

Growth Conditions of Nb₃Si, α -Nb₅Si₃ and NbSi₂ Single Crystals from High-Temperature Metal Solutions and Properties of the Crystals

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ABSTRACT

Nb₃Si (cubic), α -Nb₅Si₃ and NbSi₂ single crystals were prepared from high temperature tin or copper solutions using niobium metal powder and silicon powder as starting materials under an argon atmosphere. The growth conditions for obtaining single crystals of relatively large size were established. The results of chemical analysis and measurements of the unit cell dimensions and densities (d_m) are as follows:

From Sn solution: for α -Nb₅Si₃ (Nb₅Si_{3.08}) $a = 6.5703(2)$ Å, $c = 11.8848(6)$ Å, $d_m = 7.06(4)$ g·cm⁻³; for NbSi₂ (NbSi_{1.97}) $a = 4.7968(7)$ Å, $c = 6.5901(5)$ Å, $d_m = 5.60(4)$ g·cm⁻³.

From Cu solution: for Nb₃Si, $a = 4.2104(9)$ Å; for α -Nb₅Si₃ (Nb₅Si_{3.00}) $a = 6.5695(8)$ Å, $c = 11.8873(9)$ Å, $d_m = 7.07(3)$ g·cm⁻³.

The electrical resistivity (ρ) determined on Nb₅Si₃ and NbSi₂ crystals are as follows: for α -Nb₅Si₃: $\rho = 182$ $\mu\Omega \cdot \text{cm}$; for NbSi₂: $\rho = 1250$ $\mu\Omega \cdot \text{cm}$.

The oxidation of α -Nb₅Si₃ and NbSi₂ crystals begins to proceed at a measurable rate in the temperature range of about 430°C and 520°C, respectively. The final oxidation product is Nb₂O₅. In all cases, non-crystalline SiO₂ seemed to be formed during the oxidation reaction.

1. INTRODUCTION

The binary silicides of the transition metals have several unique chemical and physical properties. Among their attractive properties are relatively high melting points, chemical stability, and high electrical and thermal conductivity [1]. In the niobium-silicon system the intermediate phases Nb₃Si (cubic, tetragonal), α and β -Nb₅Si₃ (both tetragonal) and NbSi₂ (hexagonal) have been reported [2]. The simplest method of preparing single crystals of silicides, in terms of growth technology at low temperature, is provided by the crystal growth from solution in metallic melts. Recently we have prepared Cr₃Si, Cr₅Si₃ and CrSi₂ [3,4] or Mn₅Si₃, MnSi and Mn₂₇Si₄₇ [5] from starting material using the tin or copper solution technique. In the present work, we report the conditions for growing Nb₃Si (cubic), α -Nb₅Si₃ and NbSi₂ single crystals of relatively large size by the high-temperature tin or copper solution method. As-grown Nb₃Si (cubic), α -Nb₅Si₃ and NbSi₂ single crystals were used for chemical analysis and measurements of unit cell dimensions, densities, and electrical resistivity. Oxidation at high temperature in air was also studied.

2. EXPERIMENTAL DETAILS

2.1. Preparation of niobium silicides

The starting materials were niobium metal powder (particle size, -325 mesh; purity, 99.9%), silicon

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powder (particle size, -200 mesh; purity, 99.99%) and tin (purity, 99.9%) or copper chips (purity, 99.99%). Mixtures of the starting materials in various atomic ratios were placed in an Al_2O_3 crucible (purity, 99.5%) and heated in an argon atmosphere. The amount of niobium in the starting materials was fixed at 2.0 g throughout all the experiments. The temperature of the furnace was raised at a rate of $300^\circ C\ h^{-1}$ up to $1500^\circ C$. After the specimen had been kept at that temperature for 5 h and cooled to $1000^\circ C$ at a rate of $50^\circ C\ h^{-1}$, it was cooled to room temperature by switching off the electric power of the furnace. After cooling, the as-growth crystals in the reaction mixtures were separated from the solidified matrix by dissolving the excess Cu or Sn solutions in $8\ mol\ dm^{-3}$ nitric acid or $6\ mol\ dm^{-3}$ hydrochloric acid for 2-5 days. The experimental conditions for the obtained crystalline phases are shown in Table 1 and Table 2.

2.2. X-ray and chemical analyses

The crystalline phases and the unit cell dimensions were examined using a powder X-ray diffractometer (Rigaku RU-200) with monochromatic $CuK\alpha$ radiation

(wavelength $\lambda = 1.541743\ \text{\AA}$) or an XDC 1000 Guinier-Hägg focusing X-ray powder diffraction camera with strictly monochromatic $CuK\alpha_1$ radiation (wavelength $\lambda = 1.5405981\ \text{\AA}$) and semi-conductor grade silicon (purity, 99.9999%, $a = 5.431065\ \text{\AA}$) as internal calibration standard. The Guinier-Hägg film was used for measuring X-ray diffraction intensities which was performed with a Line Scanner (model LS-18). The relative amounts of the product phases can be assumed to be proportional to the relative intensities of the phases disregarding absorption and possibly preferred orientation effects. The non-overlapping diffraction lines I_{111} (Nb_3Si), I_{213} ($\alpha-Nb_5Si_3$) and I_{110} (Nb) for Cu solution, and I_{210} (Nb_3Sn), I_{800} ($NbSn_2$), I_{213} ($\alpha-Nb_5Si_3$), I_{111} ($NbSi_2$) and I_{111} (Si) for Sn solution were selected for calculation of the relative intensities. Some crystals were examined to collect data on crystal plane orientations or other crystal data using Weissenberg and oscillation cameras, and a four-circle type automatic diffractometer (Rigaku AFC-6), equipped with a graphite monochromator using $MoK\alpha$ radiation (wavelength $\lambda = 0.710678\ \text{\AA}$). The crystal morphology was examined by a binocular microscope and a scanning electron microscope (SEM) (Hitachi S-

Table 1
Preparation conditions of niobium silicide crystals from molten tin solution

Composition of starting material (Atomic ratio)		Phases identified
Si/Nb	Sn/Nb	
0.3	15.65	Nb_3Sn , $NbSn_2$
0.6	15.65	$NbSn_2$, Nb_3Sn , $\alpha-Nb_5Si_3$
0.8	15.65	$\alpha-Nb_5Si_3$, $NbSn_2$, $NbSi_2$
1.0	15.65	$\alpha-Nb_5Si_3$, $NbSi_2$, $NbSn_2$
1.5	15.65	$NbSi_2$, $\alpha-Nb_5Si_3$
1.8	15.65	$NbSi_2$, $\alpha-Nb_5Si_3$
2.0	15.65	$NbSi_2$, $\alpha-Nb_5Si_3$
2.1	15.65	$NbSi_2$
2.2	15.65	$NbSi_2$, Si
3.0	15.65	$NbSi_2$, Si

Nb: 2.0 g, Silicon: 0.202~1.814 g, Sn: 40 g
Soaking temperature: $1500^\circ C$, Soaking time: 5h

Table 2
Preparation conditions of niobium silicide crystals from molten copper solution

Composition of starting material (Atomic ratio)		Phases identified
Si/Nb	Cu/Nb	
0.2	29.24	α -Nb ₅ Si ₃ , Nb, Nb ₃ Si
0.3	29.24	α -Nb ₅ Si ₃ , Nb, Nb ₃ Si
0.4	29.24	α -Nb ₅ Si ₃ , Nb, Nb ₃ Si
0.5	29.24	α -Nb ₅ Si ₃ , Nb ₃ Si, Nb
0.6	29.24	α -Nb ₅ Si ₃ , Nb ₃ Si
0.7	29.24	α -Nb ₅ Si ₃ , Nb ₃ Si
1.0	29.24	α -Nb ₅ Si ₃ , Nb ₃ Si
1.5	29.24	α -Nb ₅ Si ₃ , Nb ₃ Si
1.8	29.24	α -Nb ₅ Si ₃
2.0	29.24	α -Nb ₅ Si ₃
2.5	29.24	α -Nb ₅ Si ₃
3.0	29.24	α -Nb ₅ Si ₃

Nb: 2.0 g, Silicon: 0.121~1.814 g, Cu: 40 g
Soaking temperature: 1500°C, Soaking time: 5h

4000). The chemical composition of crystals was determined by an electron probe microanalyzer (EPMA) (JEOL JSM-35C). Possible incorporation of Sn and Cu atoms into the crystals grown, which might come from the metal solutions, were checked with EPMA. The density of the crystals was measured by a pycnometer method with distilled water at room temperature. The X-ray density was determined using the results of the unit cell dimension measurements.

2.3. Properties

2.3.1. Electrical resistivity

The electrical resistivity of as-grown α -Nb₅Si₃ and NbSi₂ crystals was measured by a direct-current four-probe technique at room temperature in air.

2.3.2. Oxidation in air

Thermogravimetric (TG) analysis and differential thermal analysis (DTA) were performed up to 1200°C to study the oxidation of crystals in air. Specimens of about 25 mg were heated at a rate of 10°C·min⁻¹. The

oxidation products were analyzed by powder X-ray diffraction.

3. RESULTS AND DISCUSSION

3.1. Compounds of the Nb-Si system obtained from tin solution

The synthesis was performed under constant conditions of soaking temperature 1500°C, soaking time 5 h, cooling rate 50°C·h⁻¹ and an atomic ratio Sn/Nb = 15.65. The atomic ratio Si/Nb in the starting material was varied from 0.3 to 3.0. The X-ray evidence for the crystalline phases obtained are presented in Table 1 and Fig. 1. As seen from Table 1 and Fig. 1, five compounds, i.e., Nb₃Sn, NbSn₂, α -Nb₅Si₃, NbSi₂ and Si, were formed, while Nb₃Si and β -Nb₅Si₃ did not form from tin solution. The variation of the atomic ratio of the starting materials gave different product phases. With increased silicon concentration, more silicon-rich phases are formed. NbSi₂ crystals were obtained as a single-phase product for an atomic ratio of Si/Nb = 2.1. The α -Nb₅Si₃ crystals were

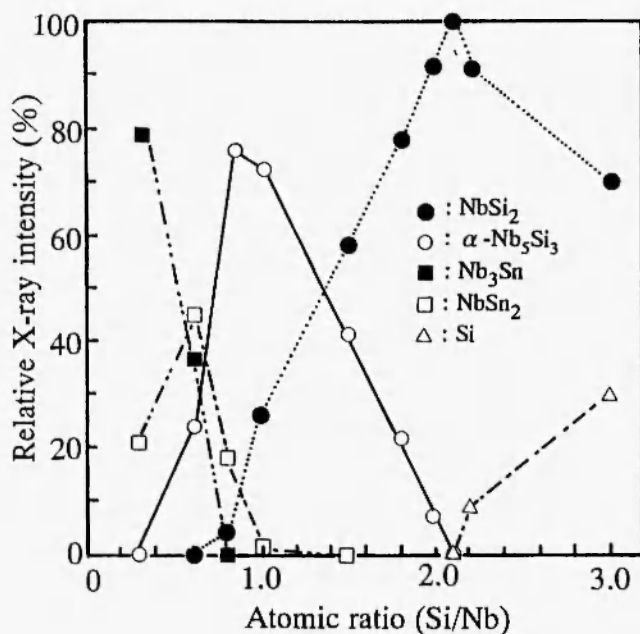


Fig. 1: Relative X-ray intensity of each phase in the products obtained from several starting materials with various compositions. The starting materials are heated at 1500°C for 5 h. (Sn solution)

invariably obtained as a phase mixture from the starting material with the atomic ratios $\text{Si/Nb} = 0.6 - 2.0$. The relative X-ray intensity of formed $\alpha\text{-Nb}_5\text{Si}_3$ became remarkably large between $\text{Si/Nb} = 0.8$ and $\text{Si/Nb} = 1.0$. However, $\alpha\text{-Nb}_5\text{Si}_3$ crystals were obtained as a phase mixture together with crystals of NbSn_2 and Nb_3Sn or NbSi_2 . The relative X-ray intensity of formed $\alpha\text{-Nb}_5\text{Si}_3$ became remarkably large for soaking temperature 1500°C, soaking time 5 h, and the atomic ratio of the starting material: $\text{Si/Nb} = 0.8$ and $\text{Sn/Nb} = 15.65$, respectively.

Most of the $\alpha\text{-Nb}_5\text{Si}_3$ crystals were obtained as cubic crystals having (001) faces (Fig. 2-A). The largest $\alpha\text{-Nb}_5\text{Si}_3$ crystals prepared had maximum dimensions of about $0.1 \text{ mm} \times 0.1 \text{ mm} \times 0.15 \text{ mm}$. The single crystals of NbSi_2 were obtained as irregularly shaped polyhedral crystals (Fig. 2-B). The largest NbSi_2 crystals prepared in the present work attained maximum dimensions of about $0.06 \text{ mm} \times 0.06 \text{ mm} \times 0.07 \text{ mm}$. The $\alpha\text{-Nb}_5\text{Si}_3$ and NbSi_2 crystals obtained from Sn solution are gray and have a metallic luster.

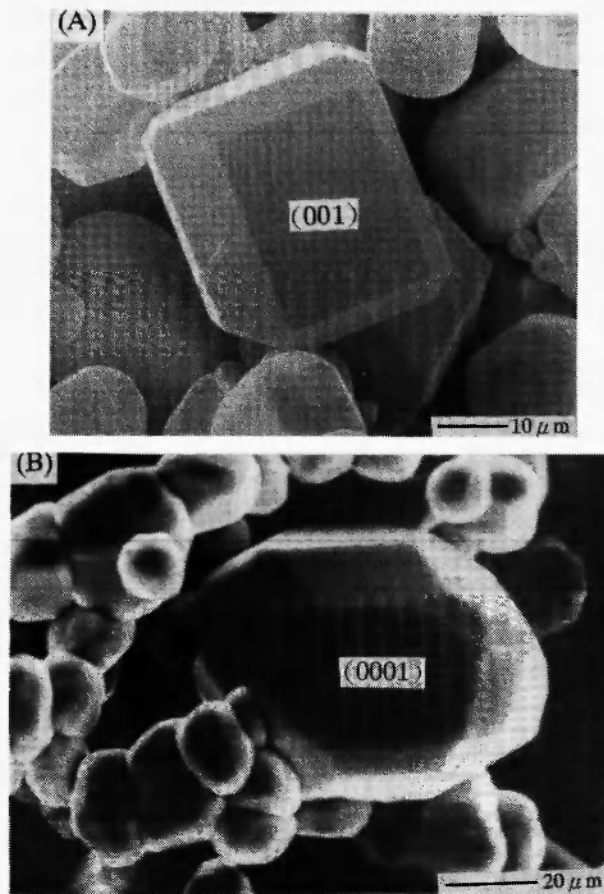


Fig. 2: SEM photographs of $\alpha\text{-Nb}_5\text{Si}_3$ (A) and NbSi_2 (B) single crystals. (Metal Sn solution)

3.2. Compounds of the Nb-Si system obtained from copper solution

The synthesis was performed under constant conditions of soaking temperature 1500°C, soaking time 5 h, cooling rate $50^\circ\text{C} \cdot \text{h}^{-1}$ and an atomic ratio $\text{Cu/Nb} = 29.24$. The atomic ratio Si/Nb in the starting material was varied from 0.2 to 3.0. The crystalline phases obtained were identified by X-ray powder diffraction. The results are listed in Table 2, and typical X-ray diffraction patterns are shown in Fig. 3. As seen from Table 2 and Fig. 3, only the two silicides Nb_3Si (cubic) and $\alpha\text{-Nb}_5\text{Si}_3$ are formed within the Si/Nb range of 0.2 to 3.0. It is shown that the more silicon-rich phases form for the larger Si/Nb values in the starting materials in a similar manner to that observed in the chromium-silicon system /4/. $\alpha\text{-Nb}_5\text{Si}_3$ crystals

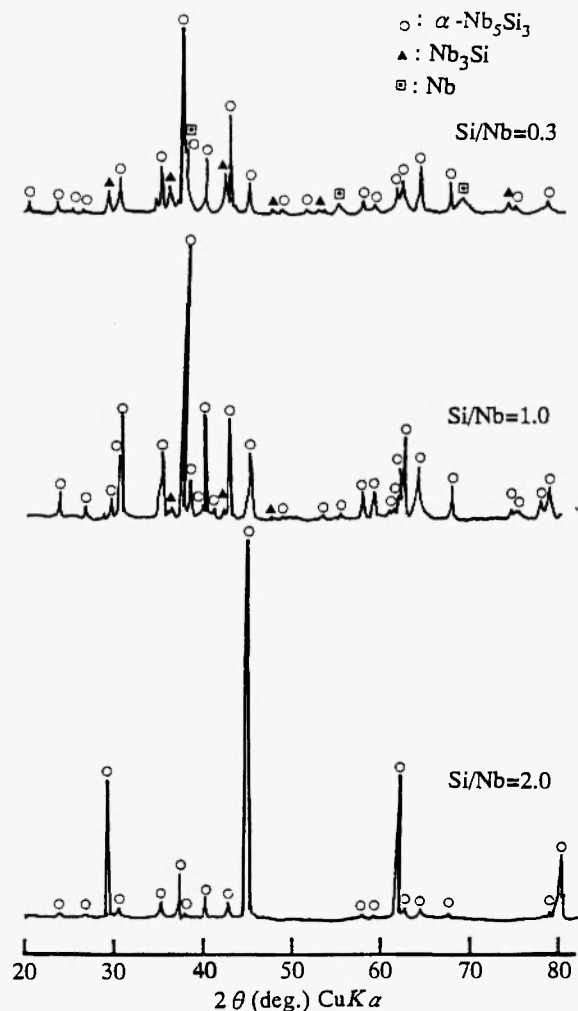


Fig. 3: X-ray diffraction patterns of compounds of Nb-Si system obtained at 1500°C for 5 h. (Cu solution).

were obtained as a single-phase product for atomic ratios Si/Nb = 1.8 - 3.0. Nb₃Si crystals were obtained from the starting material with the atomic ratios Si/Nb = 0.2 - 1.5. However, the Nb₃Si crystal was always obtained as a mixture with other phases. X-ray diffraction patterns of Nb₃Si became prominent for the product material obtained from the starting material with atomic ratio Si/Nb = 0.6.

The optimum atomic ratios of the starting materials for growing Nb₃Si single crystals are Si/Nb = 0.6 and Cu/Nb = 29.24.

The Nb₃Si crystals are gray and have a metallic luster. Cubic single crystals of Nb₃Si are surrounded by (100) and (110) faces (Fig. 4). The largest Nb₃Si

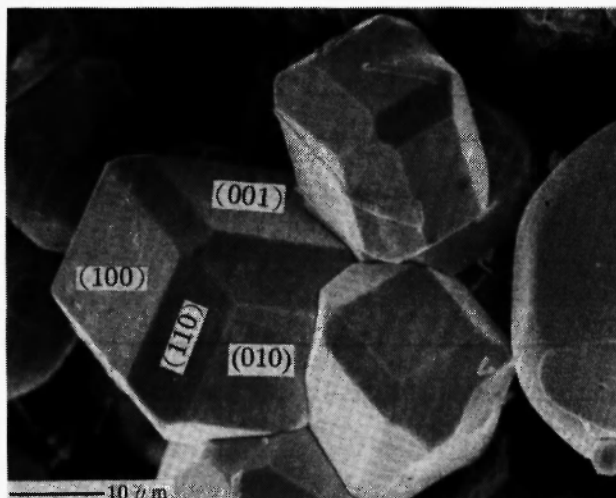


Fig. 4: SEM photograph of Nb₃Si single crystals. (Metal Cu solution)

crystals prepared had maximum dimensions of about 0.1 mm × 0.2 mm × 0.2 mm. The α-Nb₅Si₃ crystals were generally obtained in prismatic shape extending in the <001> direction and thin plate-like crystals having well-developed (001) faces (Fig. 5). The largest α-Nb₅Si₃ crystals prepared in the present work attained maximum dimensions of about 0.2 mm × 0.4 mm × 2.4 mm.

3.3. Unit cell dimensions, densities and compositions of niobium silicides

The basic crystal data, densities and chemical compositions of niobium silicides are listed in Table 3. The cell dimensions of Nb₃Si, α-Nb₅Si₃ and NbSi₂ crystals obtained are in good agreement with previously published data ($a = 4.211 \text{ \AA}$, $V = 74.67 \text{ \AA}^3$ for Nb₃Si; $a = 6.5698 \text{ \AA}$, $c = 11.887 \text{ \AA}$, $V = 513.07 \text{ \AA}^3$ for α-Nb₅Si₃; $a = 4.7971 \text{ \AA}$, $c = 6.592 \text{ \AA}$, $V = 131.37 \text{ \AA}^3$ for NbSi₂) [6]. The EPMA results seem to indicate that the niobium silicides have appreciable homogeneity ranges. The expected variations of the unit cell dimensions were, however, not observed and conclusive evidence is thus not reported. Although the impurity content of Nb₃Si, α-Nb₅Si₃ and NbSi₂ crystals was not analyzed chemically, the EPMA established the occurrence of traces of iron, calcium and aluminium, while tin and copper were found to lie below the detection limit (<0.05%). Consequently, the solid solubility of tin or

Table 3
Basic data and chemical analysis of niobium silicides

Metal solution	Cu	Cu	Sn	Sn
Formula unit	Nb_3Si	$\alpha-Nb_5Si_3$	$\alpha-Nb_5Si_3$	$NbSi_2$
Crystal system	cubic	tetragonal	tetragonal	hexagonal
a (Å)	4.2104(9)	6.5695(8)	6.5703(2)	4.7968(7)
b (Å)	-	-	-	-
c (Å)	-	11.8873(9)	11.8848(6)	6.5901(5)
V (Å ³)	74.64(2)	513.04(2)	513.05(4)	131.32(4)
Space group	Pm3m	I4/mcm	I4/mcm	P6 ₂ 22
dx -ray (g · cm ⁻³)	6.826(2)	7.105(3)	7.104(3)	5.655(1)
dm (g · cm ⁻³) ^{a)}	-	7.07(3)	7.06(4)	5.60(4)
Z	1	4	4	3
Nb (wt%) ^{b)}	-	84.65	84.30	62.63
Si (wt%) ^{b)}	-	15.35	15.70	37.37
Chemical composition	-	$Nb_5Si_{3.00}$	$Nb_5Si_{3.08}$	$NbSi_{1.97}$

^{a)} Pycnometer method

^{b)} EPMA results

Table 4
The electrical resistivity of $\alpha-Nb_5Si_3$ and $NbSi_2$ crystals

$\alpha-Nb_5Si_3$ (from Cu solution)	182 $\mu\Omega \cdot cm$
$NbSi_2$ (from Sn solution)	1250 $\mu\Omega \cdot cm$
$NbSi_2$	50.4(2.3) $\mu\Omega \cdot cm$ ^{a)}

^{a)} : G. V. Samsonov and I. M. Vinitiskii, * Handbook of Refractory Compounds*, IFI/Plenum, New York (1980) p.142

copper solution in niobium silicides is extremely low.

3.4. Properties

3.4.1. Electrical resistivity

The electrical resistivity of as-grown crystals was measured in parallel to the $\langle 001 \rangle$ direction for $\alpha-Nb_5Si_3$ and in several directions on the c planes for $NbSi_2$. The electrical resistivities are listed in Table 4 together with previously published data [6].

3.4.2. Oxidation in air

Single crystals of sizes in the range 53 - 150 μm

were used to examine the oxidation of crystals in air. The results of the TG and DTA studies are shown in Fig. 6. The oxidation reaction of the $\alpha-Nb_5Si_3$ and $NbSi_2$ crystals began to proceed at about 430°C and 520°C, respectively. In contrast, the exothermic peak of the DTA curve was found at about 450°C, 660°C, 730°C and 880°C for $\alpha-Nb_5Si_3$, and at about 720°C, 820°C and 950°C for $NbSi_2$. The crystals were heated for 5 min at temperature intervals of 50°C between 400°C and 1200°C, and the oxidation products were analyzed by a powder X-ray diffractometer at room temperature. Typical X-ray diffraction patterns of the oxidation products of $\alpha-Nb_5Si_3$ crystals are shown in Fig. 7. In all cases, the identified oxidation product was

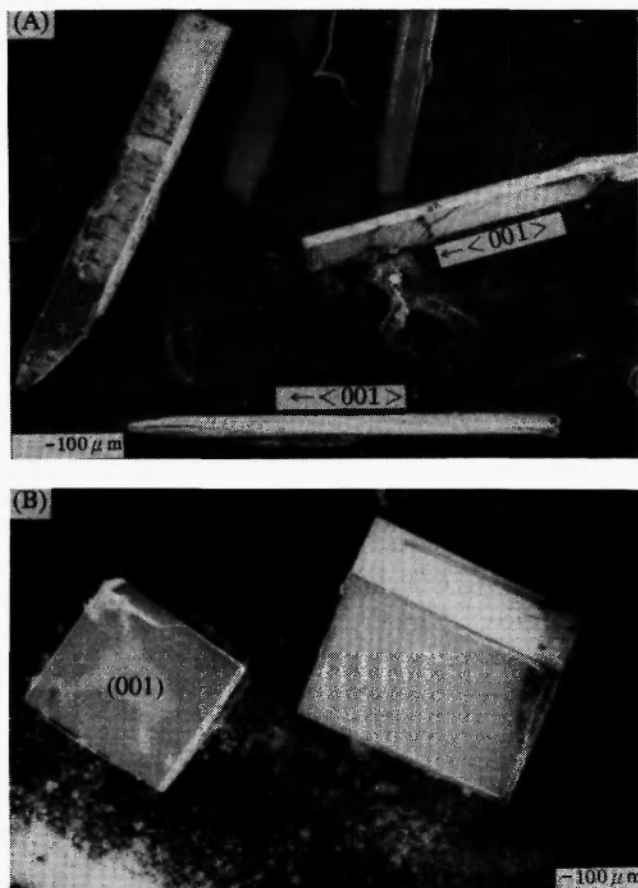


Fig. 5: SEM photographs of α -Nb₅Si₃ single crystals. (Metal Cu solution)

found to be Nb₂O₅. Although a SiO₂ phase was not detected by X-ray diffraction, noncrystalline SiO₂ was probably formed during the oxidation reaction.

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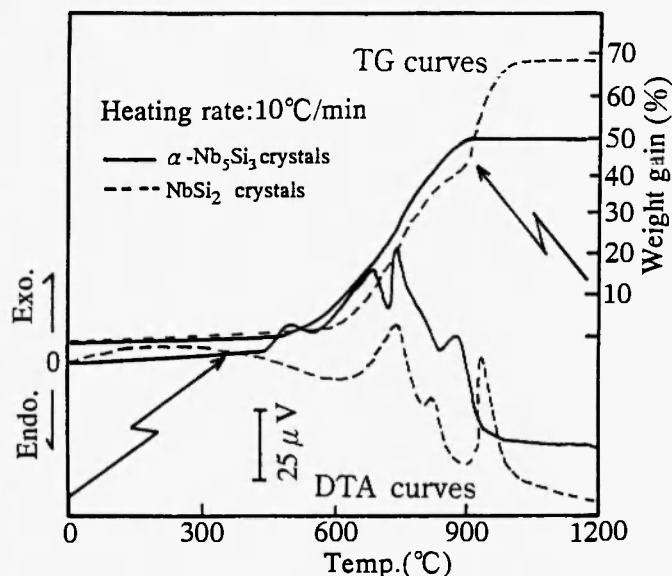


Fig. 6: Differential thermal analysis and thermal gravimetric curves of α -Nb₅Si₃ and NbSi₂ crystals heated in air.

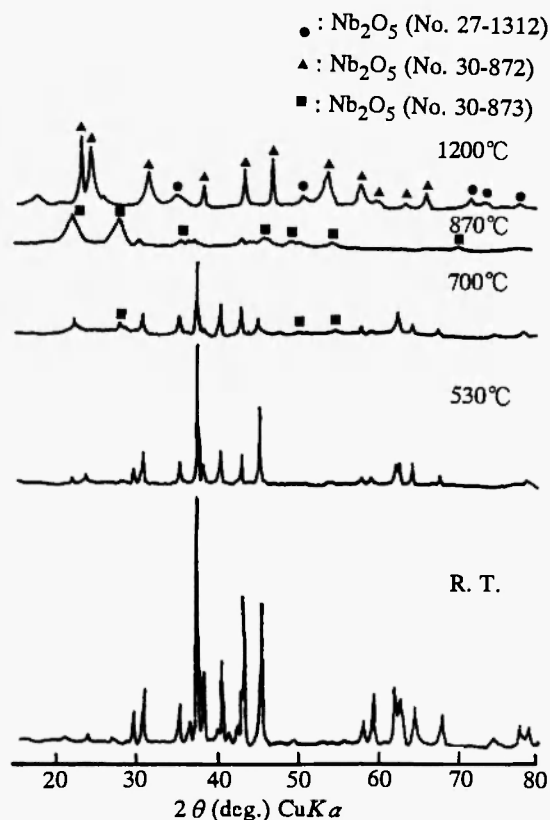


Fig. 7: X-ray diffraction patterns of oxidation products of α -Nb₅Si₃ single crystals heated at 530°C, 700°C, 870°C and 1200°C for 5 min in air.

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