Impurity Metal-Activated Crystal Growth of Niobium Monophosphide from Gas Phase

Seiji MOTOJIMA, Toyohiko IZUSHI,* Kohzo SUGIYAMA, and Yasutaka TAKAHASHI

Department of Synthetic Chemistry, Faculty of Engineering, Gifu University, Kakamigahara, Gifu 504

**Government Industrial Research Institute of Nagoya, Hirate-Machi, Kitaku, Nagoya 462*

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Niobium monophosphide single crystals were obtained by chemical vapor deposition from a gas mixture of $NbCl_5$, PCl_3, H_2, and Ar on a quartz substrate using metallic impurity. The existence of Au, Pt, Pd, and Ni resulted in the growth of whiskers or pillar crystals. Maximum whisker length of 5 mm and thickness of 30 μm were obtained at 1150 °C for an hour with the use of Pt impurity. Platelet crystals (400×1000×20 μm, max.) were obtained with the use of Pt at 1240 °C. The growth directions of the whiskers and some platelet crystals were assigned to ⟨001⟩ and a direction in (001) plane, respectively. The optimum growth conditions for the pillar crystals in the case of Ni impurity: substrate temperature 1000—1020 °C, gas flow ratio $PCl_3/(NbCl_5+PCl_3)$ of 0.7—0.75. From observation of the tip and base of pillar crystals grown with Ni, the growth mechanism seems to be base VLS followed by VS.

Of the transition metal monophosphides, niobium monophosphide (NbP, niobium phosphide hereafter) is of interest as regards thermal stability. Niobium phosphide is a greyish black material having a metallic luster and good electrical conductor ($\approx 10^{-3}\,\Omega\cdot$cm),[1] and which is moderately hard (microhardness 599 kg/mm^2)[1] and is not attacked by water or dilute acids at room temperature.[2]

The existence of two equiatomic compounds (α- and β-NbP) proposed by Schönberg[3] was disproved by Bollar and Parthe,[4] who showed that there is a single compound with a range of homogeneity 44.7—50 a/o of phosphorus. The structure is body-centered tetragonal, four formulas per unit cell, space group $I4_1md$, the lattice parameter of c slightly varying from 11.40_0 (44.7 a/o P) to 11.37_8 (50 a/o P).[4]

Niobium phosphide has been prepared by heating niobium metal with red phosphorus in sealed tube at 650—1000 °C[1,5] with tricalcium diphosphide,[1] or by electrolyzing phosphate of metals.[6] The single crystal has been prepared by Schaefer and Fuhr[7] by means of chemical vapor transport. However, no work has been reported on whisker or pillar crystal growth from a vapor phase.

We have examined the growth conditions of whisker or pillar crystals with use of metallic impurity from a gas mixture of niobium pentachloride, phosphorus trichloride, hydrogen and argon, and also physical and chemical properties of the crystals. The results are given in this paper.

Experimental

A quartz tube (7 mm I. D. and 65 mm in length) containing a SiC heater was placed as a substrate in the center of a vertical reaction tube (quartz of 35 mm I. D.) heated from outside with a nichrome heater. The quartz substrate was abraded with emery papers, rinsed with deionized water and dried. A stream of niobium pentachloride (bp 240 5.°C) prepared by chlorination of niobium powder (14 mesh) at 500—600 °C and carried by argon, and another stream of hydrogen saturated by phosphorus trichloride at a given temperature were introduced from the upper inlet of the reaction tube. Argon was used for cleaning the reaction system before each experiment. The flow rates of each gas at room temperature were measured with an orifice-type flow meter. Flow rate of niobium pentachloride was calculated from that of chlorine stream to the niobium metal, where this chlorination reaction might be considered to proceed quantitatively in a steady state.

The surface temperature of the substrate was measured with an optical pyrometer through an observation window and was corrected by means of a CA thermocouple. The ambient temperature of the reaction atmosphere was controlled between 300 and 400 °C using the CA thermocouple to keep the niobium pentachloride in gas phase. As the source of impurities to promote the crystal growth, various metals such as Mn, Fe, Co, Ni, Pd, Pt, and Au were painted on the substrate in the form of aqueous solutions of sulphates or chlorides, and were subjected to decomposition or reduction into the corresponding metals inside the reactor at a temperature below that used for the niobium phosphide crystal growth. The surface concentration of the impurity was fixed at *ca.* 0.05 mg/cm^2 of substrate area.

The range of pillar crystal length and thickness in this paper refers to about twenty of the longest samples obtained in each experiment. Crystals were observed with a scanning electron microscope. An X-ray diffractometer, a micro-analyzer and an oscillation camera were used for analysis of the grown crystals, the base of pillar crystals and a well-formed whisker, respectively.

Conductivity of whisker and platelet crystal was measured by conventional two-probe method using a Wheatstone bridge in an argon flow.

Results and Discussion

Growth Conditions of the Pillar Crystals Using Ni Metal.
Effect of Substrate Temperature: Substrate temperature influences pillar crystal growth by a great deal as shown in Fig. 1. An average length of 1.2 mm was attained at 1000—1020 °C, the length decreasing abruptly at a temperature higher or lower than 1000—1020 °C. Above the optimum temperature, pillar crystals grew to a direction perpendicular to the growth axis resulting in considerable rough surface. The lowest temperature for the growth of pillar crystals was approximately 900 °C.

Effect of the Gas Composition: The effect of the gas flow ratio of $PCl_3/(NbCl_5+PCl_3)$ on the length and thickness of pillar crystals is shown in Fig. 2, where the sum of the flow rates of niobium pentachloride and phosphorus trichloride is kept at 0.20 cm^3/s.

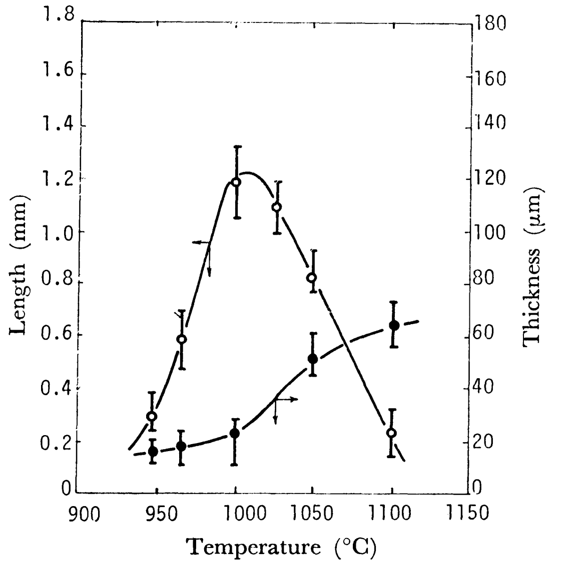

Fig. 1. Effect of substrate temperature on the length and the thickness of pillar crystals.
Impurity: Ni, reaction time: 10 min, $NbCl_5$ flow rate: 0.05 cm^3/s, PCl_3 flow rate: 0.15 cm^3/s, H_2 flow rate: 3.2 cm^3/s, Ar flow rate: 1.0 cm^3/s.

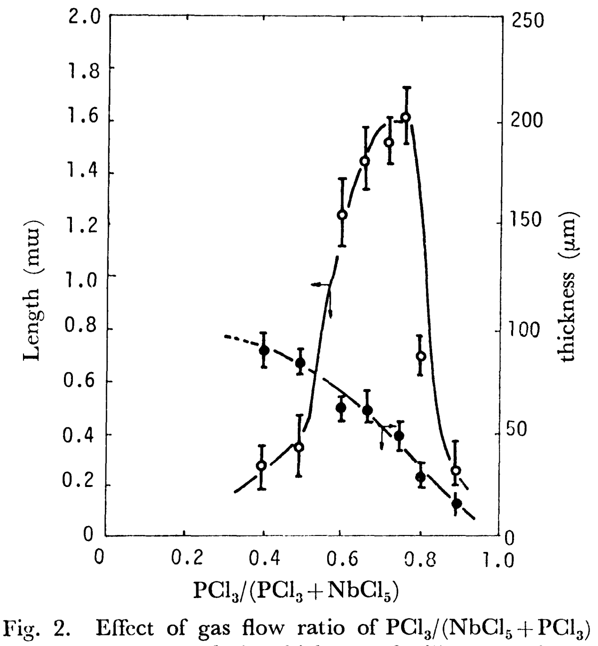

Fig. 2. Effect of gas flow ratio of $PCl_3/(NbCl_5+PCl_3)$ on the length and the thickness of pillar crystals.
Impurity: Ni, substrate temperature: 1050 °C, reaction time: 10 min, $NbCl_5+PCl_3$ flow rates: 0.20 cm^3/s, H_2 flow rate: 3.2 cm^3/s, Ar flow rate: 0.5 cm^3/s.

The length of crystals increased with increase in the ratio, and reached a maximum at a flow ratio of 0.70—0.75, decreasing abruptly above the ratio of 0.75. In contrast, the thickness of the crystals decreased linearly with increase in the ratio, pillar crystals with a well-formed and smooth surface growing preferably at the ratio of above 0.75 (Fig. 3). This optimum flow ratio declined to a PCl_3-rich region as compared with the expected reaction stoichiometry $PCl_3/(NbCl_5+PCl_3)$ of 0.5 and with the optimum flow ratio for the deposition of polycrystalline NbP by use of no impurity

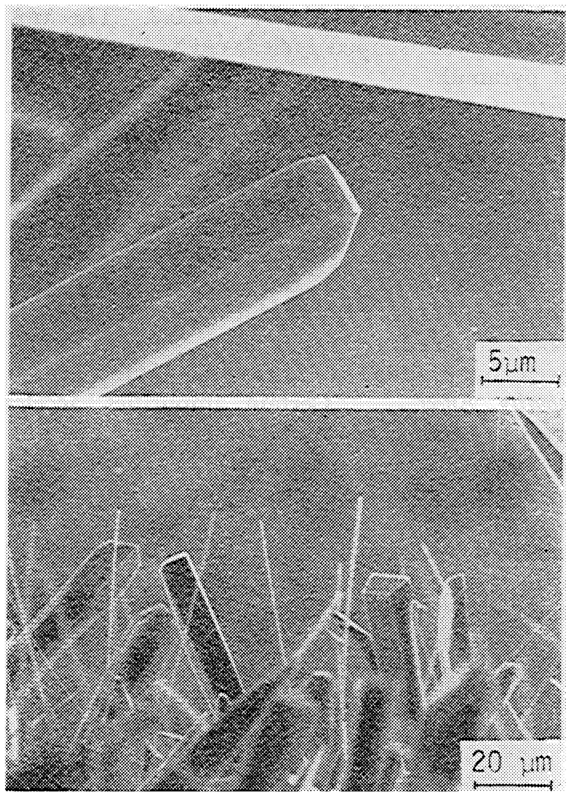

Fig. 3. Well-formed pillar crystals.
Impurity: Ni, substrate temperature: 1020 °C, reaction time: 10 min, $NbCl_5$ flow rate: 0.04 cm^3/s, PCl_3 flow rate: 0.15 cm^3/s, H_2 flow rate: 4.0 cm^3/s, Ar flow rate: 1.0 cm^3/s.

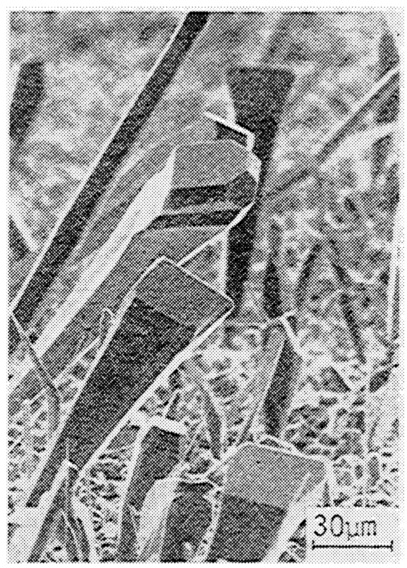

Fig. 4. Pillar crystals having a tapered form.
Impurity: Ni, substrate temperature: 1100 °C, reaction time: 30 min, $NbCl_5$ flow rate: 0.15 cm^3/s, PCl_3 flow rate: 0.15 cm^3/s, H_2 flow rate: 4.0 cm^3/s, Ar flow rate: 1.0 cm^3/s.

of 0.6. On the other hand, at a flow ratio of $PCl_3/(NbCl_5+PCl_3)$, crystals grew to a direction perpendicular to the growth axis; remarkable growth steps or a rough surface being observed. Tapered pillar crystals (Fig. 4) were obtained at 1100 °C and a flow ratio $PCl_3/(NbCl_5+PCl_3)$ of about 0.8. The tips of the crystals were shaped a clear-cut square or a tetragonal pyramid.

Effect of the Growth Time: The effect of growth time on the crystal length and thickness is shown in Fig. 5. The length of the pillar crystals increased with increase in reaction time up to 15 min after an induction time of about 5 min, and levelled off after the elapse of 15 min. In contrast, the thickness remained constant 10—15 μm until 15 min, beyond which pillar crystals grew in thickness with time. This can be explained by rapid linear growth by VLS, followed by gradual thickening by VS mechanism.

Impurity Effect. Certain impurities accelerate the growth of whiskers or pillar crystals. The growth mechanism can be explained by "VLS mechanism." The impurity effects of various metals on the crystal growth of niobium phosphide at 900—1250 °C are summarized in Table 1. Iron, cobalt, chromium, and manganese give no influence on the whisker growth for all the temperatures examined, the deposition taking place in uniform coatings or polycrystals. Gold and nickel show a conspicuous effect at 1050 °C, giving straight whiskers and pillar crystals, respectively. Platinum gives well-formed straight whiskers and platelet crystals at 1100—1200 °C and 1250 °C, respectively. Palladium gives cubic crystals mixed with thin whiskers above 1100 °C.

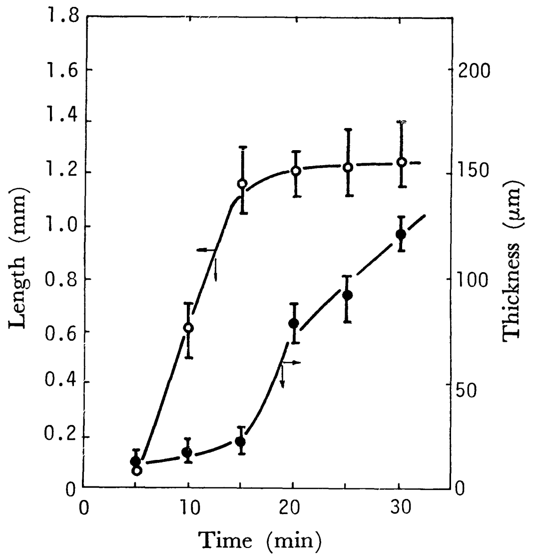

Fig. 5. Effect of reaction time on the length and the thickness of pillar crystals.
Impurity: Ni, substrate temperature: 1020 °C, $NbCl_5$ flow rate: 0.05 cm^3/s, PCl_3 flow rate: 0.15 cm^3/s, H_2 flow rate: 3.2 cm^3/s, Ar flow rate: 1.0 cm^3/s.

TABLE 1. IMPURITY EFFECTS

Impurity	Effect	Crystal morphology
Fe	−	Polycrystals
Co	−	Polycrystals
Ni	++	Pillars
Cr	−	Polycrystals
Mn	−	Polycrystals
Au	++	Whiskers
Pt	++	Whiskers and pillars (1100—1200 °C), and platelets (>1200 °C)
Pd	+	Cubic crystals (>1100 °C)

Crystal Morphologies. Typical whiskers grown with gold as an impurity are shown in Fig. 6. The whiskers have a square cross section and reach a maximum length of 1 mm and 5 μm in thickness after 2 h. Lateral surfaces are generally smooth, but a square-shaped growth depression appears occasionally (Fig. 6B). The tips of pillars is a clear-cut square (Fig. 6C). Figure 7 shows the appearance of pillar crystals grown on a platinum painted zone at 1150 °C for 15 min, polycrystal coatings depositing in the absence of platinum. Average pillar length reached 3 mm (5 mm max.) and thickness of 30 μm after

A)
B)
C)

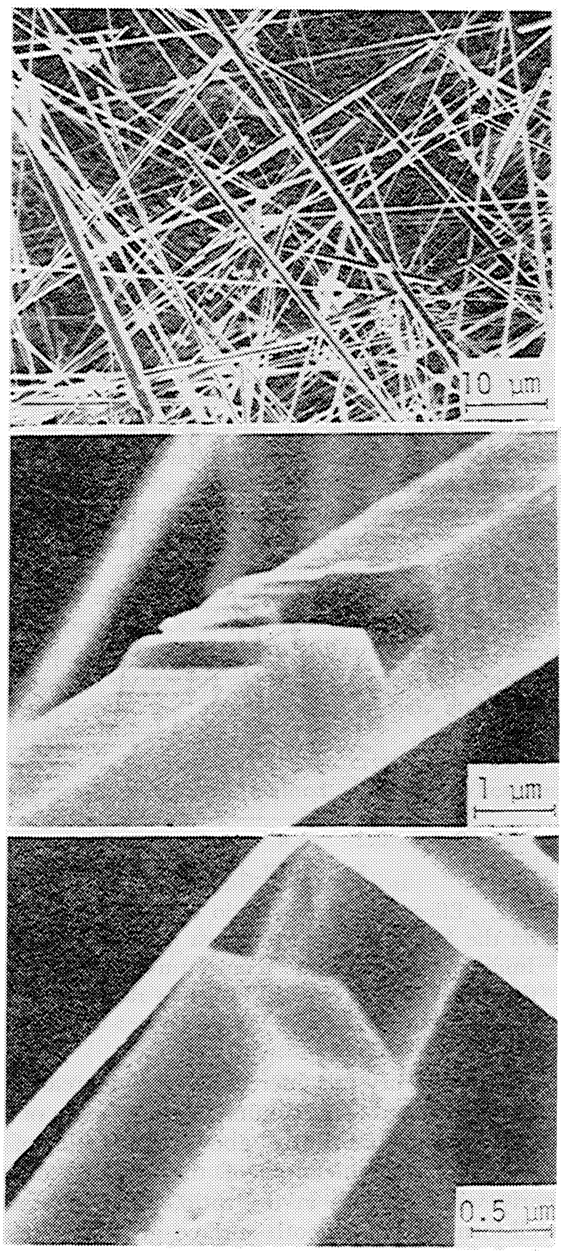

Fig. 6. Appearances of whiskers.
Impurity: Au, substrate temperature: 1050 °C, reaction time: 30 min, $NbCl_5$ flow rate: 0.04 cm^3/s, PCl_3 flow rate: 0.05 cm^3/s, H_2 flow rate: 3.5 cm^3/s, Ar flow rate: 0.5 cm^3/s.

A)

B)

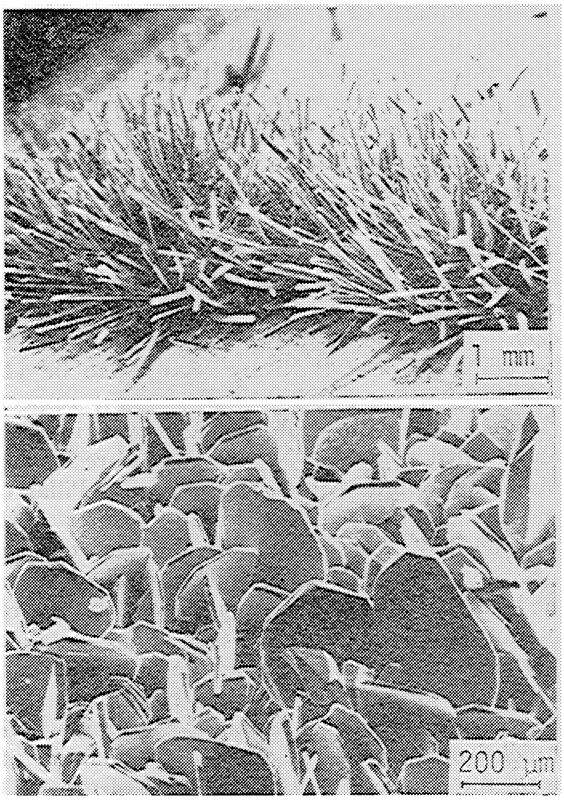

Fig. 7. Appearances of pillar and platelet crystals.
Impurity: Pt, reaction time: 15 min.
A) Substrate temperature: 1150 °C, $NbCl_5$ flow rate: 0.03 cm^3/s, PCl_3 flow rate: 0.03 cm^3/s, H_2 flow rate: 4.0 cm^3/s, Ar flow rate: 0.6 cm^3/s.
B) Substrate temperature: 1240 °C, $NbCl_5$ flow rate: 0.03 cm^3/s, PCl_3 flow rate: 0.04 cm^3/s, H_2 flow rate: 3.7 cm^3/s, Ar flow rate: 0.5 cm^3/s.

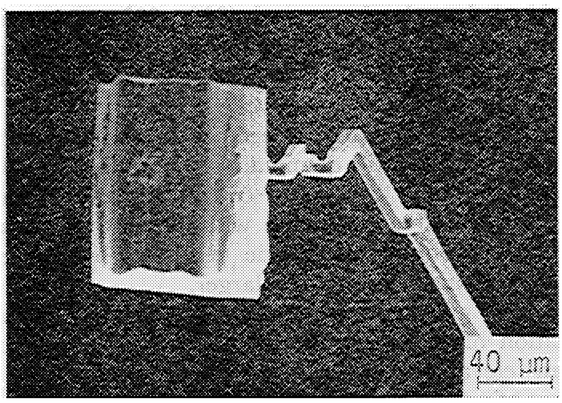

Fig. 8. Peculiar pillar crystals.
Impurity: Pt, substrate temperature: 1070 °C, reaction time: 15 min, $NbCl_5$ flow rate: 0.06 cm^3/s, PCl_3 flow rate: 0.04 cm^3/s, H_2 flow rate: 3.5 cm^3/s, Ar flow rate: 0.5 cm^3/s.

an hour. At a temperature higher than 1200 °C, thin platelet crystals 400×1000×20 μm with a smooth surface grew on the platinum painted zone (Fig. 7B). Sometimes, peculiar pillar crystals with a deformed 120×100 μm cubic crystal at the middle or the tip of the crystal were observed (Fig. 8). Well-formed 100×100×50 μm crystals deposited, sometimes mixed

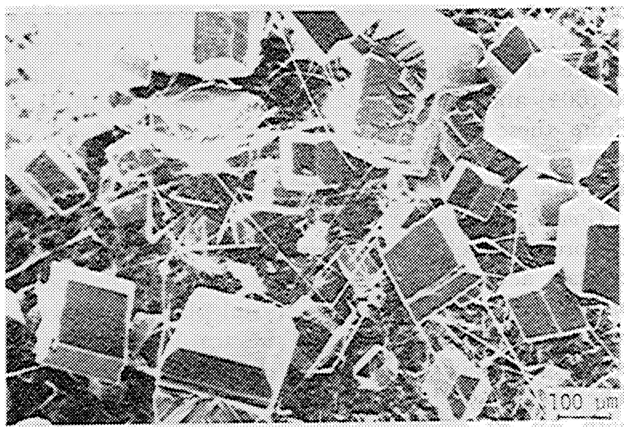

Fig. 9. Well-formed crystals.
Impurity: Pt, substrate temperature: 1145 °C, reaction time: 30 min, $NbCl_5$ flow rate: 0.04 cm^3/s, PCl_3 flow rate: 0.06 cm^3/s, H_2 flow rate: 4.1 cm^3/s, Ar flow rate: 0.6 cm^3/s.

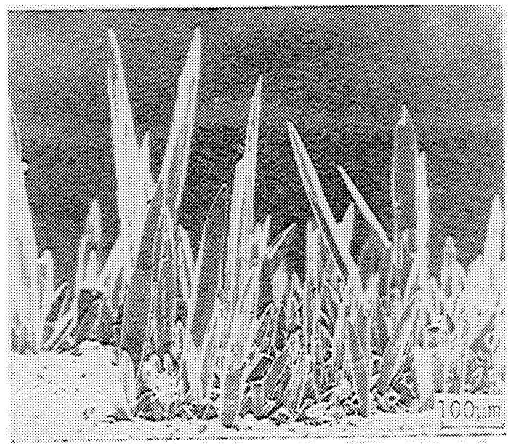

Fig. 10. Phylloid crystals.
Impurisy: Ni, substrate temperature: 1025 °C, reaction time: 15 min, $NbCl_5$ flow rate: 0.05 cm^3/s, PCl_3 flow rate: 0.10 cm^3/s, H_2 flow rate: 4.1 cm^3/s, Ar flow rate: 0.5 cm^3/s.

with thin whiskers on the platinum painted zone at 1145 °C for 30 min (Fig. 9). Similar crystals grew with palladium at 1070 °C.

Nickel impurity considerably accelerated the growth of phylloid crystals with a sharp tip, the maximum length reaching 2 mm and thickness 50 μm. A typical phylloid crystal grown at 1025 °C for 15 min is shown in Fig. 10.

The growth axis of the whisker was confirmed by full-rotation photograph. Indices of an X-ray diffraction photograph are shown in Fig. 11, in which one well-formed whisker (10 μm thick and 3 mm long) is mounted with the whisker axis perpendicular to the incident X-ray beam in an oscillation camera (diameter 57 mm).

X-Ray diffraction diagrams of whiskers (A), platelet crystals (B) and woolly whiskers (C) are shown in Fig. 12 together with that in reference (D),[8] where a collection of whiskers and platelet crystals were dispersed on a holder plate. Thus the axes of the whiskers and faces of platelets are mainly parallel to the holder plate. A strong single peak is observed on whisker diffraction which corresponds to (200) of the tetragonal lattice of niobium phosphide. Strong peaks assinged to (004) and (008) are observed on platelet diffraction. From these results and the crystal morphologies, the growth direction of whisker is supposed to be ⟨001⟩ and that of platelet in some directions on (001) plane.

Growth Mechanism of Whiskers and Pillar Crystals. In order to clarify the growth mechanism of NbP crystals activated by metallic impurities, the location of impurity on the growing crystal plays an important role, since the evidence for the tip VLS mechanism is the existence of drops of impurity on their tips. The tip part of most whiskers and pillar crystals grown with Au, Pt, or Ni impurity is commonly shaped a

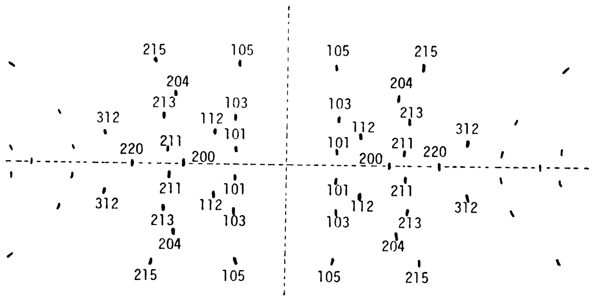

Fig. 11. Indices of the full-rotation photograph of a whisker.
Rotation axis was aligned with whisker axis (Cu$K\alpha$, diameter of camera: 57 mm).

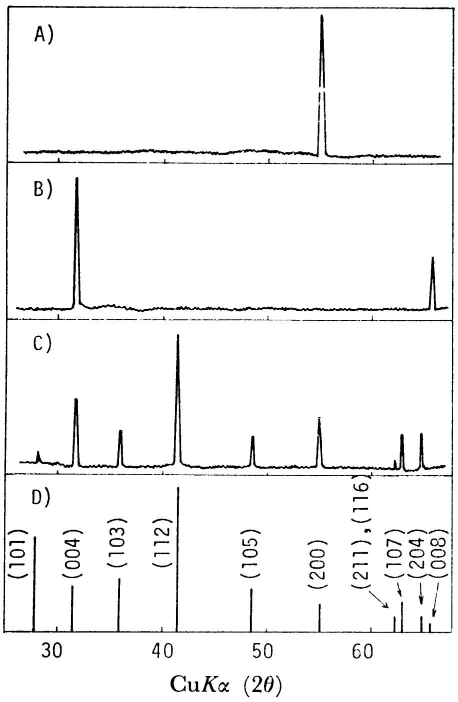

Fig. 12. X-Ray diffraction profiles.
A) A collection of whiskers placed on a holder plate along its growth direction.
B) A collection of platelet crystals dispersed on a holder plate.
C) Woolly whiskers as grown.
D) Data of NbP quoted from the Ref. 8.

clear-cut square or a long square pyramid, a drop like solid being seldom found on the tip, even in the initial stage of growth. The presence of Ni metal could not be confirmed by X-ray microanalysis of the tip of pillar crystals grown with Ni impurity. We might suppose that a tip VLS mechanism does not take part during the course of growth of whisker or pillar. The result of X-ray microanalysis on the cross section of the base of pillar crystals grown with Ni impurity is shown in Fig. 13. The layer is seen to consist of uniform composition of niobium–phosphorus–nickel. The eutectic temperatures[9] of the binary alloy of Nb–Ni and P–Ni are reported to be 1175 °C (40.2 a/o Nb) and 880 °C (19 a/o P), respectively. It seems that niobium atom is dissolved in the Ni–P melt to yield a melt of Nb–Ni–P mixture from which niobium phosphide can be crystallized. Pillar crystal growth was observed 2—5 minutes later after the substrate had been heated at a given temperature in a given reaction atmosphere. The "induction time" can be attributed to a slow diffusion rate of niobium and phosphorus into the nickel metal, or the time necessary for saturation of the drop with niobium and phosphorus. A possible mechanism for the pillar crystal growth of niobium phosphide activated by nickel metal may be base VLS mechanism at least during the course of the initial stage of growth. Appearance of a pillar crystal suggests the growth by VS mechanism. The pillar crystals might grow by base VLS mechanism followed by VS mechanism. However, another mechanism including a center axial screw dislocation mechanism or Chikawa's mechanism[10] cannot be excluded.

Properties of Niobium Phosphide Crystals. Electrical Resistivity: Electrical resistivity of a well-formed whisker (10—20 μm in diameter and 2—3 mm in length) and a platelet crystal (200—300 μm in width and 10—20 μm in thickness) along the crystal axis and some directions in (001) plane was examined in argon atmosphere, respectively. The resistivity increased with a rise in temperature in the range 20—250 °C, characteristic of metallic conduction; 9×10^{-4} for a whisker and 1×10^{-2} $\Omega\cdot$cm for a platelet crystal. The former value is in line with 0.4×10^{-3} $\Omega\cdot$cm of powdered niobium phosphide reported by Ripley,[1] the latter being considerably larger.

Stability of Oxidation in Air: Resistivity against oxidation of niobium phosphide in air was examined at an elevated temperature. Figure 14 shows the change of weight ratio with time at various temperatures between 900 and 1100 °C. The weight ratio increased with a rise in temperature above 970 °C, until the ratio attained a limiting value of *ca.* 1.64. X-Ray diffraction profiles of the products obtained at 1100 °C for an hour exhibited only the peaks of niobium phosphate ($NbPO_5$). Niobium phosphate is a light fluffy white powder and can not form a tight protecting layer on the surface of niobium phosphide crystal. It may be concluded that niobium phosphide is very stable in air up to 950 °C, but oxidizes to the phosphate at above 970 °C. Oxidation products of TiP[11] and ZrP,[12] an analogous phosphide of NbP, are a mixture of titanium pyrophosphate and titanium

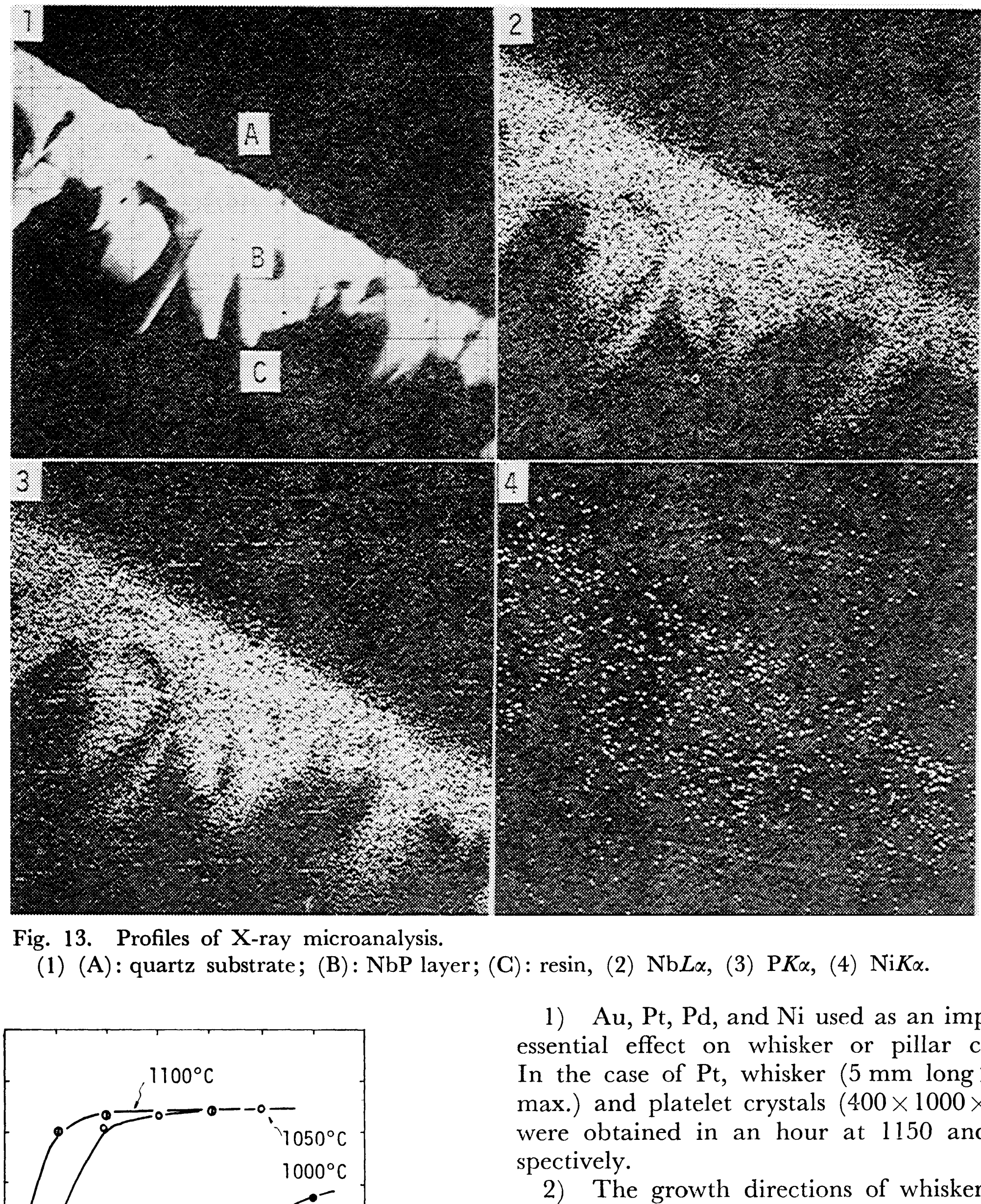

Fig. 13. Profiles of X-ray microanalysis.
(1) (A): quartz substrate; (B): NbP layer; (C): resin, (2) Nb$L\alpha$, (3) P$K\alpha$, (4) Ni$K\alpha$.

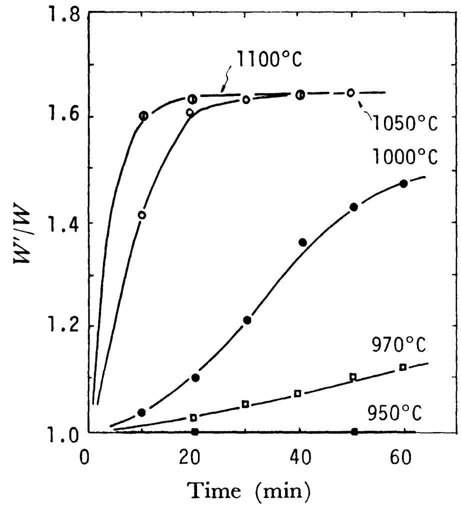

Fig. 14. Oxidation resistivity in the temperature range of 950—1100 °C

oxide, and zirconium oxide, respectively. It is of interest that oxidation products of the transition metal monophosphides differ from metal to metal.

Summary

Single crystals of NbP were obtained by the CVD method on a quartz substrate using metallic impurity.

1) Au, Pt, Pd, and Ni used as an impurity have an essential effect on whisker or pillar crystal growth. In the case of Pt, whisker (5 mm long × 30 μm thick, max.) and platelet crystals (400 × 1000 × 20 μm, max.) were obtained in an hour at 1150 and 1240 °C, respectively.

2) The growth directions of whiskers and platelet crystals were assigned to ⟨001⟩ and some direction in (001) plane, respectively.

3) In the case of Ni impurity, the longest pillar crystal was obtained at a substrate temperature of 1000—1020 °C, and $PCl_3/(NbCl_5+PCl_3)$ ratio of 0.7—0.75.

4) A drop-like solid was seldom found on the tip of most whiskers and pillar crystals, a layer with uniform Nb–P–Ni compositions being observed in the base of pillar crystals. It is presumed that base site VLS mechanism is responsible for the growth of NbP whiskers or pillar crystals rather than tip VLS mechanism.

References

1) R. L. Ripley, *J. Less-Common Met.*, **4**, 496 (1962).
2) E. Heinerth and W. Biltz, *Z. Anorg. Allg. Chem.*, **198**, 173 (1931).
3) N. Schönberg, *Acta Chem. Scand.*, **8**, 226 (1954).
4) H. Boller and E. Parthe, *Acta Crystallogr.*, **16**, 1095 (1963).

5) A. Reinecke, F. Wiechmann, M. Zumbusch, and W. Bilz, *Z. Anorg. Allg. Chem.*, **249**, 14 (1942).
6) H. Hartmann and W. Massig, *Z. Anorg. Allg. Chem.*, **266**, 98 (1951).
7) H. Schaefer and W. Fuhr, *J. Less-Common Met.*, **8**, 375 (1965).
8) L. G. Berry, "Inorg. Index to the Powder Diffraction File," Joint Committee on Powder Diffraction Standards, Pennsylvania (1971), Cards No. 17-882.
9) M. Hansen, "Constitution of Binary Alloys," McGraw-Hill, New York, Toronto, London (1958), pp. 1011, 1027.
10) J. Chikawa and T. Nakayama, *J. Appl. Phys.*, **35**, 2493 (1964).
11) S. Motojima, T. Wakamatsu, Y. Takahashi, and K. Sugiyama, *J. Electrochem. Soc.*, **123**, 290 (1976).
12) S. Motojima, Y. Takahashi, and K. Sugiyama, *J. Cryst. Growth*, **30**, 1 (1975).