Reduction of Titanium Oxide by Molten Silicon to Synthesize Titanium Silicide

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Titanium silicide was synthesized via the reaction of titanium oxide bearing slag and molten silicon. Results indicated that titanium oxide in slag was reduced by silicon with an intermetallic bulk being formed. This novel synthesis method is a three-layer refining process that is much simpler and could reduce the cost of titanium silicide production significantly. Moreover, this novel and low-cost synthesis method of Ti5Si3 provides a new way to produce high purity titanium. [doi:10.2320/mattrans.M2015264]

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1. Introduction

Titanium silicide (Ti5Si3) is a promising structural and functional material. The melting point of Ti5Si3 is as high as 2124°C. Furthermore, it exhibits high oxidation resistance at elevated temperature and shows excellent creep resistance and low specific weight. These properties make it a promising new material for very-high-temperature structural applications.1-2) Ti5Si3 is also an attractive anode material for lithium-ion batteries due to its large gravimetric and high volumetric capacity.3-6) These properties make Ti5Si3 an attractive material in applications such as graded bioactive glass coatings, refractory materials, Schottky barriers, gates and interconnects in very large scale integrated circuits, ohmic contacts, and diffusion barriers.2,7)

Historically, Ti5Si3 has been produced primarily by powder metallurgy methods.8) Though extensive research was performed on mechanical alloying9-12) and combustion synthesis (SHS),13,14) these methods use ultrapure elementary substances of Ti and Si, which are expensive. Another process using electrochemical reduction15,16) was developed in recent years, but it will take a considerably long period to be industrialized. These disadvantages could retard the development of Ti5Si3 applications.

In the present work, we propose a novel method to synthesize Ti5Si3 via a pyro-metallurgical process at high temperature, where the reagents were in liquid state. Compared to the known processes, this new method is simple, easy industrialized, and low-cost.

2. Experimental Procedure

TiO2-CaO-SiO2 ternary slag (4.46 g) was pre-melted at 1500°C from reagent-grade TiO2, SiO2 and CaO (10 : 7 : 8 mass ratio) and reacted with pure silicon melt. CaO was calcined from CaCO3 at 1000°C for 10 h in air. CaO and SiO2 were used to reduce the melting point of the slag to lower than 1500°C. Semiconductor grade silicon (1 g) was then melted on the molten slag in a graphite crucible (12 mm inner diameter) at 1500°C inside an induction furnace. This temperature is the eutectic point of Ti5Si3, one of the intermetallics in the Ti-Si binary. Argon was introduced into the furnace during the reduction. After the reaction, the sample was withdrawn from the furnace, quenched in argon gas, and subjected to characterization. The reaction times were controlled at 5 h and 17 h, respectively.

The reaction products were probed via X-ray diffraction (XRD, Rigaku Rint-2100) analysis and scanning electron microscope (JSM-6510LA, JEOL Ltd.) equipped with energy-dispersive spectroscopy (SEM/EDS).

3. Results and Discussions

3.1 Thermodynamics

In this process, TiO2 in the melt was reduced by molten silicon, which seems impossible in the view of thermodynamics because the reducibility of silicon is lower than titanium, and the titanium is reduced by as much as 74 mass% in Ti5Si3.

The Ellingham diagram indicates that little, if any, titanium can be reduced by silicon solvent. To the best of our knowledge, manganese is the only reducer developed for the synthesis of Ti5Si3 from oxides.18) However, in fact, there is no need for introducing any reducing agent except silicon. In other words, the formation of the intermetallic product can be the only driving force for titanium oxide reduction by silicon. In their research on the chemical equilibrium of the TiO2-SiO2-CaO system, Weiss et al.19) added 2 and 5 mass percent TiO2 slag to molten silicon at 1500°C and found that the titanium concentration in silicon increased to 2.7 times the square root of the titanium concentration in the slag at equilibrium. In another report, Sasabe et al.20) suggested the following chemical reaction:

\[ \text{TiO}_2 + 4\text{Si} + \text{O}_2 = \text{Ti}_5\text{Si}_3 + 2\text{SiO}_2 \]  

where Ti5Si3 is another important intermetallic product in the Ti-Si binary system. However, it can be shown thermodynamically that synthetic reaction of Ti-Si compounds can proceed without oxygen. For instance, the reaction we employed to synthesize Ti5Si3 was:

\[ (\text{TiO}_2) + 1.6(\text{Si}) = 0.2\text{Ti}_5\text{Si}_3(s) + (\text{SiO}_2) \]  

The reaction Gibbs energy of eq. (2) is \(-200 \pm 100 \text{ kJ mol}^{-1}\) within the temperature range of 900–1800°C, which indicates that the reaction is thermodynamically possible. Equation (2) is an exothermic reaction, which means that a
lower temperature enhances the reaction. Moreover, the absolute value of the enthalpy change in this reaction to produce 1 mole of Ti$_5$Si$_3$ is more than that of the reported SHS reaction using pure titanium and silicon at 1500°C. This implies that our novel process can potentially save more energy than the SHS process.

3.2 Practical reactions

Bulk intermetallic product was observed at the bottom of the graphite crucible after reaction for 17 h (Fig. 1). Intermetallic grains were measured to be approximately 20 µm. The experimental results showed that the color of the slag floating on the product turned purple after the reaction, which indicated that some Ti$^{3+}$ dissolved in the slag as by-product in the reduction.

Sections of the sample were probed by X-ray diffraction (XRD) and scanning electron microscope with energy dispersive spectrum (SEM/EDS). The statistical EDS results indicated that the mole fractions of Ti and Si in the intermetallic product were 65.0% and 35.0%, respectively; this composition is very similar to the composition of titanium silicide Ti$_5$Si$_3$ (Ti:Si = 5:3). Figure 2 shows the X-ray pattern of the cross section of the reacted sample. The peak of high intensity at 2θ = 26° is caused by graphite in the crucible, and the diffuse X-ray peak between 20 and 40° is due to the glass formed from slag during quenching. Figure 2 shows that Ti$_5$Si$_3$ intermetallic compound was obtained in this reaction and that the crystals were in a preferred orientation.

It was observed that pure silicon floated on the molten slag at the beginning of the reaction. The SEM/EDS results of a quenched sample after the reaction at 1500°C for 5 h indicated that a mixture of pure silicon, titanium-dissolved silicon (mole fraction of titanium was about 3.7%) and TiSi$_2$ were floating on the molten slag (Fig. 3(a)). The titanium silicide product dropped to the bottom of the slag. The SEM/EDS also showed that the slag contained ~5–50 µm Ti$_5$Si$_3$ particles (Fig. 3(b)). The experiment results implied that the reaction process of eq. (2) could be divided into two steps:

$$(\text{TiO}_2) + 3[\text{Si}] = \text{TiSi}_2(s) + (\text{SiO}_2)$$ (3)
The estimated density of the initial slag is \( 3.35 \text{ g} \cdot \text{cm}^{-3} \), which is higher than that of molten silicon (2.57 g cm\(^{-3}\)) but lower than the value of solid Ti\(_5\)Si\(_3\) (4.32 g cm\(^{-3}\)). This is because the slag separated the heavy products and the less-Ti-dissolving silicon during the process. The process could be described as a three-layer refining process. The floating silicon reacted with slag to produce titanium silicide particles and Ti-dissolving silicon. The solid particles and heavy liquid drops then precipitated through the molten slag and clustered at the bottom of the crucible. The reaction proceeded as the particles moved to the bottom. The three layer refining process is a key technology in the electro-refining process of silicon\(^{21-23}\). In this process, impurities could be removed effectively from the slag immediate-layer by sedimentation, yielding high purity products. In this three-layer refining process, the reduction of TiO\(_2\) could be divided into three steps: Reaction–Refining–Gathering, as shown in Fig. 4. This figure also shows the EDS scan result of the interface of Ti\(_5\)Si\(_3\) and slag. The low intensity of Ti in slag indicated that the process could extract almost all titanium in slag to the intermetallic compound after reaction for 17 h.

It is well known that impurities can be effectively removed by adjusting the slag composition and operating conditions in a pyro-metallurgical refining process. The three-layer refining technology enhances the above-mentioned effect during Ti\(_5\)Si\(_3\) synthesis, which is an additional advantage that is not possible in the SHS process. Alternatively, some other advantageous doping could be added into the products by employing the slag-silicon interface reaction in a convenient way. It has been reported that some of this doping could reduce the ignition temperature for SHS of titanium silicide\(^{24,25}\) or improve the performance of the materials.\(^{1,3,26}\) The dopants in the SHS method were usually in the form of extra pure materials, rendering this process cost ineffective. In contrast, the dopants in the pyro metallurgical process can be low purity or inexpensive crude compounds, resulting in reduced expense. In the reaction, the doping materials transferred from the slag to the Ti\(_5\)Si\(_3\) product, and the impurities were simultaneously removed from the product to the slag.

This novel and low-cost synthesis method of Ti\(_5\)Si\(_3\) provides a new way to produce high purity titanium (Fig. 5). In this process, silicon reduced from SiO\(_2\) by carbon was used as the reducer of titanium. The silicon acted as an intermediate for the transfer of electrons from carbon to titanium oxide and prevented the transfer of carbon in the direct reduction of titanium oxide. This produced an abundance of titanium carbide as the principal product, which was one of the main reasons why carbon could not be used to reduce titanium in practice. The next step was the extraction of pure titanium from Ti\(_5\)Si\(_3\). There are several possible methods to do this. We suggest molten salt
electrolysis refining, as shown in Fig. 5. The electronegativity of Ti is lower than Si.27 Thus in the electrochemical production of Ti from Ti5Si3, Si will not anodically dissolve in the electrolyte, and the two elements will be separated. However, limited research has been done in the field of electrolytic separation pure elements from intermetallic compounds. The development of the process needs more investigation in the future.

4. Conclusion

In summary, we introduce a novel synthesis method of Ti5Si3 bulk. Titanium-oxide-bearing slag was reacted with molten silicon to reduce titanium oxide to an intermetallic product. During the reduction, the formed products dropped through the slag and then deposited at the bottom of a crucible to form bulk material. This reaction can be described as a three-layer refining process. This process can be used to synthesize titanium silicide intermetallic compound with dopants in a convenient way. Finally, we also propose that this novel and low-cost synthesis method of Ti5Si3 provides a new way to produce high purity titanium.

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