PREPARATION OF TITANIUM DISILICIDE SINGLE CRYSTALS BY CHEMICAL VAPOUR TRANSPORT WITH HALOGENS*

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Summary

The preparation of TiSi_2 single crystals by chemical transport in the presence of halogens is studied. It is shown that the tetrahalides formed during the interaction of TiSi_2 with halogens, and above all the tetrahalides of titanium, TiX_4 , are the transporting agents. The gas phase composition is complex in all cases, but according to thermodynamic analysis silicon should be transported in the form of a dihalide, SiX_2 , whereas titanium transport should occur through TiX_3 and TiX_2 , the contribution of the latter increasing in the sequence chlorine \rightarrow bromine \rightarrow iodine. Single crystals of TiSi_2 are obtained in the presence of the three halogens, but transport with chlorine is found to be the most efficient. The conditions for the preparation of TiSi_2 single crystals in the form of needles, polyhedra or plates with maximum dimensions of 10 mm, 4 mm and 5 mm, respectively, and a composition close to the stoichiometric are established.

1. Introduction

Transition metals form a large number of binary phases with silicon with various structures. Some metal silicides have important applications because of their specific properties. However, most of these compounds are not studied enough or the data available in the literature on them are contradictory. This is mainly due to the lack of sufficiently large single crystals, whose study could give reliable information on their properties and the ways in which they are modified [1].

The phase diagram of the Ti-Si system has been studied in detail by Svechnikov *et al.* [2] and five binary compounds (Ti₃Si, Ti₅Si₃, Ti₅Si₄, TiSi and TiSi₂) have been found. The existence of a pure Ti₃Si binary phase reported first in ref. 3 is not accepted by some authors [4]. In addition, the phases Ti₅Si₄ and TiSi are each found to possess two polymorphous modifications [4].

^{*}Paper presented at the 8th International Symposium on Boron, Borides, Carbides, Nitrides and Related Compounds, Tbilisi, October 8 - 12, 1984.

The subject of the present investigation was the highest titanium silicide, TiSi_2 . This silicide has a face-centered orthorhombic structure, type C54 (space group, *Fddd*) with parameters a = 8.2664 Å, b = 4.7987 Å and c = 8.5503 Å [5], and is known to melt congruently at temperatures between 1500 °C [2] and 1540 °C [6]. This permits the growth of single crystals from a melt. For this purpose, Beaudouin [7] has used the Czochralski method and obtained TiSi₂ crystals with a poor quality and a considerable deficiency of silicon with respect to the stoichiometric composition (compositions ranging from TiSi_{1.8} to TiSi_{1.93}).

Using electrolysis of a melt of alkali silicofluoride and TiO_2 , Chernov et al. [8] have obtained $TiSi_2$ crystals with maximum dimensions of 1 mm. Chemical vapour deposition according to the reaction

$$TiCl_{4(g)} + 2SiCl_{4(g)} + 6H_{2(g)} = TiSi_{2(s)} + 12HCl_{(g)}$$

proceeding on a heated tungsten filament [9] or on a graphite substrate [4] has yielded even smaller single crystals (0.1 - 0.2 mm). Gurin *et al.* [10] have obtained whiskers and isometric crystals (0.1 - 0.2 mm) of TiSi₂ by crystal-lization from a solution in molten zinc.

Titanium and silicon have halides with a high volatility, which makes it possible to obtain $TiSi_2$ single crystals by chemical vapour transport with halogens. This possibility was studied in a paper of Nickl and Koukoussas [11]. At source and crystallization zone temperatures in a sealed silica tube of 1000 °C and 800 °C, respectively, under a pressure of 100 Torr of bromine as a transporting agent, these authors obtained single crystals with a maximum volume of 1 mm³. No data on the rate of transport with bromine and no experimental results from chemical transport with other halogens are presented. It is only stated that chlorine is less efficient as transporting agent than is bromine. For this reason, in the present work we carried out a detailed study of the chemical transport processes in the presence of chlorine, bromine and iodine with varying process parameters (temperature in the two zones, temperature difference and initial concentration of the halogen). This permitted an estimation of the relative efficiency of the three halogens and their effect on the habit and size of the crystals obtained.

2. A thermodynamic consideration of the chemical transport of titanium disilicide with halogens

The chemical transport processes of elemental silicon with halogens were studied in the early papers of Schaefer and coworkers [12, 13]. These authors showed that the transporting agent in this case was the SiX_4 (X \equiv Cl, Br and I) formed in the system and not the halogen itself. Silicon is transported by a lower halide according to the reaction

$$Si_{(s)} + SiX_{4(g)} = 2SiX_{2(g)}$$

(1)

Using thermodynamic data from the literature [14 - 16], one can easily show that the chemical transport of titanium should not proceed according to the reaction

$$Ti_{(s)} + 2X_{2(g)} = TiX_{4(g)}$$
 (2)

but according to another reaction involving the formation of a lower halide and the participation of TiX_4 as a transporting agent.

In a system containing titanium silicide, interaction of titanium and silicon with the gaseous halogen occurs, which may result in the formation of TiX_4 and SiX_4 , each of them playing the role of a transporting agent of both titanium and silicon. However, a comparison of the heats of formation of TiX_4 and SiX_4 as well as of the temperature dependences of these heats shows that the halogen introduced into the system should be utilized mainly for the formation of TiX_4 .

2.1. Transport with the participation of chlorine

During transport of TiSi_2 with chlorine as a transporting agent a large number of equilibria are established in the gas phase, in which the following gaseous species are participating: Cl_2 , TiCl_2 , TiCl_3 , Ti_2Cl_6 , TiCl_4 , SiCl_3 , SiCl_2 , SiCl_3 and SiCl_4 . We have taken into consideration only reactions whose equilibrium constants are larger than 10^{-6} . For the transport of titanium and silicon, respectively, these reactions are:

$$Ti_{(s)} + 3TiCl_{4(g)} = 4TiCl_{3(g)}$$
(3)

$$\operatorname{Ti}_{(s)} + 3\operatorname{TiCl}_{4(g)} = 2\operatorname{Ti}_2\operatorname{Cl}_{6(g)}$$

$$\tag{4}$$

$$\operatorname{Ti}_{(s)} + \operatorname{TiCl}_{4(g)} = 2\operatorname{TiCl}_{2(g)}$$
(5)

$$Ti_{(s)} + 1.5SiCl_{4(g)} = TiCl_{3(g)} + 1.5SiCl_{2(g)}$$
 (6)

$$Ti_{(s)} + 1.5SiCl_{4(g)} = 0.5Ti_2Cl_{6(g)} + 1.5SiCl_{2(g)}$$
(7)

$$\operatorname{Ti}_{(s)} + \operatorname{SiCl}_{4(g)} = \operatorname{TiCl}_{2(g)} + \operatorname{SiCl}_{2(g)}$$
(8)

$$\operatorname{Si}_{(s)} + \operatorname{SiCl}_{4(g)} = 2\operatorname{SiCl}_{2(g)}$$
(9)

$$\operatorname{Si}_{(s)} + 2\operatorname{TiCl}_{4(g)} = 2\operatorname{TiCl}_{3(g)} + \operatorname{SiCl}_{2(g)}$$
(10)

$$Si_{(s)} + 2TiCl_{4(g)} = Ti_2Cl_{6(g)} + SiCl_{2(g)}$$
 (11)

$$\operatorname{Si}_{(s)} + \operatorname{TiCl}_{4(g)} = \operatorname{SiCl}_{2(g)} + \operatorname{TiCl}_{2(g)}$$
(12)

Reaction (4) was not taken into account in our study since, in contrast with the remaining reactions, it is exothermic and titanium is transferred in a direction opposite to the usual one, *i.e.* from the cold to the hot zone. The $\lg K_p$ values for the remaining reactions at 1200 K are presented in Table 1.

Taking into account the fact that $TiCl_4$ rather than $SiCl_4$ should be the transporting agent, the main role in the transport of titanium and silicon will

TABLE 1

Values of $\lg K_p$ (12)	00 K) for t	the chemical	transport	reactions	of	titanium	and	silicon	in
the presence of chlo	orine								

Reaction	(3)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
$\lg K_{\rm p} (1200 K)$	3.22	0.30	2.38	2.09	1.20	-3.13	-2.57	-3.13	-4.03

obviously be played by reactions (3), (5), (10) and (11), silicon being transferred as a dichloride, and titanium as a trichloride, or, to a smaller extent, as a dichloride.

2.2. Transport with the participation of bromine and iodine

When bromine or iodine is used for the transport of $TiSi_2$, in the gas phase there are equilibria in which the following species may participate: Br_2 , Br, I_2 , I, TiBr, $TiBr_2$, $TiBr_3$, $TiBr_4$, TiI, TiI_2 , TiI_3 , TiI_4 , $SiBr_2$, $SiBr_4$, SiI_2 and SiI_4 . The silicide components will be transported according to the following reactions:

$$Ti_{(s)} + 3TiX_{4(g)} = 4TiX_{3(g)}$$
 (13)

$$Ti_{(s)} + TiX_{4(g)} = 2TiX_{2(g)}$$
 (14)

$$Ti_{(s)} + 1.5SiX_{4(g)} = TiX_{3(g)} + 1.5SiX_{2(g)}$$
 (15)

$$Ti_{(s)} + SiX_{4(g)} = TiX_{2(g)} + SiX_{2(g)}$$
 (16)

$$Si_{(s)} + SiX_{4(g)} = 2SiX_{2(g)}$$
 (17)

$$Si_{(s)} + 2TiX_{4(g)} = 2TiX_{3(g)} + SiX_{2(g)}$$
 (18)

$$Si_{(s)} + TiX_{4(g)} = SiX_{2(g)} + TiX_{2(g)}$$
 (19)

where $X \equiv Br$ or I.

The values of $\lg K_p$ at 1200 K for reactions (13) - (19) and (13') - (19') with the participation of bromine or iodine respectively, are given in Table 2.

When the main transporting agent is $TiBr_4$ or TiI_4 in the presence of bromine reactions (13) and (18) should be most important, whereas with

TABLE 2

Values of $\lg K_p$ (1200 K) for the chemical transport reactions of titanium and silicon in the presence of bromine and iodine (')

					the second se		
Reaction	(13)	(14)	(15)	(16)	(17)	(18)	(19)
lg K _p (1200 K)	4.40	1.48	3.05	2.04	-3.56	-2.67	-4.12
Reaction	(13')	(14')	(15')	(16')	(17')	(18') -5.26	(19')
lg K _p (1200 K)	—1.04	2.72	—1.05	0.83	-5.27		—3.38

iodine in the system this most important part will be played by reactions (14') and (19'), *i.e.* silicon should be transported as a dihalide, which is analogous to the case of chlorine. However, titanium is transported with bromine mainly in the form of TiBr₃ (or as TiBr₂ according to reaction (14)), whereas with iodine transport of titanium is achieved via TiI₂.

The above qualitative considerations show that all three halogens should be appropriate agents for the chemical transport of compounds of the Ti–Si system.

3. Experimental details

The investigations were carried out using a titanium sponge (Ventron; purity, 99.9%) and powdery silicon (Fluka; purity, 99.9%) in an atomic ratio of 1:2. Chlorine (Merck) came from a steel cylinder and was of laboratory grade purity. Bromine and iodine were ultra-high pure (Merck, Suprapure). The transport proceeded in sealed silica tubes with an outer diameter of 20 mm and a length of about 150 mm. The synthesis of $TiSi_2$ occurred in the ampoules by back transport for 24 h. The phase composition of the crystals obtained was controlled by X-ray analysis, while gravimetric methods were used for establishing the chemical composition. Titanium was determined as titanium cupferronate, and silicon as SiO_2 [17].

4. Results and discussion

In the first series of experiments the effect of the initial halogen concentration (varying between 0.2 and 5 mg cm⁻³) on the transport rate, habit and size of the crystals obtained was investigated at constant temperatures in the source zone ($T_1 = 1000$ °C) and in the crystallization zone ($T_2 = 800$ °C) and at the same process duration ($\tau = 96$ h). It was established that in all cases the transport rate increased with increasing initial concentration of the halogen. The lowest transport rates were established in the presence of iodine and the highest in the presence of chlorine. In the latter case the rate was already rather high at relatively low initial chlorine concentrations (of the order of 1 mg cm⁻³), sufficiently large TiSi₂ single crystals in needle and polyhedra forms (Fig. 1) being obtained. This result contradicts the statement of Nickl and Koukoussas [11] according to which TiSi₂ transport with chlorine is less efficient than that with bromine.

A general tendency in the habit of the crystals formed is that the amount of the polyhedra decreases at the expense of an increase in amount of needles when the halogen concentration becomes higher. This is shown in Figs. 2 and 3 which present typical crystals obtained at the lowest and the highest initial concentrations of bromine and iodine respectively.

The fact that the chemical transport of titanium disilicide was most efficient in the presence of chlorine was the reason for carrying out a second



Fig. 1. TiSi₂ single crystals obtained in the presence of chlorine ($C_{Cl_2}^{\circ} = 1 \text{ mg cm}^{-3}$; $T_1 = 1000 \text{ °C}$; $T_2 = 800 \text{ °C}$; $\tau = 96 \text{ h}$; TR = 7.7 mg h⁻¹ (grid distance 2 mm)).

Fig. 2. TiSi₂ single crystals obtained in the presence of bromine ($C_{Br_2}^{\circ} = 0.2 \text{ mg cm}^{-3}$; $T_1 = 1000 \text{ °C}$; $T_2 = 800 \text{ °C}$; $\tau = 96 \text{ h}$; TR = 1.3 mg h⁻¹ (grid distance 2 mm)).



Fig. 3. TiSi₂ single crystals obtained in the presence of iodine ($C_{1_2}^{c} = 5 \text{ mg cm}^{-3}$; $T_1 = 1000 \text{ °C}$; $T_2 = 800 \text{ °C}$; $\tau = 96 \text{ h}$; TR = 1.3 mg h⁻¹ (grid distance 2 mm)).

Fig. 4. TiSi₂ single crystals obtained in the presence of chlorine ($C_{Cl_2}^{\circ} = 3 \text{ mg cm}^{-3}$; $T_1 = 1000 \text{ °C}$; $T_2 = 950 \text{ °C}$; $\tau = 96 \text{ h}$; TR = 2.8 mg h⁻¹ (grid distance 2 mm)).

series of experiments using this transporting agent alone, with an initial concentration $C_{Cl_2}^{\circ} = 3 \text{ mg cm}^{-3}$, a constant duration of the transport process $\tau = 96$ h, varying temperatures in the source and crystallization zones $(T_1$ and $T_2)$ and a varying temperature difference ΔT . Some results of these experiments are summarized in Table 3.

As was to be expected, the decrease in temperature at a constant temperature difference led to a decrease in the transport rate. The same effect was observed when the crystallization proceeded at the same temperature, but the temperature difference was decreased. However, the application of a lower temperature difference between the source and crystallization zones permitted the formation of better-shaped crystals with larger sized polyhedra. At a crystallization temperature of 950 °C and $\Delta T = 50$ °C, TiSi₂ plates with a maximum linear dimension of up to 5 mm appeared together with the needles and polyhedra (Fig. 4).

The chemical analysis of some of the single crystals obtained showed some silicon deficiency with respect to stoichiometric proportions. This

Number	Temperature in the crystallization zone	Temperature difference	Transport rate	Shape and maximum size	Phase composition of the crystals	Chemical composition of the crystals (Si:Ti
	(C)	(°C)	$(mg h^{-1})$	of the crystals (mm)	(X-ray analysis data)	ratio from analytical determinations)
1	006	200	8.44	Needles 6 - 8 Polyhedra 2	TiSi ₂	1.92
2	800	200	7.70	Needles 5 - 7 Polvhedra 1.5	$TiSi_2$	I
со С	200	200	7.07	Needles 3 - 4 Polvhedra 1	$TiSi_2$	I
4	600	200	4.95	Needles 3 - 4 Polvhedra 1	TiSi_2	1.97
5	006	100	6.18	Needles 5 - 6 Polvhedra 3	$TiSi_2$	1.98
9	1050	50	4.49	Needles 8 - 10 Polvhedra 3	${ m TiSi}_2$	1
7	1000	50	3.16	Needles 5 - 8 Polvhedra 3	TiSi_2	ł
œ	950	50	2.76	Needles 5 - 8 Polyhedra 3 - 4 Plates 4 - 5	TiSi ₂	I

Results of experiments on chemical transport of titanium disilicide with chlorine

TABLE 3

 $C_{\text{Cl}_2}^\circ = 3 \text{ mg cm}^{-3}; \tau = 96 \text{ h.}$

deficiency was larger when the temperature in the source zone exceeded 1000 °C. At 1000 °C and below this temperature, the deviation from the stoichiometric composition of the crystals was much smaller than that of the TiSi₂ crystals obtained by the Czochralski method [7].

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