc began at 7 GPa, and the three phases coexisted up to 3.6 GPa. At 2.6 GPa, the hcp phase disappeared, and bcc and fcc coexisted. On further decompression, the sample formed a single bcc phase.

(2) bcc–hcp+fcc–hcp transition

The bcc phase of the 25% Ni alloy transformed into a state in which hcp and fcc coexisted when the pressure was increased. The onset pressure of the transition was 12.1(2) GPa, and the offset pressure was 14.5(5) GPa, which is a slightly higher than that for the 23% Ni alloy. When the two-phase coexistence state was further pressurized, the fcc began to transform to hcp. However, this transition was sluggish and was complete at 36 GPa. Since for the 27% Ni alloy, bcc transformed to fcc rather than hcp, 25% Ni appeared to be the boundary composition between hcp and fcc. During decompression, the reverse transition to fcc began at 9.7 GPa and was almost complete at 5.7 GPa. The transition to bcc then resumed at 1.8 GPa, and at normal pressure, the bcc phase almost restored.

(3) bcc–fcc–hcp transition

As the pressure increased, the bcc phase of the Fe–27% Ni alloy began to transform to fcc at 10.2(2) GPa and formed a single fcc phase at 12.8(5) GPa. On further pressurization, it began to transform to hcp at 20.5(5) GPa. However, the transition was sluggish and a pressure exceeding 50 GPa was required to complete the transition to hcp. During decompression, the sample formed a single fcc phase at 8.5(5) GPa. Even when the pressure was reduced to normal pressure, only a weak bcc peak was observed. Most of the high-pressure fcc phase was recovered to normal pressure.

(4) fcc–hcp phase transition

The fcc phase of the 29.9% Ni alloy started to transform to hcp at 25(1) GPa, but the volume fraction of hcp estimated from the peak intensity at 29 GPa was only about 20%. The progress of the phase transition due to compression was slow, and it appeared that a pressure exceeding 50 GPa was required to form a single hcp phase. Since hcp and fcc coexisted within a wide pressure range, the difference in Gibbs free energy between the two phases was considered small from a thermodynamic viewpoint. In fact, both phases had a close-packed structure, and their atomic volumes estimated from the observed diffraction patterns were almost the same, the difference being below 1%. A previous high-temperature and high-pressure experiments reported the observation of the hcp phase at 30 GPa.¹⁰⁾ Furthermore, in the 31.6% Ni alloy, the onset of the transition to hcp rapidly increased to about 40 GPa, and the volume fraction of fcc was about 50% even at 65 GPa.

3.2 Pressure–composition phase diagram

Figure 4 shows the pressure–composition phase diagram obtained from this study. The blue symbols indicate increasing pressure and the red ones decreasing pressure. The onset pressure of the phase transition is indicated by a circle and the offset pressure by a triangle. Phase boundaries between the three solid phases, bcc, hcp, and fcc were obtained. From this figure, as the Ni content increased, the onset pressure of the bcc–hcp transition decreased with a negative coefficient, -0.2 GPa/at% Ni for the 15% Ni content, and then reached a constant value of 11.0 GPa. This phase boundary is consistent with pure iron data reported in the previous study.⁷⁾ The reverse transition on decompression

Fig. 4 The pressure–composition phase diagram of the Fe-rich portion for the Fe–Ni alloy system under compression (blue) and decompression (red) at 298 K. Lines are guides to the eye.

showed a large hysteresis with respect to the pressure, and the transition pressure also decreased as the Ni content increased.

For 25% Ni, three solid phases coexisted at 11.2 GPa. Furthermore, for 27% Ni, the bcc phase transformed to fcc and then hcp. The hcp phase reverted to fcc when the pressure was reduced. The fcc phase Furthermore, the fcc phase was preserved at normal pressure, although a small amount of bcc appeared. The transition pressure from bcc to fcc rapidly decreased as the Ni content increased. The stable region of the fcc phase extends to the lower Ni composition side under pressure.

For alloys with Ni contents exceeding 30%, the fcc phase was stable over a wide pressure range, and the transition pressure to hcp rapidly increased with the Ni content. It is interesting that the present pressure–composition phase diagram corresponded to the P – T phase diagram of pure iron^{1,2)} when the composition axis was replaced with temperature in this phase diagram.

3.3 Pressure dependence of atomic volume

Figure 5 shows the pressure dependence of the atomic volume for the bcc and hcp phases of the 20%Ni alloy estimated from diffraction patterns shown in Fig. 2. Circles and triangles indicate data for increasing and decreasing pressure, respectively. A relatively large volume reduction was observed at the phase transition. Based on the pressure–volume (P – V) data observed in the bcc and hcp phases for each composition obtained in this study, the bulk modulus: K_0 was estimated using the Vinet equation of state as shown in eq. (1).¹⁸⁾

$$P = 3K_0 \left(\frac{V}{V_0} \right)^{-\frac{2}{3}} \left[1 - \left(\frac{V}{V_0} \right)^{\frac{1}{3}} \right] \times \exp \left\{ \frac{3}{2} (K'_0 - 1) \left[1 - \left(\frac{V}{V_0} \right)^{\frac{1}{3}} \right] \right\}, \quad (1)$$

where V_0 is the atomic volume at normal pressure. At this time, values of 5.29 and 5.38^{7,19)} were assumed for the pressure derivative of bulk modulus: K'_0 for pure iron at

Fig. 5 The pressure dependence of the atomic volumes of the bcc (green) and hcp (blue) phases for the Fe–20% Ni alloy shown in Fig. 2. Circles and triangles correspond to increasing and decreasing pressure.

normal pressure for bcc and hcp, respectively. For bcc, only the P – V data before the phase transition was used. The values of V_0 and K_0 are summarized in Table 1. The obtained equations of state for both phases are shown in Fig. 5 by solid lines. The value of K_0 for bcc obtained for each alloy was approximately 160 GPa, which was almost constant within the error range.

From the solid lines for the 20% Ni alloy, the atomic volumes of bcc and hcp at 10 GPa were estimated as 11.17

and 10.75 Å^3 , respectively. The volume reduction, $-\Delta V$, accompanying the bcc–hcp phase transition was 0.42 Å^3 , corresponding to 3.9% of the bcc volume before the phase transition. This value was smaller than that of 4.8% for pure iron. This was due to an increase in the atomic volume of the hcp high-pressure phase as the Ni content increased. Figure 1(b) shows the composition dependence of the atomic volumes of bcc and hcp estimated at 10 GPa. The atomic volume of the hcp high-pressure phase showed a relatively large increase as the Ni content increased, while the composition dependence for bcc at 10 GPa was similar to that at atmospheric pressure. Consequently, the volume reduction of the bcc–hcp transition decreased with the Ni content. The lattice constant: c for hcp became 0.6% larger than that of pure iron, while a for hcp was almost equal to that of pure iron. The c/a ratio increased with the Ni content and reached 1.614 for 20% Ni, which is larger than that of 1.604 for pure iron.

The large volume reduction of pure iron is considered to be due to the magnetic–non-magnetic transition. The hcp phase of pure iron is non-magnetic and shows superconductivity at low temperature.²⁰⁾ Therefore, there is interest in whether the high-pressure hcp phase of Fe–Ni alloys is a non-magnetic superconductor.

Equations of state for the fcc phases for 27%, 29.9%, and 31.6% Ni are also listed in Table 1. The fcc phase with a Ni content close to the bcc–fcc martensitic transition line showed an Invar effect. Previous high-pressure XRD^{21–23)} and theoretical²⁴⁾ studies reported that the Invar alloy exhibits a significantly lower K_0 value than those of pure iron⁷⁾ and

Table 1 The values of the atomic volume at normal pressure: V_0 , the bulk modulus: K_0 , and the pressure derivative of bulk modulus: K_0' for the bcc, hcp and fcc phases of Fe–Ni alloy samples, together with previous data for pure iron and nickel.

bcc				hcp		
Sample	V_0	K_0	K_0'	V_0	K_0	K_0'
0%Ni*	11.76*	165*	5.29*	11.214*	163.4*	5.38*
5%Ni	11.830(7)	166(4)	5.29	11.25(2)	184(8)	5.38
5.3%Ni	11.827(9)	160(4)	5.29	11.22(3)	183(12)	5.38
10%Ni	11.837(11)	160(5)	5.29	11.24(2)	178(9)	5.38
15%Ni	11.792(11)	161(14)	5.29	11.20(2)	188(7)	5.38
20%Ni	11.791(8)	158(6)	5.29	11.33(3)	172(12)	5.38
20%Ni He	11.814(5)	152(5)	5.29	11.33(1)	154(4)	5.38
23%Ni	11.814(9)	152(10)	5.29	11.44(4)	139(18)	5.38
25%Ni	11.810(5)	164(20)	5.29	11.40(3)	146(6)	5.38
27%Ni	11.774(9)	155(7)	5.29	-	-	-
fcc						
Sample	V_0	K_0	K_0'			
27%Ni	11.469(9)	133(2)	7(5)			
29.9%Ni	11.470(20)	136(5)	4(2)			
31.6%Ni	11.568(4)	109(2)	10(4)			
100%Ni**	10.94	181**	5.2**			

*: Dewaele *et al.*[6]

** : P. Lazor [23]

Fig. 6 The compression curves for (a) Fe-29.9% Ni and (b) Fe-31.6% Ni.

nickel²⁵⁾ listed in Table 1. Presently observed low K_0 values suggest that these fcc phases are Invar alloys at ambient pressure.

Compression curves of 29.9% Ni and 31.6% Ni shown in Fig. 6 exhibit an anomaly at 2.0 and 2.9 GPa, respectively. The values of K_0 obtained by linearly approximating the P - V data before and after these pressure points are 122 and 175 GPa for 29.9% Ni, and 112 and 170 GPa for 31.6% Ni, respectively. The discontinuous change of bulk modulus suggests the second order phase transition. Such behavior reported from the previous XRD study by Oomi and Mori.^{21,22)} From a previous study of magnetization measurements for 31.9% Ni alloy, a ferromagnetic to spin glass-like phase transition has been proposed at room temperature and 4 GPa.²⁶⁾ Therefore, the compression anomaly would be attributed to the magnetic transition.

4. Conclusion

In this study, structural phase transitions in the Fe-rich portion of the Fe-Ni alloy system were investigated under hydrostatic pressure conditions at 298 K by examining the XRD patterns of polycrystalline samples, and the pressure-composition phase diagram was determined in the pressure range of 0–15 GPa. The diagram comprised three structural phases: bcc, fcc, and hcp, and these coexisted in 25% Ni at 11 GPa during compression. Alloys with Ni contents reaching 23% showed the bcc-hcp transition at high pressure. The onset pressure of the phase transition decreased with a

negative coefficient, -0.2 GPa/at% Ni up to the 15% Ni content, and reached a constant value of 11.0 GPa. The 27% Ni alloy showed a two-stage transition: bcc-fcc-hcp, and the fcc phase was quenched to ambient pressure. The transition pressure from fcc to hcp rapidly increased with the Ni content.

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