Preparation of Ni_2P and Fe_2P single crystals by the floating-zone method

Shigeki OTANI[†] and Naoki OHASHI

Environment and Energy Materials Division, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Single crystals of Ni_2P and Fe_2P were prepared at an argon pressure of 0.4 MPa by the RF-heated floating-zone method. The grown crystals, about 1 cm in diameter and 4–6 cm in length, had a near-stoichiometric composition.

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1. Introduction

Recently, transition-metal phosphides such as Fe_2P , MoP, WP, CoP, and Ni_2P have been identified as a new class of catalysts active for the hydrosulfurization reaction, that is, removal of sulfur from crude oil.^{1)–4)} Among them, nickel phosphide (Ni_2P) had the best catalytic activity, and its activity and selectivity were superior to those of the commercially available NiMoS and CoMoS catalysts in model experiments.^{4),5)} Extensive research has been carried out to investigate the mechanism of sulfur removal and to improve the catalytic properties.^{6)–8)} Atomic-scale studies of the catalyst surface, which require the use of single crystals, are important for understanding the origin of the catalytic activity of transition-metal phosphides. So far, only Fe_2P crystals have been prepared by thermal annealing at temperatures just below the melting point, for magnetic property evaluation, but the details of crystal growth have not been reported.⁹⁾ The catalytic activity of Fe_2P is not so high as that of Ni_2P , but Fe_2P crystals are also useful for analyzing the catalytic properties of the phosphides, especially in comparison with Ni_2P crystals. Therefore, in this study, single crystals of Ni_2P and Fe_2P were prepared by the floating-zone method because high purity crystals are obtained due to melting without crucibles.

2. Experimental

Commercial Ni_2P and Fe_2P powders were placed in rubber bags and isostatically pressed at 200 MPa. The pressed rods were then heated in a boron nitride (BN) crucible in vacuum at 800°C for 30 min. The diameter and length of the sintered rods were 1.2 cm and 12–13 cm, respectively.

Crystals were prepared at an argon pressure of 0.4 MPa by the RF-heated floating-zone method, using a three-turn/two-step work coil with an inner diameter of 1.8 cm. The crystal growth rate was 1 cm/h. Only the growing crystal (the lower shaft) was rotated at the rate of 6 rpm. The details are described elsewhere.¹⁰⁾

The lattice constants were determined by X-ray powder diffraction analysis using silicon as the internal standard. The accuracy of the results was ± 0.00008 nm. The crystal quality and orientations were verified by the X-ray back-Laue method. Chemical analysis was carried out by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Oxygen impurity was determined by an automatic analyzer (LECO, TC-436).

3. Results and discussion

Ni_2P and Fe_2P phases have been reported to melt congruently at 1110 and 1370°C, respectively,¹¹⁾ but crystal growth from the melt has not yet been reported for these compounds. In this study, the floating-zone method was adopted for crystal growth. During zone pass, $\text{Ni}_2\text{P}_2\text{O}_7$ and $\text{Fe}_3(\text{PO}_4)_2$ floated on the surface of the molten zone. When the amount increased, the molten zone became unstable. Therefore, the starting materials with fewer oxygen impurities were considered suitable for crystal growth.

The obtained Ni_2P crystal is shown in Fig. 1(a); the length and diameter of the crystals were 6 cm and 1.1 cm, respectively. The (0001) cross section of the crystal is shown in Fig. 1(b). The peripheral region included subgrain boundaries, but the central portion consisted of high-quality single crystal without splitting of the Laue spots. Although the crystal growth was initiated by spontaneous nucleation, most of the crystals grew in the vicinity of the (0001) direction, less than 30 degrees off. Accordingly, the (0001) cross section was almost circular, as shown in Fig. 1(b). The crystals were ductile without internal cracks.

Fig. 1. (a) Ni_2P crystal rod and (b) (0001) cross section. The marker indicates 1 cm.

[†] Corresponding author: S. Otani; E-mail: OTANI.shigeki@nims.go.jp

Table 1. Analytical results for Ni₂P crystal rod

	Content (wt %)		Composition
	Ni	P	Ni/P
Feed rod	78.6 ± 0.2	20.6 ± 0.1	2.01 ± 0.02
Molten zone	79.5	20.2	2.08
Crystal	79.3	20.7	2.02

The results of chemical analysis are shown in **Table 1**. The crystals had a stoichiometric composition within the analytical error. The Ni₂P phase was confirmed to melt congruently, as shown by the phase diagram,¹¹⁾ because the molten zone had almost the same composition as the crystal.

The lattice constants of the Ni₂P crystal were $a = 0.58630$ nm and $c = 0.33894$ nm of a hexagonal lattice. The transition-metal phosphides are reported to have nonstoichiometric composition ranges because of several atomic per cent of metal defects.¹²⁾ Accordingly, the chemical formula is represented as Ni_{2-x}P or Fe_{2-x}P, for example. The lattice constants of the a -axis and c -axis clearly increased with an increase in the metal content, that is, with a decrease in the concentration of metal defects. The lattice constants of the obtained crystals corresponded with those of the Ni₂P phase coexisting with the Ni₁₂P₅ phase, which has higher nickel content than the Ni₂P phase, $a = 0.5865 \pm 0.0002$ nm and $c = 0.3387 \pm 0.0002$ nm.¹³⁾ Therefore, the crystal was found to have a stoichiometric composition.

Figure 2(a) shows an Fe₂P crystal, with a diameter and length of 1 and 4 cm, respectively. The hollows on the crystal surface are tracks of Fe₃(PO₄)₂, which floated on the surface of the molten zone during crystal growth and subsequently attached to the crystal surface. The phosphate could be easily removed from the crystal surface after the growth, owing to the difference in the thermal expansion coefficients. The phosphate was produced from the oxygen impurity in the feed rod, as shown in **Table 2**.

The Fe₂P crystals were brittle and contained cracks, especially in the peripheral part, as shown by the cross-sectional image in **Fig. 2(b)**. The peripheral part broke easily because of the presence of cracks, while the central part included high-quality crystals. The growth directions of the crystals were in the vicinity of the (10–11) direction.

The analytical results are shown in **Table 2**. The molten zone had an iron-excessive composition, with an Fe/P composition ratio of 2.27. This was because of phosphate formation from the oxygen impurity in the feed rod, 1.74 wt %. The obtained crystal had a stoichiometric composition within the experimental error. The concentration of the oxygen impurity was 200 ppm in the crystal.

The lattice constants of the crystal were $a = 0.58649$ nm and $c = 0.34573$ nm of a hexagonal lattice, which corresponded to the composition Fe_{1.995}P, as estimated from the relationship between the composition and the lattice constants.¹³⁾ The lattice constants of the Fe₂P phase in the iron-rich molten zone (Fe/P = 2.27), which consisted of Fe₂P and Fe₃P phases, were $a = 0.58665$ nm and $c = 0.34576$ nm, which corresponded to those for the stoichiometric composition, $a = 0.58674$ nm and $c = 0.34581$ nm.¹³⁾

In summary, crystal growth could be easily effected, as long as the amount of phosphates did not increase during the growth. Oxygen impurity in the starting material played an important role in the growth of Ni₂P and Fe₂P crystals. It was important to choose the starting materials.

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Fig. 2. (a) Fe₂P crystal rod and (b) cross section. The marker indicates 1 cm.

Table 2. Analytical results for Fe₂P crystal rod

	Content (wt %)			Composition
	Fe	P	O	Fe/P
Feed rod	77.2 ± 0.1	21.1 ± 0.1	1.74	2.03 ± 0.01
Molten zone	80.3	19.6		2.27*
Crystal	78.1	21.7	0.02	2.00

(*: Fe₂P and Fe₃P)

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References

- 1) W. Li, B. Dhandapani and S. T. Oyama, *Chem. Lett.*, 3, 207–208 (1998).
- 2) P. Clark, W. Li and S. T. Oyama, *J. Catal.*, 200, 140–147 (2001).
- 3) C. Stinner, R. Prins and Th. Weber, *J. Catal.*, 202, 187–194 (2001).
- 4) S. T. Oyama, X. Wang, F. G. Requejo, T. Sata and Y. Yoshimura, *J. Catal.*, 209, 1–5 (2002).
- 5) S. T. Oyama, *J. Catal.*, 216, 343–352 (2003).
- 6) Md. G. Moula, S. Suzuki, W.-J. Chun, S. Otani, S. T. Oyama and K. Asakura, *Chem. Lett.*, 35, 90–91 (2006).
- 7) K. Edamoto, H. Inomata, K. Ozawa, Y. Nakagawa, K. Asakura and S. Otani, *Solid State Commun.*, 150, 1120–1123 (2010).
- 8) A. B. Hernandez, H. Ariga, S. Takakusagi, K. Kinoshita, S. Suzuki, S. Otani, S. T. Oyama and K. Asakura, *Chem. Phys. Lett.*, 513, 48–52 (2011).
- 9) H. Fujii, T. Hokabe, T. Kamigaichi and T. Okamoto, *J. Phys. Soc. Jpn.*, 43, 41–45 (1977).
- 10) S. Otani and Y. Ishizawa, *Prog. Crystal Growth and Charct.*, 23, 153–177 (1991).
- 11) “Binary Alloy Phase diagram”, 2nd ed., Ed. by T. B. Massalski, ASM, OH (1990) p. 2835.
- 12) B. Carlsson, M. Golin and S. Rundqvist, *J. Solid State Chem.*, 8, 57–67 (1973).
- 13) S. Rundqvist, *Acta Chem. Scand.*, 16, 992–998 (1962).