Growth of CaSi₂ single-phase polycrystalline ingots using the phase relationship
between CaSi₂ and associated phases

Ritsuko Yaokawa^a, Hideyuki Nakano^{a, b}, Masataka Ohashi^a

^a *TOYOTA CENTRAL R&D LABS., INC. Nagakute 480-1192, Japan*

^b *JST PRESTO, Kawaguchi 332-0012, Japan*

Abstract

The phase relationship between CaSi₂ and associated phases was studied in order to fabricate CaSi₂ single-phase polycrystalline ingots. The phase diagram of the Ca-Si binary system around CaSi₂ (Ca_xSi₂; 0.9 ≤ x ≤ 1.1) was obtained by identifying the phases in samples of varying composition and DTA analysis of the phase transitions. CaSi₂ was treated as an incongruent-melting material that precipitates through two peritectic reactions, namely CaSi + liquid → Ca₁₄Si₁₉ and Ca₁₄Si₁₉ + liquid → CaSi₂, according to the currently accepted phase diagram. However, at the CaSi₂ stoichiometric composition, the stable peritectic reaction Ca₁₄Si₁₉ + liquid → CaSi₂ occurs only in the presence of impurities such as Ta, B or P. In contrast, only CaSi + liquid → CaSi₂ occurs as the metastable peritectic reaction in a high-purity melt. The undercooling required for CaSi₂ precipitation is less than 5°C. Therefore, single-phase CaSi₂ could be produced from a

high-purity stoichiometric CaSi_2 melt with a small amount of undercooling, and a rod-like coupled structure of CaSi_2 and CaSi phases formed by peritectic coupled growth (PCG) in a high-purity Ca-rich ingot. The present study also investigates the fabrication process for CaSi_2 single-phase polycrystalline ingots. These can be obtained by high-cooling-rate casting ($1\text{-}100^\circ\text{C}/\text{min}$) of high-purity, stoichiometric CaSi_2 melts using new Ta crucibles.

Keywords: Single crystal; transformation; solidification microstructure; phase diagram; nucleation and growth

1. Introduction

Calcium disilicide, CaSi_2 , is a so-called Zintl phase [1,2], i.e., an intermetallic compound formed between a strongly electropositive metal, such as alkali metals, alkaline earth metals, and lanthanides, and a somewhat less electropositive metal. In a Zintl silicide, silicon is the anionic part of the structure and fulfills the simple role of typical valence compounds, which results in a variety of sub-network structures with Si-Si covalent bonds; each Si atom achieves an octet shell with covalent bonds and lone-pair electrons according to the 8-N rule.

CaSi_2 has a 2D silicon sub-network resembling buckled Si (111) planes, in which the Si_6 rings are interconnected with sp^3 bonds; the puckered $(\text{Si}^-)_n$ polyanion layers are

separated by planar monolayers of Ca^{2+} .

CaSi_2 has a trigonal structure (space group $R\bar{3}m$) at ambient pressure, which can only vary in its stacking sequence: tr6 ($a=3.855\text{\AA}$, $c=30.62\text{\AA}$) [6] and tr3 ($a=3.829\text{\AA}$, $c=15.90\text{\AA}$) [7]. In the tr6 structure, the stacking of trigonal Ca layers follows an AABBC sequence with a six-layer repeat distance. The tr3 structure has a three-layer repeat distance, with Ca layers stacked in an ABC sequence. CaSi_2 ingots typically have the tr6 structure. In addition, CaSi_2 has a tetragonal phase ($\alpha\text{-ThSi}_2$ -type, space group $I4_1/amd$, $a=4.3\text{\AA}$, $c=13.5\text{\AA}$) [6], in which the Si atoms are connected by a three-dimensional network of sp^2 bonds, obtained through a high-pressure treatment. For tetragonal CaSi_2 , superconductivity occurs at high pressure, and T_c was experimentally found to increase as a function of pressure, reaching 14 K [8, 9]. This was attributed to flattening of the Si planes, resulting from an sp^3 - sp^2 phase transition above 16 GPa.

The covalent bonding of the silicon sub-networks of Zintl silicides is very stable and versatile and can be chemically modified by oxidation, i.e., removal of metals [10]. Therefore, a layered polysilane $(\text{SiH})_n$ isomorphous with fluorographite $(\text{CF})_n$ can be derived from tr6 or tr3 CaSi_2 by treating CaSi_2 with ice-cold concentrated aqueous HCl [11]. We have achieved several varieties of Si nanosheets by the organic modification of $(\text{SiH})_n$ [12-14]. Si nanosheets have a 2D silicon sub-network, and various properties can be imparted to them through the use of surface dangling bonds modified with an organic

group. The most promising use of CaSi_2 is as a starting material for Si nanosheets, owing to its 2D silicon puckered sheet. When used as the starting material for Si nanosheets, CaSi_2 needs to be free of Si and other phases in order for the yield of Si nanosheet synthesis to be high.

The currently accepted Ca-Si binary phase diagram is shown in Fig. 1 [18], and was constructed by Gröbner et al. on the basis of three sets of experimental data [15-17] and thermodynamic data [18]. According to this phase diagram, CaSi_2 is an incongruent-melting compound with two peritectic reactions ($\text{Ca}_{14}\text{Si}_{19} + \text{liquid} \rightarrow \text{CaSi}_2$ at 1028°C , and $\text{CaSi} + \text{liquid} \rightarrow \text{Ca}_{14}\text{Si}_{19}$ at 1083°C), and its liquidus point is about 1150°C . Thus, an undercooling of over 120°C is required to obtain single-phase CaSi_2 ingots, and it is expected that for smaller amounts of undercooling, not only the CaSi_2 phase but also other phases such as CaSi , $\text{Ca}_{14}\text{Si}_{19}$ and Si would precipitate. For CaSi_2 precipitation as the primary phase, the melt composition during cooling must ideally be within the narrow region between a and b in Fig. 1; the primary phase is the CaSi_2 phase. However, evaporation of Ca from the CaSi_2 melt makes it difficult to control the melt composition in the slow cooling stage.

On the other hand, Evers et al. [19] and Yamanaka et al. [20] obtained, respectively, 8×8 mm and 5×5 mm single crystal specimens from ingots cooled slowly at a rate of $0.167^\circ\text{C}/\text{min}$ ($10^\circ\text{C}/\text{h}$). However, these specimens seem to have been taken from polycrystalline ingots having very coarse grains, although there is no detailed statement

in their report.

About 20 years ago, Hirano fabricated a CaSi_2 single crystal with a diameter of 10 mm and length of 100 mm by the floating zone (FZ) method using a seed crystal [21]. It is also difficult to generate an undercooling of over 120°C in the melt in order to grow CaSi_2 single crystals by the FZ method. The fact that a CaSi_2 single crystal could be grown directly from the melt by the FZ method shows that the requisite undercooling is not so high. Thus, there is a discrepancy between the phase diagram in Fig. 1 and the crystal growth results.

In the present study, in order to fabricate a single-phase CaSi_2 ingot, we studied CaSi_2 ingot casting at higher cooling rates in order to facilitate the process, because Ca evaporation could then be reduced. As a result, single-phase CaSi_2 ingots were successfully obtained from the stoichiometric $\text{Ca}_{1.00}\text{Si}_2$ melt at cooling rates from 1 to $100^\circ\text{C}/\text{min}$. In addition, it was found that Ta, B, and P contamination in the melt affected precipitation of the $\text{Ca}_{14}\text{Si}_{19}$ phase. We determined the phase relationship between CaSi_2 and associated phases by metallographic, X-ray diffraction (XRD) and differential thermal analysis (DTA) and revised the phase diagram for this system accordingly.

2. Experimental

2.1 Polycrystalline CaSi_2 ingot casting at high cooling rates (1, 10, 100°C/min)

Polycrystalline CaSi_2 ingots were fabricated by high-cooling-rate casting (1, 10, 100°C/min). 99.999 wt% Si and 99.99 wt% Ca were weighed and placed in a new Ta crucible (20 mm in diameter, 20 mm in height) under an argon atmosphere. These raw materials were melted by high-frequency induction heating. Once the material was completely melted, it was held at the temperature for 10 min, cooled at 1, 10, or 100°C/min to 900°C, where the melt solidified completely, and then cooled to room temperature at 10°C/min. The cooling rate was monitored by thermocouples located under the Ta crucible. The initial compositions were Ca_xSi_2 ($x=0.90, 0.97$ to 1.05 at increments of 0.01 and 1.10) for 10°C/min cooling, and $\text{Ca}_{0.90}\text{Si}_2$, $\text{Ca}_{1.00}\text{Si}_2$, and $\text{Ca}_{1.05}\text{Si}_2$ for 1 and 100°C/min cooling.

2.2 Polycrystalline CaSi_2 ingot casting with Ta impurities

A thin layer of Ta_3Si phase formed on the Ta crucible surface during fabrication of the polycrystalline CaSi_2 ingots. An impurity phase of this sort affects the phases that precipitate from the CaSi_2 melts. Therefore, in order to investigate the influence of Ta impurities on the solidification process, Ta crucibles that were used once were reused (hereafter called second-use Ta crucibles). The initial compositions were Ca_xSi_2 ($x=0.90, 0.99$ to 1.02 in increments of $0.01, 1.05$, and 1.10). We note that the amount of Ta_3Si on the second-use Ta crucible was not that large: The change in the x value of the initial

composition due to the Ta_3Si impurity was less than 0.01. The cooling rate was $10^\circ\text{C}/\text{min}$.

2.3 Polycrystalline CaSi_2 ingot casting with B and P

It is thought that some impurities in the melt other than Ta affect the solidification of the CaSi_2 polycrystal. In order to investigate the influence of other impurities on the precipitation phases, 100 ppm B- or P-doped Si substrates were used as Si raw material, and polycrystalline $\text{Ca}_{1.05}\text{Si}_2$ ingots containing 66 ppm B or P were obtained by casting at $100^\circ\text{C}/\text{min}$ with new Ta crucibles.

2.4 Microstructural characterization and phase identification

Optical microscopy (Olympus PMG3) was used for microstructural characterization of the specimens. In addition, SEM (Hitachi High-Technologies S-3600; accelerating voltage: 15 kV) with backscattered electrons (BSE) and energy-dispersed X-ray spectroscopy (EDX) were used for characterization and local chemical analysis of the microstructure.

The precipitation phases in the single-crystalline and polycrystalline CaSi_2 ingots were characterized using XRD (Rigaku RINT-TTR, scan rate: θ - 2θ method, $2^\circ/\text{min}$, $\text{Cu-K}\alpha$, 50 kV, 300 mA). The orientations of the CaSi_2 crystals were also determined by XRD.

2.5 Differential thermal analysis

DTA was performed to investigate the relationship between melting points, eutectic and peritectic points, and the melt composition. DTA samples comprised ca. 8 mg of Ca_xSi_2 ($x=0.9$ to 1.1) polycrystals. Measurements were performed using molybdenum pans (5 mm in diameter, 5 mm in height) under an Ar atmosphere. In order to prevent oxidation of the melt during the measurements, the apparatus was evacuated prior to the measurements. The heating rate was $20^\circ\text{C}/\text{min}$ from room temperature to 1000°C and $5^\circ\text{C}/\text{min}$ from 1000 to 1200°C .

3. Results

3.1. CaSi_2 polycrystals fabricated by high-cooling-rate casting

Figs. 2(a) to 2(i) show the top surfaces of $\text{Ca}_{1.05}\text{Si}_2$, $\text{Ca}_{1.00}\text{Si}_2$, and $\text{Ca}_{0.90}\text{Si}_2$ ingots cooled at a rate of 1, 10, and $100^\circ\text{C}/\text{min}$, respectively. Plate-like large grains grew on the surface of the $\text{Ca}_{1.00}\text{Si}_2$ ingot cooled at $10^\circ\text{C}/\text{min}$ (Fig. 2(e)). XRD analysis revealed that these plate-like grains consisted of single-phase CaSi_2 whose crystal orientation coincided with the $\{001\}$ facet planes. Similarly, CaSi_2 grains covered the entire surface of all $\text{Ca}_{1.00}\text{Si}_2$ and $\text{Ca}_{0.90}\text{Si}_2$ ingots, and plate-like CaSi_2 grains were found in ingots cooled at 10 and $100^\circ\text{C}/\text{min}$. In contrast, hardly any plate-like CaSi_2 grains were formed on the surface of the $\text{Ca}_{1.05}\text{Si}_2$ ingot.

Figs. 3(a) and 3(b) show XRD patterns for powdered $\text{Ca}_{1.00}\text{Si}_2$ and $\text{Ca}_{1.05}\text{Si}_2$ ingots cooled at 1, 10, and $100^\circ\text{C}/\text{min}$, respectively, where the patterns have been magnified to show weaker peaks. For all cooling rates, $\text{Ca}_{1.00}\text{Si}_2$ ingots were composed entirely of the CaSi_2 (tr6) phase, while $\text{Ca}_{1.05}\text{Si}_2$ ingots consisted of the phases CaSi_2 , CaSi , and Si . It should be mentioned that the CaSi_2 single-phase ingot can be obtained from the stoichiometric composition. In addition, single-phase CaSi_2 means that the composition of the $\text{Ca}_{1.00}\text{Si}_2$ ingots was almost the same as that of the initial ingot, since CaSi_2 is a line compound that has no solid solution range. Thus, Ca evaporation from the CaSi_2 melt is negligible at the cooling rates of 1, 10, and $100^\circ\text{C}/\text{min}$.

Figs. 4(a) and 4(b) show, respectively, an optical micrograph and BSE image of a cross section of a $\text{Ca}_{1.05}\text{Si}_2$ ingot cooled at $10^\circ\text{C}/\text{min}$. A rod-like coupled structure is observed. Chemical composition analysis by EDX indicated that the rod-like precipitates (bright gray phase in Fig. 4(b)) were the CaSi phase, and the matrix (dark gray phase in Fig. 4(b)) was the CaSi_2 phase.

Fig. 5 shows a BSE image of a cross section of the $\text{Ca}_{0.90}\text{Si}_2$ specimen cooled at $10^\circ\text{C}/\text{min}$. In contrast to the $\text{Ca}_{1.05}\text{Si}_2$ specimen, the microstructure is seen to consist of large single-phase CaSi_2 grains and a eutectic structure of CaSi_2 and Si . This suggests that in the case of the $\text{Ca}_{0.90}\text{Si}_2$ composition, CaSi_2 is the primary phase and that the eutectic structure of CaSi_2 and Si forms later.

Fig. 6 shows a BSE image of a cross-section of the $\text{Ca}_{1.00}\text{Si}_2$ specimen cooled at

10°C/min. This specimen clearly consisted of single-phase CaSi_2 , although several voids had formed in the ingot.

3.2. Precipitation phases in CaSi_2 polycrystals

XRD measurements were performed on ten powdered Ca_xSi_2 ($x=0.9$ to 1.1) ingots cooled at 10°C/min to determine the precipitation phases. Fig. 7(a) shows XRD patterns for $\text{Ca}_{0.97}\text{Si}_2$, $\text{Ca}_{1.00}\text{Si}_2$, and $\text{Ca}_{1.03}\text{Si}_2$ ingots cooled at 10°C/min, again magnified to show weaker peaks. The stoichiometric $\text{Ca}_{1.00}\text{Si}_2$ ingot was composed entirely of the CaSi_2 phase, while the Ca-poor $\text{Ca}_{0.97}\text{Si}_2$ ingot contained both CaSi_2 and Si phases. The Ca-rich $\text{Ca}_{1.03}\text{Si}_2$ ingot consisted of three phases, namely CaSi_2 , CaSi , and Si. In the Ca-rich ingot, the Si phase detected by XRD was not found in the SEM observations, presumably because the amount of the Si phase was too little or because it occurred at the grain boundaries.

Fig. 7(b) shows the precipitation phase map around the composition CaSi_2 . The CaSi_2 and Si phases occur on the Ca-poor side and the three phases CaSi_2 , CaSi , and Si, on the Ca-rich side. Single-phase CaSi_2 was obtained only in the stoichiometric $\text{Ca}_{1.00}\text{Si}_2$ ingot. These features of the precipitation phase were the same at the other cooling rates, 1°C/min and 100°C/min, as shown in Fig. 2.

According to the phase diagram reported by Manfrinetti et al. [15], not only the CaSi_2 , CaSi , and Si phases, but also the $\text{Ca}_{14}\text{Si}_{19}$ phase would precipitate around the CaSi_2

stoichiometric composition. However, no $\text{Ca}_{14}\text{Si}_{19}$ precipitation was observed in any of the ingots when a new Ta crucible was used. This finding will be discussed in the following section.

3.3. Precipitation phases in CaSi_2 polycrystals with impurities

3.3.1. CaSi_2 polycrystals with Ta impurities

The precipitation phases varied depending on whether the polycrystalline CaSi_2 ingot was fabricated with a second-use or new Ta crucible. Fig. 8(a) shows magnified powder XRD patterns for $\text{Ca}_{1.02}\text{Si}_2$, $\text{Ca}_{1.00}\text{Si}_2$, and $\text{Ca}_{0.99}\text{Si}_2$ ingots cooled at $10^\circ\text{C}/\text{min}$ fabricated with second-use Ta crucibles, and Fig. 8(b) shows the precipitation phase map obtained on the basis of these XRD patterns. There were three main differences between the new and second-use Ta crucible cases. First, the TaSi_2 phase was found in all ingots fabricated with a second-use Ta crucible. Secondly, some $\text{Ca}_{14}\text{Si}_{19}$ peaks (31.24° , 38.78° , etc.) [22] were detected in the XRD patterns for Ca-rich $\text{Ca}_{1.02}\text{Si}_2$ ingots. Indeed, the $\text{Ca}_{14}\text{Si}_{19}$ phase was present in all Ca-rich ingots, although no $\text{Ca}_{14}\text{Si}_{19}$ precipitation was observed in any of the ingots when a new Ta crucible was used. Thirdly, the stoichiometric $\text{Ca}_{1.00}\text{Si}_2$ ingot was not single-phase CaSi_2 ; rather, very weak peaks due to Si, CaSi, and $\text{Ca}_{14}\text{Si}_{19}$ phases were detected.

The Si in the Ca-Si melt and the Ta crucible react to form several kinds of Ta_xSi compounds (TaSi_2 , Ta_5Si_3 , Ta_2Si , and Ta_3Si) [23]. In the present investigation, the Ta_3Si

phase formed on the Ta crucible surface during the first melting. This reaction made the surface of the second-use Ta crucible rougher than that of the new one. As a result, the second-use Ta crucible reacted with the Ca-Si melt more easily. Formation of the Ta_3Si phase would promote Ta diffusion into the melt, leading to the formation of the TaSi_2 phase in CaSi_2 polycrystals.

According to the Ca-Si binary system phase diagrams reported by Gröbner et al. [18], the $\text{Ca}_{14}\text{Si}_{19}$ phase is expected to precipitate around the CaSi_2 stoichiometric composition below the peritectic temperature of 1083°C via the reaction $\text{CaSi} + \text{liquid} \rightarrow \text{Ca}_{14}\text{Si}_{19}$. The precipitation of $\text{Ca}_{14}\text{Si}_{19}$ in the case of the second-use Ta crucible was consistent with this expectation. On the other hand, no $\text{Ca}_{14}\text{Si}_{19}$ phase precipitated in the case of the new Ta crucible, which implies that $\text{Ca}_{14}\text{Si}_{19}$ was more difficult to nucleate compared to other phases. Owing to this limitation of $\text{Ca}_{14}\text{Si}_{19}$ precipitation, the coupled structure of CaSi_2 and CaSi phases was observed in ingots fabricated using new Ta crucibles.

3.3.2. CaSi_2 polycrystals with B or P impurity

The precipitation phases also changed when the melt contained other impurities. Figure 9 shows magnified powder XRD patterns for Ca-rich $\text{Ca}_{1.05}\text{Si}_2$ ingots with 66 ppm B or P fabricated at $100^\circ\text{C}/\text{min}$ cooling using new Ta crucibles. $\text{Ca}_{1.05}\text{Si}_2$ ingots containing B or P consisted of $\text{Ca}_{14}\text{Si}_{19}$, CaSi_2 , CaSi , and Si phases, similarly to ingots

fabricated with second-use Ta crucibles. In contrast, since new Ta crucibles were used, no TaSi_2 phase was detected in $\text{Ca}_{1.05}\text{Si}_2$ ingots containing B or P. These results indicated that the impurities Ta (TaSi_2), B, and P promoted the nucleation of the $\text{Ca}_{14}\text{Si}_{19}$ phase. However, the nucleation mechanism of $\text{Ca}_{14}\text{Si}_{19}$ remains unclear.

3.4. DTA analysis results

According to the results of microstructural observation and XRD analysis, single-phase CaSi_2 precipitated from the stoichiometric CaSi_2 composition melt without impurities, namely, via a congruent-like reaction. However, according to the phase diagram reported by Gröbner et al. [18], the temperature difference between the liquidus point and the peritectic temperature of the $\text{Ca}_{14}\text{Si}_{19}$, CaSi_2 , and liquid phases is above 120°C at the stoichiometric CaSi_2 composition. Normally, it is difficult to achieve such high undercooling in this system. Therefore, in order to revise the phase diagram for this system around the CaSi_2 composition, the liquidus point or other invariant reaction temperatures were determined by DTA conducted during the heating process on several Ca_xSi_2 ($x = 0.9$ to 1.1) samples. DTA samples were polycrystalline CaSi_2 ingots using second-use Ta crucibles. These ingots consisted of CaSi_2 and Si phases in the case of Ca-poor compositions, and CaSi , $\text{Ca}_{14}\text{Si}_{19}$, CaSi_2 , and Si phases at the stoichiometric composition ($\text{Ca}_{1.00}\text{Si}_2$) and Ca-rich compositions. The DTA results are shown in Fig. 10(a). The invariant reaction temperatures were chosen as the temperatures at the onset

of the heat flow signals, i.e., the intersection of a baseline and the maximum incline of the endothermic peak.

There were peaks at about 1024°C in all samples, which corresponds to the eutectic point of the CaSi_2 , Si, and liquid phases. In Ca-rich samples, the peaks at 1042°C represent the peritectic reaction of the $\text{Ca}_{14}\text{Si}_{19}$, CaSi_2 , and liquid phases, while the peaks at 1088°C are due to the peritectic reaction of the CaSi, $\text{Ca}_{14}\text{Si}_{19}$, and liquid phases. In the $\text{Ca}_{1.00}\text{Si}_2$ and $\text{Ca}_{0.90}\text{Si}_2$ heat flow profiles, it is difficult to determine the liquidus temperature because the onset points are hidden under other peaks. It is customary to select the peak temperature of the last thermal event during heating as the liquidus temperature [24]. Thus, the peak temperature, i.e., the derived liquidus temperature, is 1047°C for $\text{Ca}_{1.00}\text{Si}_2$ and 1041°C for $\text{Ca}_{0.90}\text{Si}_2$.

Figure 10(b) shows a revised Ca-Si phase diagram around the CaSi_2 composition, determined on the basis of DTA analysis results. In the $\text{Ca}_{0.90}\text{Si}_2$ sample, there are two endothermic peaks at 1024°C and 1041°C. The former is the eutectic point of the CaSi_2 , Si, and liquid phases, and the later is the liquidus. As mentioned above, the microstructure of the $\text{Ca}_{0.90}\text{Si}_2$ ingot suggested that the primary phase was not Si, but rather, CaSi_2 . Thus, the eutectic composition of the CaSi_2 , Si, and liquid phases is Si-richer than $\text{Ca}_{0.90}\text{Si}_2$.

Peaks at 1024°C were also observed at Ca-rich and stoichiometric CaSi_2 compositions. However, these peaks seem to be due to the non-equilibrium eutectic reaction, because

on the basis of the Gibb's phase rule, Si is not the equilibrium phase at these compositions. The formation mechanism for the Si phase from Ca-rich and stoichiometric CaSi_2 melts is assumed to be solute partitioning during the peritectic reaction and will be discussed later. In the Ca-rich samples, the endothermic peaks at 1042°C represent the peritectic reaction of the $\text{Ca}_{14}\text{Si}_{19}$, CaSi_2 , and liquid phases, and the endothermic peaks at 1088°C represent the peritectic reaction of the CaSi , $\text{Ca}_{14}\text{Si}_{19}$, and liquid phases. In the stoichiometric samples, the liquidus peak is found to consist of two overlapped endothermic peaks, one at 1042°C , associated with the peritectic reaction of the $\text{Ca}_{14}\text{Si}_{19}$, CaSi_2 , and liquid phases, and the other at 1047°C , associated with the liquidus point.

4. Discussion

4.1. Revision of the Ca-Si binary system phase diagram around CaSi_2

Figure 10(b) can explain the mechanism of the non-equilibrium Si phase formation from Ca-rich melts or the CaSi_2 stoichiometric melt with second-use Ta crucibles. When the Ca-rich or CaSi_2 stoichiometric melt start to solidify, the $\text{Ca}_{14}\text{Si}_{19}$ phase precipitates below the peritectic temperature 1088°C or the $\text{Ca}_{14}\text{Si}_{19}$ liquidus line, depending on the initial composition of the melt. Then, the local composition of the liquid phase that

contacts the $\text{Ca}_{14}\text{Si}_{19}$ phase becomes slightly more Si-rich than the CaSi_2 stoichiometric composition by solute partitioning before the start of CaSi_2 precipitation. This Si-rich liquid solidifies with the precipitation of Si and CaSi_2 when the melt temperature decreases to the eutectic temperature of 1024°C . Therefore, a small amount of the non-equilibrium Si phase is present in the Ca-rich or CaSi_2 stoichiometric composition ingots. It is important that the invariant reaction of $\text{Ca}_{14}\text{Si}_{19}$, liquid, and CaSi_2 must not be the eutectic liquid $\rightarrow \text{Ca}_{14}\text{Si}_{19} + \text{CaSi}_2$ but the peritectic $\text{Ca}_{14}\text{Si}_{19} + \text{liquid} \rightarrow \text{CaSi}_2$ because if the CaSi_2 solidification occurs as the eutectic, the Si phase cannot form from the Ca-rich melt. Similarly, the non-equilibrium Si phase forms from Ca-rich melts with new Ta crucibles. As mentioned above, the $\text{Ca}_{14}\text{Si}_{19}$ phase is very difficult to precipitate, compared to the CaSi_2 and CaSi phases, in the case of the new Ta crucible. Thus, only CaSi is formed, following the metastable extension of the CaSi liquidus line below 1088°C . This metastable CaSi liquidus is also plotted as a broken line in Fig. 10(b), which lies below the stable $\text{Ca}_{14}\text{Si}_{19}$ liquidus line. During the solidification of the Ca-rich melt, the local composition of the liquid near the primary CaSi precipitates becomes more Si-rich than the CaSi_2 stoichiometric composition by solute partitioning, and thus, a small amount of the non-equilibrium Si phase forms. Note that the metastable invariant reaction of CaSi , liquid, and CaSi_2 must not be the eutectic liquid $\rightarrow \text{CaSi} + \text{CaSi}_2$ but the peritectic $\text{CaSi} + \text{liquid} \rightarrow \text{CaSi}_2$ because the Si phase also forms in the Ca-rich specimens. The temperature of the metastable peritectic $\text{CaSi} +$

liquid $\rightarrow$ CaSi_2 was not measured in this study, but it is presumably slightly below that for the stable peritectic $\text{Ca}_{14}\text{Si}_{19} + \text{liquid} \rightarrow \text{CaSi}_2$.

Figure 10(b) can also explain the formation mechanisms for two characteristic solidification structures observed in the case of ingots fabricated with a new Ta crucible,

i.e., the coupled structure of CaSi_2 and CaSi phases obtained from Ca-rich melts (Fig. 4) and the single-phase CaSi_2 structure obtained from the stoichiometric CaSi_2 melt (Fig.

6). When the Ca-rich melt solidifies inside the new Ta crucible, the CaSi phase precipitates as the primary phase. However, the $\text{Ca}_{14}\text{Si}_{19}$ phase is not likely to precipitate. As a result, the primary CaSi phase precipitation is followed by precipitation of the CaSi_2 phase, and thus a coupled structure of CaSi_2 and CaSi is formed instead.

When the high-purity stoichiometric CaSi_2 melt solidifies, CaSi is the primary phase.

However, its liquidus point is below 1047°C . The undercooling required for CaSi_2 precipitation, i.e., the temperature difference between the metastable CaSi_2 melting point and the metastable peritectic reaction $\text{CaSi} + \text{liquid} \rightarrow \text{CaSi}_2$ is less than 5°C .

Therefore, single-phase CaSi_2 can be obtained from the high-purity stoichiometric CaSi_2 melt.

Note that the peritectic reaction $\text{CaSi} + \text{liquid} \rightarrow \text{Ca}_{14}\text{Si}_{19}$ occurs over the composition range from the Ca-rich to the Ca-poor side of the phase diagram proposed by Gröbner et al. [18], shown in Fig. 1. According to this phase diagram, it is necessary to prevent the nucleation of the CaSi phase as well as the $\text{Ca}_{14}\text{Si}_{19}$ phase in order to obtain a

single-phase CaSi_2 ingot. Furthermore, the undercooling required to obtain a single-phase CaSi_2 ingot, i.e., the temperature difference between the liquidus and the peritectic reaction $\text{Ca}_{14}\text{Si}_{19} + \text{liquid} \rightarrow \text{CaSi}_2$ on the CaSi_2 stoichiometric composition, is more than 120°C . However, it seems difficult to inhibit CaSi precipitation under such high undercooling because the CaSi phase precipitates readily, as shown in the present study. Thus, the phase diagram in Fig. 1 must be modified from this perspective. Indeed, the revised phase diagram in Fig. 10(b) demonstrates that the peritectic reaction $\text{CaSi} + \text{liquid} \rightarrow \text{Ca}_{14}\text{Si}_{19}$ occurs only on the Ca-rich side. For the CaSi_2 stoichiometric composition, the primary phase is $\text{Ca}_{14}\text{Si}_{19}$ and the undercooling required for CaSi_2 precipitation is only about 5°C . Therefore, single-phase CaSi_2 can be obtained from the CaSi_2 stoichiometric melt. This is arguably one of the most important features of the revised phase diagram.

The most recent Ca-Si binary phase diagram based on DTA results was developed by Manfrinetti et al. [15]. The differences between the phase diagrams presented in our study and in their study [15] are presumably due to differences in experimental conditions. For example, in their DTA measurements, Manfrinetti et al. sealed the raw materials Si and Ca in a Mo crucible by arc welding, which prevented Ca evaporation and oxidation. However, the sample was subjected to heating and cooling cycles in Mo pans, and the highest temperature during these cycles was at least 1120°C in the case of the Ca-70at%Si sample, which had the lowest liquidus temperature around the CaSi_2

stoichiometric composition. Heating at such elevated temperatures promotes the formation of Mo silicides (MoSi_2 , Mo_5Si_3 , etc.) [25]. This results in the consumption of Si, which in turn changes the melt composition from Ca-poor to Ca-rich, leading to an increase in the liquidus temperature and nucleation of the $\text{Ca}_{14}\text{Si}_{19}$ phase. Si consumption has a large effect on the melt composition, especially in small specimens, such as DTA samples.

Since the liquidus line temperature increases with increasing Ca composition, a Ca-rich melt composition might promote Ca evaporation and TaSi_x formation in our experiment. However, our XRD results indicated that CaSi_2 stoichiometric composition ingots were single-phase CaSi_2 , and the CaSi phase volume increased with increasing Ca content in the case of new Ta crucibles. Thus, it is thought that the influence of Ca evaporation and TaSi_x formation on melt composition was small.

Figure 1 plots experimental data presented in other studies [16, 17]. Ca vapor pressure measurements by Wynnyckyj and Pigeon [17] determined liquidus temperatures, and Schürmann et al. reported a Ca-Si phase diagram based on thermal analysis and metallography [16]. The experimental results in Fig. 1 show a considerable discrepancy: the CaSi liquidus line obtained by Manfrinetti et al. [15] is much higher than that reported in other studies [16, 17], and the eutectic point of CaSi_2 and Si reported in [15] occurs at a more Si-rich composition than those in [16] and [17]. The liquidus lines in the present study are closer to the data in [16] and [17] than they are to the data in [15].

On the other hand, Evers et al. [19] and Yamanaka et al. [20] presumably obtained millimeter-sized CaSi_2 single crystals by the precipitation of CaSi_2 as the primary phase in ingots cooled at a rate of $0.167^\circ\text{C}/\text{min}$ ($10^\circ\text{C}/\text{h}$). Yamanaka et al. obtained CaSi_2 single crystals from a melt of silicon and calcium (about 20% excess, i.e., about $\text{Ca}_{1.2}\text{Si}_2$ composition) at 1350°C by $0.167^\circ\text{C}/\text{min}$ ($10^\circ\text{C}/\text{h}$) cooling [20]. In their case, Ca evaporation occurred, as a result of which the melt composition changed from Ca-rich to Ca-poor. Also, Evers et al. obtained a CaSi_2 single crystal by $0.167^\circ\text{C}/\text{min}$ ($10^\circ\text{C}/\text{h}$) cooling. As mentioned above, the composition range over which CaSi_2 could precipitate as the primary phase is about 0.5 at%, i.e., between a and b in Fig. 1, but Ca evaporation from the CaSi_2 melt makes it difficult to control the melt composition in such a narrow composition range during the slow cooling stage. In contrast, the range from the stoichiometric composition to the eutectic point of CaSi_2 and Si in Fig. 10(b) is above 2.5 at%. Therefore, we concluded that the revised phase diagram in Fig. 10(b) was more suitable for their results.

4.2. Peritectic coupled growth of CaSi_2 and CaSi phases

A rod-like coupled structure of the phases CaSi_2 and CaSi , like a eutectic structure, was obtained from Ca-rich composition melts as shown in Fig. 4. Nevertheless, the metastable reaction $\text{CaSi} + \text{liquid} \rightarrow \text{CaSi}_2$ is peritectic (Fig. 10(b)). It is thought that this rod-type structure is created by peritectic coupled growth (PCG). In the peritectic

Fe-Ni binary phase diagram, where three phases, liquid, and primary δ form an invariant equilibrium with peritectic γ , Dobler et al. investigated variations in the morphology of the coupled δ/γ structure with alloy composition, growth rate (v) and temperature gradient (G) [26]. Coupled δ/γ bulks have banded, lamellar and rod structures. Similarly to eutectics, both lamellar and rod morphologies have been observed, and the lamellar-to-rod transition is induced by a reduction in the phase fraction. Dobler et al. reported that a necessary condition for lamellar PCG is a G/v ratio that is close to or above the critical value for morphological stability of the primary phase. Rod (fibrous) coupled growth requires a slightly lower G/v ratio than lamellar coupled growth. In addition, they explained that the key for PCG was that the solidification interval was very small, and consequently, the critical velocity for morphological instability was relatively high, on the order of 15 $\mu\text{m/s}$ in the Fe–Ni system.

In our results, the solidification interval (i.e., the temperature difference between the metastable liquidus point and metastable peritectic reaction) of CaSi_2 is less than 5°C in the Ca-Si system. Thus, PCG of the CaSi_2 and CaSi phases seems to have occurred, following which a rod-like coupled structure formed in Ca-rich ingots.

5. Conclusion

The equilibrium phase diagram around CaSi_2 (Ca_xSi_2 ; $0.9 \leq x \leq 1.1$) was obtained by identifying the phases in samples of varying composition and by DTA analysis of phase

transitions. CaSi_2 was treated as an incongruent-melting material that precipitated via the two peritectic reactions $\text{CaSi} + \text{liquid} \rightarrow \text{Ca}_{14}\text{Si}_{19}$ and $\text{Ca}_{14}\text{Si}_{19} + \text{liquid} \rightarrow \text{CaSi}_2$, and an undercooling of over 120°C was required to obtain single-phase CaSi_2 ingots, according to the currently accepted phase diagram. However, the peritectic reaction changed into a stable or metastable reaction, depending on the presence of impurities in the melt. If the melt contained some impurities, such as Ta, B or P, the stable peritectic reaction $\text{Ca}_{14}\text{Si}_{19} + \text{liquid} \rightarrow \text{CaSi}_2$ occurred at the CaSi_2 stoichiometric composition. In contrast, only $\text{CaSi} + \text{liquid} \rightarrow \text{CaSi}_2$ occurred as a metastable peritectic reaction in the high-purity melt, following the metastable extension of the CaSi liquidus line below 1088°C down to 1042°C . The undercooling required for CaSi_2 precipitation, i.e., the temperature difference between the metastable CaSi_2 melting point and the metastable peritectic reaction $\text{CaSi} + \text{liquid} \rightarrow \text{CaSi}_2$ was less than 5°C . Thus, single-phase CaSi_2 could be obtained from the stoichiometric CaSi_2 melt at a small undercooling. In addition, a rod-like coupled structure of the CaSi_2 and CaSi phases could form through PCG in high-purity Ca-rich ingots, via a metastable peritectic reaction.

The fabrication process for a single-phase CaSi_2 polycrystal was investigated as well. Such a polycrystal could be obtained by high-cooling-rate casting ($1\text{--}100^\circ\text{C}/\text{min}$) of a high-purity CaSi_2 stoichiometric melt using a new Ta crucible. Under these conditions, the formation of the $\text{Ca}_{14}\text{Si}_{19}$ phase was suppressed. In addition, rapid cooling was found to be important because it prevented compositional change due to Ca evaporation.

ACKNOWLEDGEMENTS

This work was supported in part by PRESTO, the Japan Science and Technology Agency.

References

- [1] Zintl E. *Angew Chem* 1939;52:1.
- [2] Schäfer H, Eisenmann B, Müller W. *Angew Chem Int Ed Engl* 1973;12:694.
- [3] Mayer IP, Banks E, Post B. *J Phys Chem* 1962;66:693.
- [4] Koleshko VM, Belitsky VF, Khodin AA. *Thin Solid Films* 1986;141:277.
- [5] Pierre J, Siaud E, Frachon D. *J Less-Common Metals* 1988;139:321.
- [6] Evers J. *J Solid State Chem* 1979;28:369.
- [7] Dick S, Öhlinger G. *Z Krist-New Cryst St* 1998;213:232.
- [8] Sanfilippo S, Elsinger H, Núñez-Regueiro M, Laborde O, LeFloch S, Affronte M, Olcese GL, Palenzona A. *Phys Rev B* 2000;61:R3800.
- [9] Bordet P, Affronte M, Sanfilippo S, Núñez-Regueiro M, Laborde O, Olcese GL, Palenzona A, LeFloch S, Levi D, Hanfland M. *Phys Rev B* 2000; 62:11392.
- [10] Tamanaka S, *Dalton Trans* 2010;39:1901.
- [11] Brandt MS, Vogg G, Stutzmann M, *Silicon Chemistry: From the Atom to Extended Systems* (Eds.: P. Jutzi, U. Schubert), Wiley-VCH, Weinheim, 2003;194-213.

- [12] Nakano H, Mitsuoka T, Harada M, Horibuchi K, Nozaki H, Takahashi N, Nonaka T, Seno Y, Nakamura H, Angew Chem 2006;118:6451; Angew Chem Int Ed 2006;45:6303.
- [13] Okamoto H, Kumai Y, Sugiyama Y, Mitsuoka T, Nakanishi K, Ohta T, Nozaki H, Yamaguchi S, Shirai S, Nakano H. J Am Chem Soc 2010;132:2710.
- [14] Sugiyama Y, Okamoto H, Mitsuoka T, Morikawa T, Nakanishi K, Ohta T, Nakano H. J Am Chem Soc 2010;132:5946.
- [15] Manfrinetti P, Fornasini ML, Palenzona A. Intermetallics 2000;8:223.
- [16] Schürmann E, Litterscheidt H, Fünders P. Arch Eisenhüttenwes 1974;45:367.
- [17] Wynnyckyj JR, Pigeon LM. Metall Trans 1971;2:975.
- [18] Gröbner J, Chumak I, Schmid-Fetzer R. Intermetallics 2003;11:1065.
- [19] Evers J, Weiss A. Mat Res Bull 1974;9:549.
- [20] Yamanaka S, Suehiro F, Sasaki K, Hattori M. Physica 1981;105B:230.
- [21] Hirano T. J Less-Common Metals, 1991;167:329.
- [22] Currao A, Wengert S, Nesper R, Curda J, Hillebrecht H. Z Anorg Allg Chem 1996;622:501.
- [23] Schlesinger ME, Binary Alloy Phase Diagrams, Second Edition, Ed. T.B. Massalski, ASM International, Materials Park, Ohio, 1990;3:3364.
- [24] Boettinger WJ, Kattner UR, Moon K-W, Perepezko JH, DTA and Heat-flux DSC Measurements of Alloy Melting and Freezing, NIST Special Publication 960-15, U.S.

Department of Commerce, Washington; 2006.

[25] Gokhale AB, Abbaschian GJ, Binary Alloy Phase Diagrams, Second Edition, Ed. T.B. Massalski, ASM International, Materials Park, Ohio, 1990;3:2664.

[26] Dobler S, Lo TS, Plapp M, Karma A, Kurz W, Acta Mater 2004;52:2795.

Figure captions

Fig. 1. Calculated phase diagram of the binary Ca-Si system with the experimental data [15-17] in [18].

Fig. 2. (a)-(i) Top surface of ingots fabricated from $\text{Ca}_{1.05}\text{Si}_2$, $\text{Ca}_{1.00}\text{Si}_2$, and $\text{Ca}_{0.90}\text{Si}_2$ composition melts at a cooling rate of 1, 10, and 100°C/min, respectively.

Fig. 3. The weak-peak-magnified powder XRD patterns of polycrystalline (a) $\text{Ca}_{1.00}\text{Si}_2$ and (b) $\text{Ca}_{1.05}\text{Si}_2$ ingots cooled at 1, 10, and 100°C/min, respectively, using new Ta crucibles.

Fig. 4. Cross-sectional (a) optical micrograph and (b) BSE image of a $\text{Ca}_{1.05}\text{Si}_2$ ingot cooled at 10°C/min.

Fig. 5. Cross-sectional BSE image of a $\text{Ca}_{0.90}\text{Si}_2$ ingot cooled at 10°C/min.

Fig. 6. Cross-sectional BSE image of a $\text{Ca}_{1.00}\text{Si}_2$ ingot cooled at $10^\circ\text{C}/\text{min}$.

Fig. 7. (a) The weak-peak-magnified XRD patterns of $\text{Ca}_{0.97}\text{Si}_2$, $\text{Ca}_{1.00}\text{Si}_2$, and $\text{Ca}_{1.03}\text{Si}_2$ polycrystals cooled at $10^\circ\text{C}/\text{min}$ using new Ta crucibles (no Ta contamination), and (b) the precipitation phase map around the composition CaSi_2 , obtained on the basis of XRD patterns.

Fig. 8. (a) The weak-peak-magnified XRD patterns of $\text{Ca}_{1.02}\text{Si}_2$, $\text{Ca}_{1.00}\text{Si}_2$, and $\text{Ca}_{0.99}\text{Si}_2$ cooled at $10^\circ\text{C}/\text{min}$ using second-use Ta crucibles (with Ta contamination), and (b) the precipitation phase map around the composition CaSi_2 , obtained on the basis of XRD patterns.

Fig. 9. The weak-peak-magnified powder XRD patterns of 100-ppm B- or P-doped $\text{Ca}_{1.05}\text{Si}_2$ ingots cooled at $100^\circ\text{C}/\text{min}$.

Fig. 10. (a) DTA analysis results for Ca_xSi_2 ingots with compositions in the range $0.90 < x < 1.1$. (b) Phase diagram of the Ca-Si binary system around CaSi_2 , obtained on the basis of DTA analysis results.

Fig. 1.

Fig. 2.

(a)

(b)

Fig. 3.

(a)

(b)

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

(a)

(b)

Fig. 8.

Fig. 9

Fig. 10.