

Single Crystals of Vanadium Silicides Prepared by High-Temperature Metal Flux Method and Property Measurements

Shigeru OKADA*¹, Kunio KUDOU*² and Masaaki MIYAMOTO*³

高温度金属フラックス法で合成したバナジウムケイ化物単結晶と特性測定

岡田 繁*¹・工藤 邦男*²・宮本 正章*³

Abstracts: Crystals of binary vanadium silicides were grown from high-temperature tin and copper metal fluxes under an argon atmosphere using vanadium metal chips and silicon powder as starting materials. The crystals grown were V_3Si , V_5Si_3 and VSi_2 . The growth conditions for obtaining single crystals of relatively large size were established. The as-grown V_3Si , V_5Si_3 and VSi_2 crystals were used for chemical analysis and measurements of unit cell parameters. The chemical analyses of the crystals are discussed. Densities, micro-Vickers hardness and electrical resistivity were determined on V_5Si_3 crystals, and oxidation at high temperature in air was studied for V_5Si_3 and VSi_2 crystals. The unit cell parameters are as follows:

From Sn flux: for V_5Si_3 $a=0.9429(1)\text{nm}$, $c=0.4758(1)\text{nm}$, $V=422.9(1)\times 10^{-3}\text{nm}^3$; for VSi_2 $a=0.4573(1)\text{nm}$, $c=0.6372(1)\text{nm}$, $V=115.4(1)\times 10^{-3}\text{nm}^3$.

From Cu flux: for V_3Si $a=0.4725(1)\text{nm}$, $V=105.5(1)\times 10^{-3}\text{nm}^3$; for V_5Si_3 $a=0.9428(1)\text{nm}$, $c=0.4757(1)\text{nm}$, $V=422.9(1)\times 10^{-3}\text{nm}^3$.

The largest crystals were obtained of V_5Si_3 (about $0.2\text{mm}\times 0.2\text{mm}\times 10.3\text{mm}$), but for the other phases the crystals were smaller. The micro-Vickers hardness value on (110) planes of V_5Si_3 is $12.3(1)\text{GPa}$. The electrical resistivity determined on V_5Si_3 crystal is $17.6(\pm 0.7)\mu\Omega\text{cm}$. The oxidation of V_5Si_3 and VSi_2 crystals starts to proceed at a measurable rate in the temperature range of about 355°C and 515°C , respectively. The final oxidation product is V_2O_5 . In all cases, non-crystalline SiO_2 seemed to be formed during the oxidation reaction.

Keywords: V_3Si , V_5Si_3 , VSi_2 , Tin-flux, Copper-flux, Single crystal, Morphology, Unit cell parameter, Chemical analysis, Oxidation in air

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, high thermal stability, and high elec-

trical and thermal conductivity^{1),2)}. However, the data available on these properties are in most cases obtained from measurements on sintered samples or polycrystalline layers and they are often contradictory. It is therefore necessary to grow crystals, the study of which could provide reliable information on the properties and the ways in which they can be modified³⁾. In the vanadium-silicon system the intermediate phases V_3Si (cubic; space group $Pm\bar{3}n$), V_5Si_3 (tetragonal; space group $I4/mcm$), V_6Si_5 (tetragonal; space group $Immm$ or $Ibam$) and VSi_2 (hexagonal; space group $P6_222$) have been reported⁴⁾⁵⁾. The V-Si diagram shown in Fig. 1 is that given by Smith (1989)⁴⁾. The binary silicides have been synthesized by solid state reaction, chemical vapour deposition, Bridgman method, floating zone

*¹ 工学部土木工学科 助教授 工学博士
Department of Civil Engineering, Faculty of Engineering, Associate Professor, Dr. of Engineering

*² 神奈川大学工学部機械工学科 助手 工学博士
Department of Mechanical Engineering, Faculty of Engineering, Kanagawa University, Research Associate, Dr. of Engineering

*³ 工学部電気工学科 教授
Department of Electrical Engineering, Faculty of Engineering, Professor

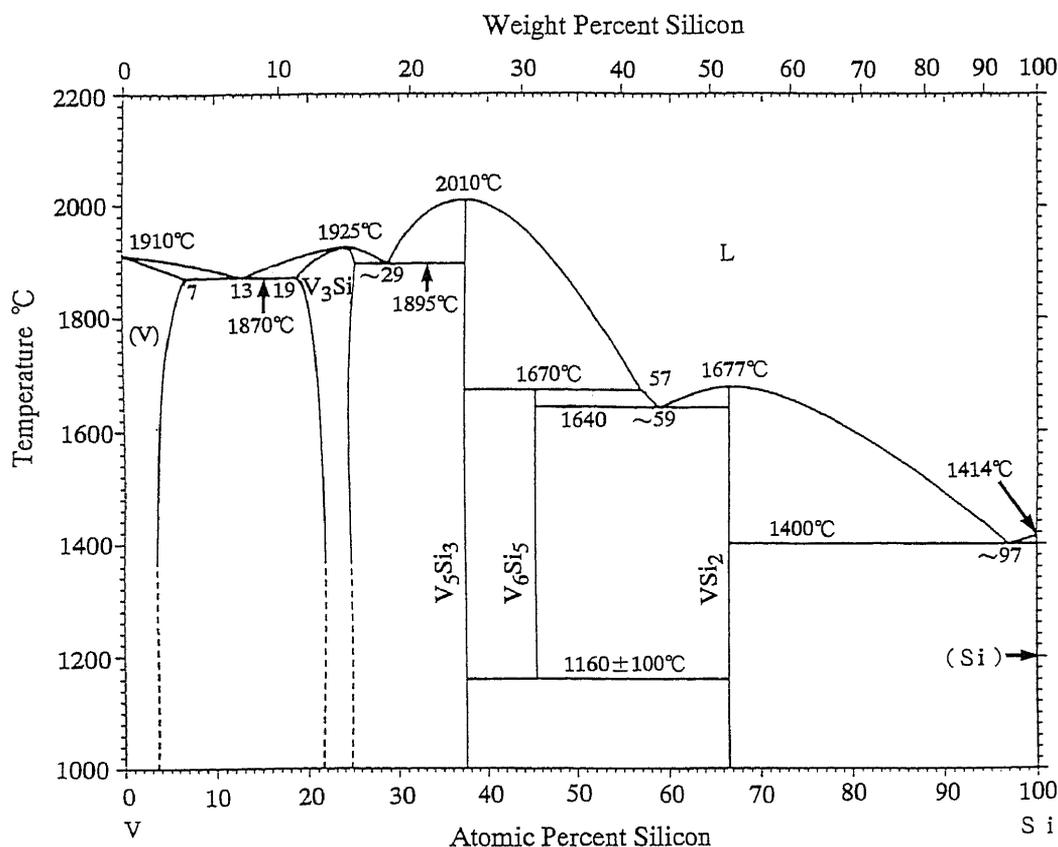


Fig. 1 V-Si phase diagram.

method and from a flux in metallic melts. The simplest method of preparing single crystals of metal silicides, in terms of growth technology at low temperature, is provided by the crystal growth from flux in metallic melts. Recently we have prepared Cr₃Si, Cr₅Si₃ and CrSi₂^{6,7)}, Mn₅Si₃, MnSi and Mn₂₇Si₄₇⁸⁾, Nb₃Si, α -Nb₅Si₃ and NbSi₂⁹⁾ from starting material using the tin or copper flux method. In the present work, we report the conditions for growing V₃Si, V₅Si₃ and VSi₂ single crystals were characterized as regards crystal size, crystal morphology, chemical composition, unit cell parameters. Micro-Vickers hardness and electrical resistivity of the crystals were measured and the oxidation at high temperature in air was examined.

2. Experimental Details

2.1 Sample preparation of vanadium silicides

The starting materials were vanadium metal chips (purity, 99.5%), silicon powder (purity, 99.99%, particle size, <75 μ m) and tin (purity, 99.9%) or copper chips (purity, 99.99%). The amount of vanadium in the starting materials was fixed at 2.0 g throughout all the experiments. Mixtures of the starting materials in various atomic ratios were placed in a dense Al₂O₃ crucible (purity, 99.5%).

The crucible was inserted into a vertical electric furnace. Purified Ar gas flowed in the furnace as a protecting atmosphere against oxidation^{10)~12)}. The temperature of the furnace was heated at a rate of 300°C h⁻¹ and held at 1400°C for 5 h. The solution was cooled to room temperature at a rate of 50°C h⁻¹. After cooling, the as-grown crystals in the reaction mixtures were separated from the solidified matrix by dissolving the excess Cu or Sn solutions in dilute nitric acid or hydrochloric acid. The experimental conditions for the obtained crystalline phases are shown in Table 1 and Table 2.

2.2 Characterization

The crystalline phases and the unit cell parameters were examined using a powder X-ray diffractometer (Rigaku RU-200) with monochromatic CuK α radiation ($\lambda=0.154183$ nm) or an XDC-700 Guinier-Hägg focusing X-ray powder diffraction camera with strictly monochromatic CrK α_1 radiation ($\lambda=0.228975$ nm) and ultra-pure silicon powder (purity, 99.9999%, $a=0.357107$ nm) as an internal calibration standard¹³⁾. The unit cell parameters were refined by the least-squares method using the local program UNITCELL¹⁴⁾. The relative amounts of the product phases can be assumed to be proportional to the relative intensities of the phases disregarding

Table 1 Preparation conditions of vanadium silicide crystals from molten tin flux

Composition of starting material (atomic ratio)		Phases identified
Si/V	Sn/V	
0.3	6.44	V ₅ Si ₃ , V ₂ Sn ₃ , V
0.5	6.44	VSi ₂ , V ₅ Si ₃ , V
0.8	6.44	VSi ₂ , V ₅ Si ₃ , V
1.0	6.44	VSi ₂ , V ₅ Si ₃
1.5	6.44	VSi ₂ , V ₅ Si ₃
1.8	6.44	VSi ₂ , V ₅ Si ₃
2.0	6.44	VSi ₂
2.2	6.44	VSi ₂ , Si
2.5	6.44	VSi ₂ , Si
3.0	6.44	VSi ₂ , Si

Soaking temperature: 1400°C, Soaking time: 5 h.

Table 2 Preparation conditions of vanadium silicide crystals from molten copper flux

Composition of starting material (atomic ratio)		Phases identified
Si/V	Cu/V	
0.3	12.92	V ₃ Si, V ₅ Si ₃ , V
0.5	12.92	V ₃ Si, V ₅ Si ₃ , V
0.8	12.92	V ₃ Si, V ₅ Si ₃ , V
1.0	12.92	V ₅ Si ₃ , V ₃ Si
1.5	12.92	V ₅ Si ₃ , V ₃ Si
1.8	12.92	V ₅ Si ₃ , V ₃ Si
2.0	12.92	V ₅ Si ₃ , V ₃ Si
2.2	12.92	V ₅ Si ₃ , V ₃ Si
2.5	12.92	V ₅ Si ₃
3.0	12.92	V ₅ Si ₃

Soaking temperature: 1400°C, Soaking time: 5 h.

ing absorption and possible preferred orientation effects. The non-overlapping diffraction lines I_{211} (V₃Si), I_{411} (V₅Si₃) and I_{110} (V) for Cu solution, and I_{411} (V₅Si₃), I_{111} (VSi₂) 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 α radiation ($\lambda=0.071078$ nm). The crystals morphology was examined in a binocular microscope and a scanning electron microscope (SEM) (Hitachi S-4000). Electron microprobe analysis was performed in a scanning electron microscope equipped with an energy-dispersive detector (EDX) (Horiba EMAX-2770) to perform elemental analysis on the final samples. Five or six samples were prepared with different compositions within each atomic ratio of the starting materials (Table 1 and Table 2) and one of them was used as representative in the phase analysis. Possible incorporation of Sn and Cu atoms into the crystals grown, which might come from the metal solutions, were checked with EDX. The X-ray density was calculated using the results of the unit cell parameter measurements. The micro-Vickers hardness (MVH) of the as-grown V₅Si₃ single crystals was measured using a Vickers diamond indenter at room temperature. A load of 0.98 N was applied for 15 sec at about 5 to 8 points of crystal, and values obtained were averaged. The electrical resistivity of as-grown V₅Si₃ crystal was measured by a direct-current four-probe technique at room temperature in air. Thermogravimetric (TG) analy-

sis and differential thermal analysis (DTA) were performed between room temperature and 1200°C to study the oxidation resistivity of crystals in air. Powders were prepared by grinding in an agate mortar. A pulverized specimen of about 25 mg was heated at a rate of 10°C min⁻¹.

3. Results and discussion

3.1 Compounds of the V-Si system obtained from tin flux

The synthesis was performed under constant conditions of soaking temperature 1400°C, soaking time 5 h, cooling rate 50°C h⁻¹ and an atomic ratio Sn/V=6.44. The atomic ratio Si/V in the starting material was varied from 0.3 to 2.0. The X-ray phase analytical data are presented in Table 1. As seen from Table 1, V₅Si₃, VSi₂, V₂Sn₃ (orthorhombic; space group *Fddd*), V (cubic; space group *Im3m*) and Si (cubic; space group *Ia3*) were formed in silicon-poor compositions, while V₃Si, V₆Si₅ and V₃Sn (hexagonal) crystals were not detected. VSi₂ crystals were obtained as single phase product for atomic ratio Si/V=2.0. The relative X-ray intensity of formed V₅Si₃ reached a maximum at Si/V=0.3. However, V₅Si₃ crystals were obtained as a phase mixture together with crystals of V and V₂Sn₃ (at Si/V=0.3) or VSi₂ and V (at Si/V=0.5–0.8). VSi₂ was obtained together with V₅Si₃ for Si/V=1.0–1.8 and Si for Si/V=2.2–3.0. The relative X-ray intensity of formed V₅Si₃ displayed its maximum for soaking temperature 1400°C, soaking time 5 h, and the atomic ratios of the starting material: Si/V=0.3 and Sn/V=6.44, respectively.

The V₅Si₃ and VSi₂ crystals are silver-grey in

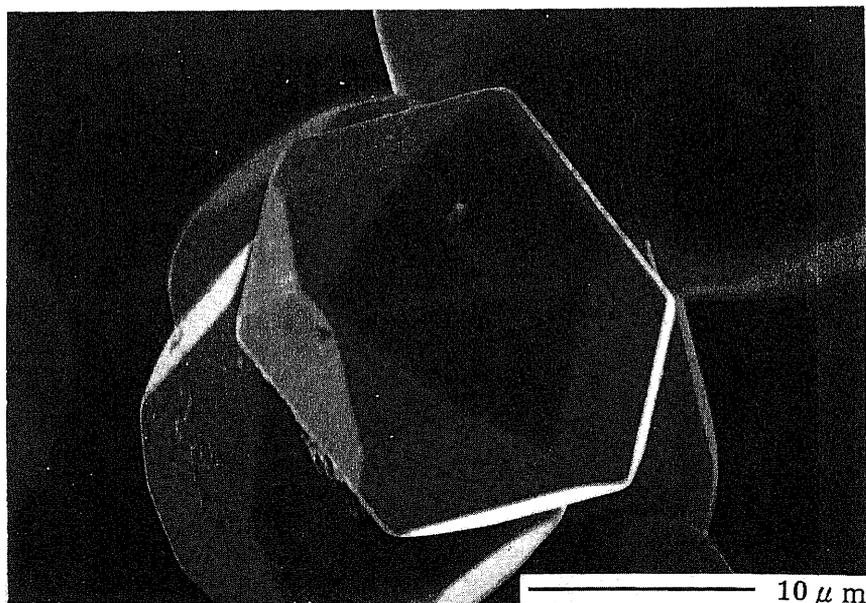


Fig. 2 SEM photograph of VSi_2 crystal. (Sn flux)

colour and have a metallic luster. The V_5Si_3 crystals were obtained as irregularly shaped polyhedral crystals. The single crystals of VSi_2 are obtained as hexagonal polyhedral crystals (Fig. 2). The V_5Si_3 and VSi_2 crystals prepared had maximum dimensions of 20–30 μm .

3.2 Compounds of the V-Si system obtained from copper flux

The synthesis was performed under constant conditions of soaking temperature 1400°C, soaking time 5 h, cooling rate 50°C h⁻¹ an atomic ratio Cu/V=12.92, and the atomic ratio Si/V=0.3–3.0. 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 binary silicides V_3Si (cubic) and V_5Si_3 (tetragonal) are formed within the Si/V range of 0.3 to 3.0. V_3Si crystals were obtained from the starting materials with the atomic ratios Si/V=0.3 to 2.0. However, the V_3Si crystal was always obtained as a mixture with other phases. The relative X-ray diffraction intensities of V_3Si had a maximum, when the product was obtained from the starting material with atomic ratio Si/V=0.3. The optimum atomic ratios of the starting materials for growing V_3Si single crystals are Si/V=0.3 and Cu/V=12.92. V_5Si_3 crystals were obtained as a single phase product for atomic ratios Si/V=2.5–3.0.

The V_3Si and V_5Si_3 crystals are silver-grey in colour and have a metallic luster. The V_3Si crystals were obtained as polyhedral crystals having (110) faces (Fig. 4). The largest V_3Si crystals prepared had maximum dimensions of about 30 μm . The single

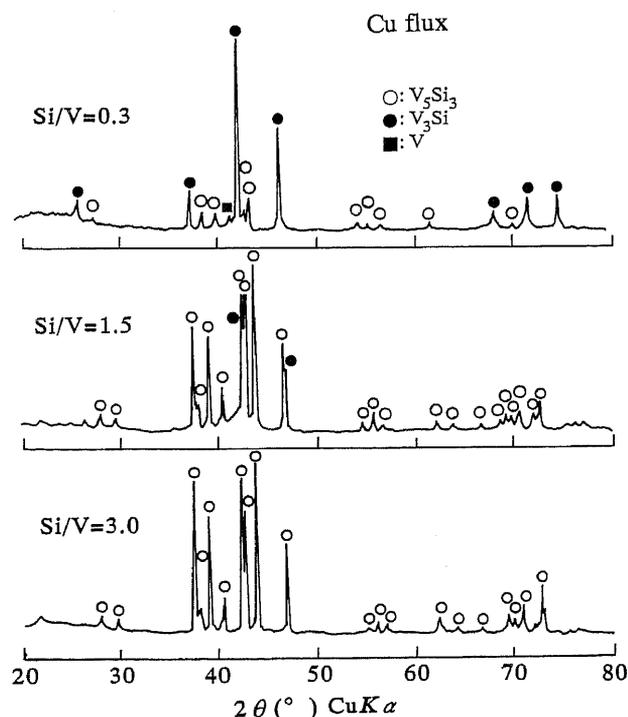


Fig. 3 X-ray diffraction patterns for compounds of V-Si system prepared at 1400°C for 5 h.

crystals of V_5Si_3 obtained in prismatic shape extending in the $\langle 001 \rangle$ direction (Fig. 5). The largest V_5Si_3 crystal obtained had maximum dimensions of about 0.2 mm × 0.2 mm × 10.3 mm.

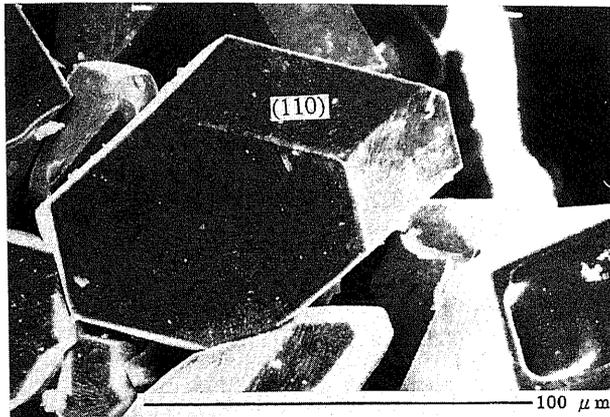


Fig. 4 SEM photograph of V_3Si crystal. (Cu flux)

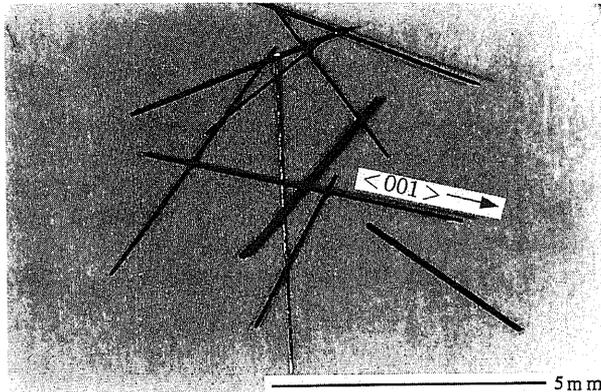


Fig. 5 Stereomicroscope photograph of V_5Si_3 crystals. (Cu flux)

3.3 Unit cell parameters, densities and compositions of vanadium silicides

The basic crystal data, densities and chemical compositions of vanadium silicides are listed in **Table 3** and **Table 4**. The unit cell parameters of V_3Si , V_5Si_3 and VSi_2 crystals obtained are in good agreement with previously published data ($a=0.47253$ nm, $V=105.5 \times 10^{-3}$ nm³ for V_3Si ; $a=0.47276$ nm, $c=0.47555$ nm, $V=422.7 \times 10^{-3}$ nm³ for V_5Si_3 ; $a=0.45723(2)$ nm, $c=0.63730(4)$ nm, $V=115.4(2) \times 10^{-3}$ nm³ for VSi_2)¹⁵. The EPMA results seem to indicate that the vanadium silicides have appreciable homogeneity ranges. The expected variations of the unit cell parameters with composition were not observed, and thus conclusive evidence for homogeneity ranges is not reported. Although the impurity content of V_3Si , V_5Si_3 and VSi_2 crystals was not analyzed chemically, the EPMA established the occurrence of traces of calcium, magnesium, iron and aluminum, while tin and copper were found to lie below the detection limit ($<0.05\%$). Consequently, the solid solubility of tin or copper in vanadium silicides is extremely low.

Table 3 The unit cell parameters and densities of vanadium silicides

Metal flux	Sn	Sn	Cu	Cu
Formula unit	V_5Si_3	VSi_2	V_3Si	V_5Si_3
Crystal system	tetragonal	hexagonal	cubic	tetragonal
a (nm)	0.9429(1)	0.4573(1)	0.4725(1)	0.9428(1)
b (nm)	-	-	-	-
c (nm)	0.4758(1)	0.6372(1)	-	0.4757(1)
V ($\times 10^{-3}$ nm ³)	422.9(1)	115.4(1)	105.5(1)	422.9(1)
Space group	$I4/mcm$	$P6_222$	$Pm3n$	$I4/mcm$
Z	4	3	2	4
dx-ray (g cm ⁻³)	5.323(3)	4.623(3)	5.694(2)	5.322(2)
dm (g cm ⁻³ *)	-	4.59(3)	-	5.28(3)

*): Pycnometer method

Table 4 The results of the chemical analysis of vanadium silicides

Metal flux	Sn	Sn	Cu	Cu
Formula unit	V_5Si_3	VSi_2	V_3Si	V_5Si_3
V (wt%)*	75.5	47.3	-	75.3
Si (wt%)*	24.5	52.7	-	24.7
Chemical composition	$V_5Si_{2.94}$	$VSi_{2.02}$	-	$V_5Si_{2.97}$

*): EPMA results

3.4 Properties

The micro-Vickers hardness (MVH) of the as-grown V_5Si_3 (Si/V=1.5) crystals was measured in several direction on the (110) plane. The MVH values as measured on the (110) plane of V_5Si_3 crystals are found to be $12.3(\pm 0.1)$ GPa, which is somewhat lower than the value of $14.3(\pm 0.8)$ GPa reported in Ref. 15. The literature values, however, probably refer to polycrystalline samples.

The electrical resistivity of as-grown crystals was measured in parallel to the $\langle 001 \rangle$ direction for V_5Si_3 . The electrical resistivity value of V_5Si_3 crystals was found to be $17.6(\pm 0.7)\mu\Omega\text{cm}$, which is an order of magnitude smaller than the earlier reported values of $114.5(\pm 8.5)\mu\Omega\text{cm}$ ¹⁵. The literature values of V_5Si_3 appear to have been obtained from a polycrystalline sample.

Single crystals of sizes in the range 45–180 μm were used to examine the oxidation of crystals in air. The oxidation process of V_5Si_3 and VSi_2 crystals was studied at temperatures below 1200°C by TG and DTA, as shown in Fig. 6. According to the TG curve, the oxidation reaction of the V_5Si_3 and VSi_2

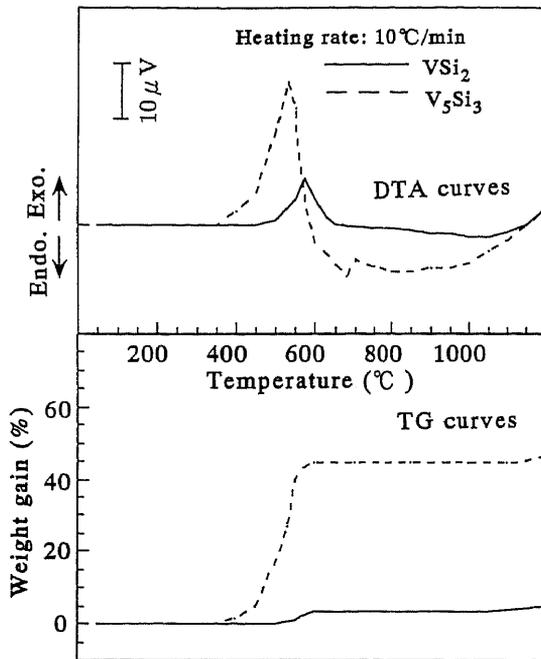


Fig. 6 TG and DTA curves of V_5Si_3 and VSi_2 crystals heated in air.

crystals starts at about 355°C and 515°C, respectively. However, a large exothermic peak of the DTA curve was found at about 530°C for V_5Si_3 , and at about 570°C for VSi_2 . Since a small endothermic peak of the DTA curve was found at about 680°C for V_5Si_3 , it would be reasonable to assume that V_2O_5 (melting point: about 670°C)¹⁶⁾ is formed as an oxidation product. For two compounds, V_2O_5 was identified as the main oxidation product by powder X-ray diffraction at room temperature. It is likely that non-crystalline SiO_2 was formed during the oxidation process, although this could not be verified by the diffraction methods available to the authors. Raman spectroscopy would, however, be profitable.

4. Conclusions

In this investigation single crystals of the vanadium silicides V_3Si , V_5Si_3 and VSi_2 were grown from high-temperature tin and copper fluxes. The largest crystals were obtained of V_5Si_3 (about 0.2 mm × 0.2 mm × 10.3 mm), but for the other phases the crystals were smaller, and not always sufficiently large for property measurements. The oxidation in air sets in at relatively low temperatures for V_5Si_3 and

VSi_2 , namely at 355°C and 515°C, respectively.

In the study of materials properties single crystals are generally preferable to sintered bodies or melted polycrystalline specimens. In this study, for instance, the electrical resistance of V_5Si_3 single crystals was found to be an order of magnitude smaller than earlier reported, based on sintered bodies¹⁵⁾. The difference in micro-Vickers hardness between the single crystalline and the sintered materials was, however, smaller.

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