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Na–Si binary phase diagram and solution growth of silicon crystals

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ABSTRACT

In the present study, a Na–Si binary phase diagram was first presented from the results of differential thermal analysis and X-ray diffraction. Based on the phase diagram, we performed low-temperature formation of single crystals, film and porous bulk of Si by vaporizing Na from a Na–Si melt at 800 or 900 °C.

1. Introduction

Phase diagrams provide essential information for the conditions of materials synthesis and crystal growth. Although many binary phase diagrams, including those for the Li–Si [1] and Na–Ge [2] systems, were reported in the last century, that for Na–Si has not yet been established. NaSi [3,4], $NaSi_2$ [5] and clathrate compounds Na_xSi_{136} ($x = 0$–24) [6,7] have been reported in the Na–Si binary system [8]. However, there has been no report on the melting points of these Na–Si compounds.

Recently, we succeeded in the formation of silicon carbide (SiC) nanopowder [9] and porous ceramics [10] by the reaction of silicon and amorphous carbon powders with Na at 700 °C. A high-temperature condition over 1200 °C is generally required to synthesize SiC from Si and carbon. β-Type iron silicide ($FeSi_2$) was also prepared at 500–900 °C by using Na as a flux [11]. In these studies, we surmised that a melt of Na–Si played an important role in the low-temperature formation of SiC and β-$FeSi_2$. In order to clarify the details of these low-temperature syntheses, we decided to study the Na–Si binary system. The growth of Si crystals from the Na–Si solution was also demonstrated based on the Na–Si phase diagram in the present study.

2. Experimental

The samples for the thermal analysis to construct the binary phase diagram were prepared with starting materials of Si powder (High Purity Chemicals, 99.999% purity) and Na (Nippon Soda, 99.95% purity). Predetermined amounts (total 400 mg) of these materials were weighed in an Ar gas-filled glove box (O_2 and $H_2O < 1$ ppm) and charged in boron nitride (BN) crucibles (Showa Denko; 99.5%; inside diameter, 6 mm; depth, 18 mm). Each crucible was sealed in a stainless-steel tube (inside diameter, 10 mm; length, 80 mm) to prevent the vaporization and composition change during heating (vapor pressure of Na at 727 °C was 0.1874 atm [12]). The sealed tube was heated at 700 °C for 24 h in an electric furnace. The amount of evaporated Na from the sample during the heating was confirmed to be less than 0.5 mol% by weighing the sample in the BN crucible.

The obtained samples were analyzed up to 850–900 °C by using DTA setup in which a sample in a BN crucible and a stainless steel sheathed thermocouple (alumel–chromel) were sealed in a stainless steel tube (inside diameter, 8 mm; length, 32 mm) under Ar atmosphere in the glove box. Two sealed tubes, one containing a sample in a BN crucible and the other containing a BN crucible without a sample for reference, were heated in air in an electric furnace. The heating and cooling rates were 20 °C/min. The accuracy of the measured temperatures was confirmed to be ±2 °C by measuring the melting points of Na (98 °C), In (157 °C), and Al (660 °C) [13]. No apparent reaction between the samples and the boron nitride of the crucible was observed by DTA nor by the naked eye. During the heating and cooling of the DTA measurement from room temperature to 900 °C, the amount of Na which evaporated from the sample was less than 1 mol%.

The crystalline phases in the sample before and after the thermal analysis were identified by powder X-ray diffraction (XRD; RINT2500, Rigaku). The high-temperature powder XRD measurements were carried out by using a Bruker AXS D8 Vario-1 equipped with a capillary heater stage (mri, Physikalische Gerate GmbH). The sample for the XRD measurement was kept in Ar atmosphere by using a cell with a window of kapton film or by sealing it in a quartz capillary tube with Ar gas.

3. Results and discussions

The Na–Si binary phase diagram based on the results of the DTA and XRD of the samples prepared with various compositions is shown in Fig. 1. The formation of NaSi (monoclinic, $a = 1.219$, $b = 0.655$, $c = 1.118$ nm, $\beta = 119.0°$, space group $C2/c$) [3] was confirmed. $NaSi_2$ reported by Nowotny and Scheil [5] was not obtained.

Fig. 2 shows the DTA curves of Na–25, 50, 60 mol% Si on heating process. In the DTA measurement for the sample of 50 mol% Si, two endothermic peaks were observed with heating, one at 612 °C and

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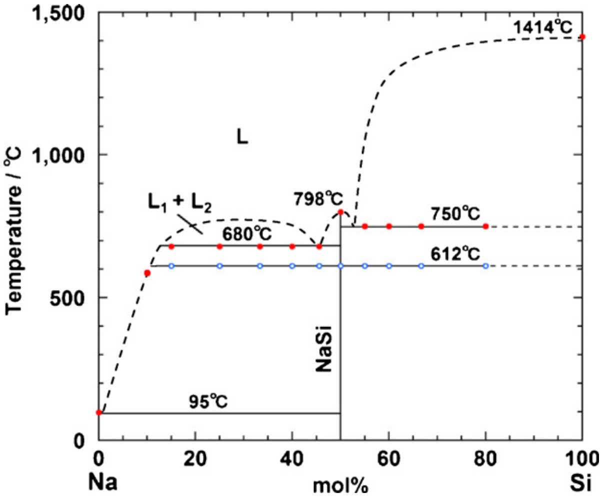

Fig. 1. Na–Si binary phase diagram.

the other at 798 °C. The sample heated to 700 °C maintained its shape, while that heated to 900 °C completely melted. Therefore, the melting point of NaSi was determined to be 798 °C.

An endothermic peak was also observed at heating to around 612 °C for other samples prepared with compositions of 25–80 mol% Si. A high-temperature XRD pattern measured for the sample of NaSi at 580 °C still showed the diffraction pattern of NaSi. Diffraction peaks were also observed at 630 °C, but the XRD pattern was different from that of NaSi observed at and below 580 °C. An exothermic peak was also observed upon cooling to around 612 °C for all the samples. Therefore, we concluded that a reversible phase transition of NaSi occurred at 612 °C. The crystal structure of the high-temperature phase is now under investigation.

A eutectic point at the composition close to 0 mol% Si was observed at 95 °C, which is 3 °C lower than the melting point of Na. The samples with the compositions of 25–45 mol% Si exhibited another endothermic peak upon heating to 680 °C. A mixture of Na and Si (molar ratio Na:Si = 2:1) completely melted when heated to 700 °C. From these results, we expected an area of two liquid phases, L$_1$ and L$_2$, with a eutectic point of 680 °C. Similar two liquid phase regions have been reported in binary phase diagrams containing Na, for example, in the diagram of Na-NaCl [14].

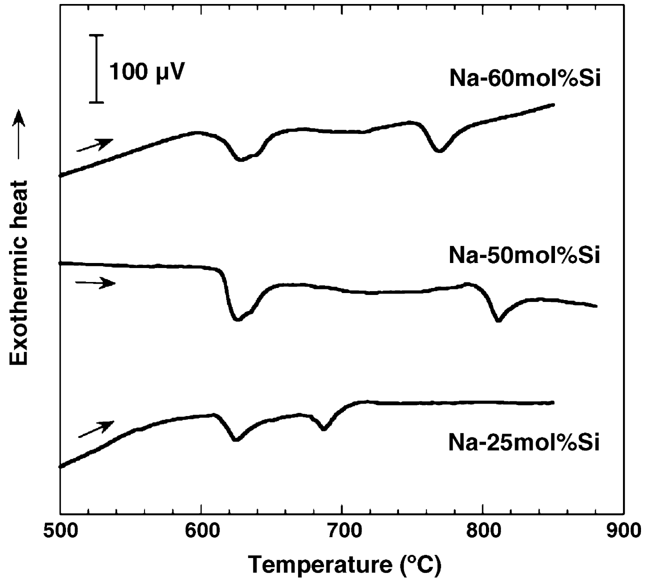

Fig. 2. DTA curves of the samples with compositions Na–25, 50, and 60 mol% Si on heating process.

In the DTA measurements for the samples of 55–80 mol% Si, another endothermic peak was observed upon heating to 750 °C. The partial melting of the samples of 60 and 67 mol% Si was observed after heating to 800 °C. Thus, the eutectic point was determined to be 750 °C in the composition over 50 mol% Si. The liquidus temperature at the composition of 55 mol% Si was determined to be between 1000 and 1100 °C because the sample heated at 1000 °C kept the shape as prepared and the sample heated at 1100 °C completely melted. The liquidus line was drawn toward the melting point of Si (1414 °C) [13]. The samples of 55–80 mol% Si obtained after DTA measurements were a mixture of Si and NaSi, and no other phase such as clathrate compounds [6,7] was detected by XRD. These clathrate compounds have been synthesized only by decomposition of NaSi and volatilization of Na in a vacuum at temperature around 375–450 °C [6,7].

The phase diagram of Na–Si clearly shows that the Na–Si melt exists above 680 °C at a Na-rich composition and above 750 °C at a Si-rich composition. These are consistent with the temperature of 700 °C and higher for the synthesis of SiC with Na in the previous studies [9,10]. The present phase diagram will be useful for the synthesis of Si containing materials at low temperature with a Na flux or a Na–Si solution. It also indicates the possibility of silicon formation from the Si containing Na solution.

Since the liquidus curve is steep at the composition around 55% Si and we had observed Na evaporation from the Na–Si melts by heating in an open system, we attempted low temperature solution growth of Si crystals by Na solvent vaporization. First, we prepared a homogeneous starting mixture of Na and NaSi by heating Si powder and Na metal (40 mol% Si) at 700 °C for 24 h in the BN crucible sealed in the stainless-steel tube. The sample of 40 mol% Si completely melts at this temperature. After cooling the sample in a furnace, the sample in the crucible was replaced and sealed in a long stainless-steel tube (inside diameter, 10 mm; length 200 mm) in the glove box. The BN crucible in the tube was heated at 800 or 900 °C for 24 h with an electric furnace. The other side of the tube was out of the furnace and cooled in air. Na was vaporized from the sample and condensed at the cooler side in the tube. The composition of the sample was changed toward the liquidus line at around 53 mol% Si at 800 and 900 °C by Na evaporation, and then crystallization of Si was started. After heating for 24 h, Na was not contained in the BN crucible. Fig. 3 shows the optical microscope and scanning electron microscope (SEM; Philips, ESEM XL30) photographs of the samples prepared at 800 °C (a) and (b) and 900 °C (c) and (d). The XRD peaks from the samples were indexed with the cell parameter of Si (cubic *Fd*-3*m*, $a = 0.543$ nm) [15].

The inside-wall of the BN crucible was coated with a silicon film with a thickness of 10–20 μm by heating at 800 °C. The film consisted of domains with a size of 200–400 μm. Radial growth of fine needle Si crystals was observed in the domains (Fig. 3(b)). On the other hand, Si crystals with a grain size of 100–200 μm grew on the BN crucible wall at 900 °C (Fig. 3(c) and (d)). Each grain has a square pyramidal shape with many step edges on pyramidal facets and a smooth rectangular facet on the top. The Si grains were easily separated from the BN crucible wall.

After washing the samples with distilled water, the samples were analyzed with an energy dispersive X-ray analyzer (EDX, EDAX) installed on the SEM. Only a characteristic X-ray peak of Si appeared in the EDX spectrum. Na and other impurity elements could not be detected by EDX.

We could also prepare porous bulk Si by using a mixture of NaSi and Si (molar ratio Na:Si = 1:2) powders. The mixture was pressed into a rectangular parallelepiped of 3 mm × 3 mm × 14 mm with a die in an Ar gas-filled glove box. It was set in a BN crucible, sealed in the long stainless-steel tube, and heated at 800 °C for 24 h by

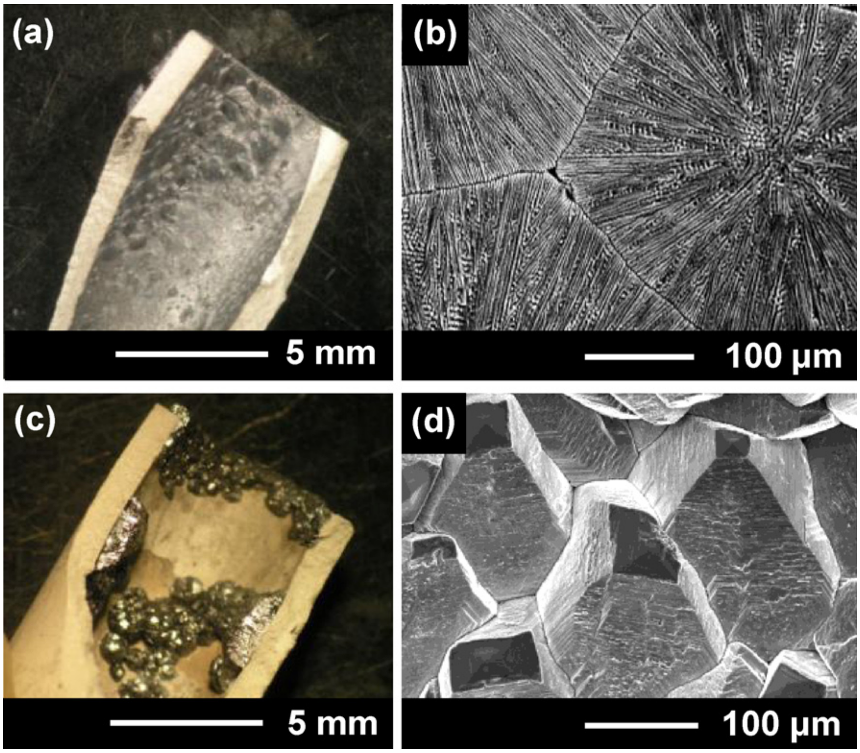

Fig. 3. Photographs and SEM images of the samples formed on the inside wall of the BN crucible by vaporizing Na from Na-40 mol% Si at 800 °C (a), (b) and 900 °C (c), (d).

the electric furnace. This temperature is above the eutectic point of 750 °C at the Si-rich compositions. The NaSi grains melted at this temperature and changed into Si grains by Na evaporation, bonding the premixed Si grains in the sample. Fig. 4 shows the photograph and SEM image of the porous Si in which Si grains with a size of a few μm aggregate and form agglomerates. The density of this sample was 1.1 Mg/m^3, which was 48% of the density of Si (2.3 Mg/m^3) [13].

Solar cell attracts attention as one of the last cards of the global warming countermeasure, and the market spreads rapidly. To expand use of Si solar cells, the development of a low-cost method to produce bulk, plate, and film of single crystalline or polycrystalline Si is necessary. The melt growth of Si crystal expends much thermal energy because of the high melting point of Si at 1414 °C [13]. It has been reported that metals having a low melting point, such as Ga [16], In [17], and Al [18,19] were used as solvents and Si crystallized from the metal solutions. However, Ga and In metals are expensive, and it is difficult to remove Ga, In, and Al from the products. Therefore, it is worth noting that crystals, film and porous Si bulk can be formed at 800–900 °C by Na solvent evaporation. Na is easily removed from the products and reused by vaporizing and condensing. The melting and boiling points of Na are 98 and 881 °C at 1 atm, respectively [13]. Low-temperature Si crystal formation would also be possible with a Li–Si melt because of a similar liquidus curve in the Li–Si binary phase diagram [1]. However, Li has a higher boiling point of 1347 °C [13].

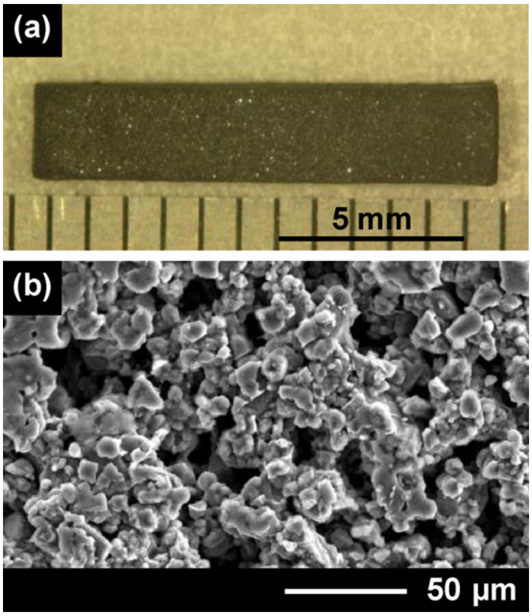

Fig. 4. Photograph (a) and SEM image (b) of the porous Si prepared by heating a mixture of NaSi and Si (Na:Si = 1:2) and by vaporizing Na at 800 °C for 24 h.

According to MacCaldin et al., the concentration of Na introduced from a Na–Si melt into Si at 800 °C is the order of 3×10^{17} cm^{-3} and no donor properties were observed by the Na introduction [20]. Although further investigation is needed to reveal the amounts of trace impurities introduced in the present process and the effect of the impurities to the application, we believe that the present process of low temperature Si crystal formation will be applied to low-cost and low-environmental-load manufacture of Si and Si-containing materials in the future.

4. Conclusions

We studied the Na–Si binary phase diagram which showed the melting point of NaSi at 798 °C and the existence of Na–Si melt over this temperature. Si crystal formation from a Na solution was demonstrated by solvent evaporation. This solution process could be applied to prepare film, crystals, and porous bulk of Si at 800 and 900 °C.

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References

[1] C. van der Marel, G.J.B. Vinke, W. van der Lugt, Solid State Commun. 54 (1985) 917–919.
[2] M.E. Drits, V.F. Potemkin, L.L. Zusman, Inorg. Mater. 18 (1982) 969–971.
[3] E. Hohmann, Z. Anorg. Allg. Chem. 257 (1948) 113–126.
[4] J. Witte, H.G. Schenering, Z. Anorg. Allg. Chem. 327 (1964) 260–273.
[5] H. Nowotny, E. Scheil, Z. Metallkd. 38 (1947) 76–80.
[6] C. Cros, M. Pouchard, P. Hagenmuller, J. Solid State Chem. 2 (1970) 570–581.
[7] G.K. Ramachandran, J. Dong, J. Diefenbacher, J. Gryko, R.F. Marzke, O.F. Sankey, P.F. McMillan, J. Solid State Chem. 145 (1999) 716–730.
[8] J. Sangster, A.D. Pelton, J. Phase Equilibr. 13 (1992) 67–69.
[9] F. Kawamura, H. Yamane, T. Yamada, S. Yin, T. Sato, J. Ceram. Soc. Jpn. 115 (2007) 74–76.
[10] F. Kawamura, H. Yamane, T. Yamada, S. Yin, T. Sato, J. Am. Ceram. Soc. 91 (2008) 51–55.
[11] T. Yamada, H. Yamane, Chem. Mater. 19 (2007) 6047–6051.
[12] W.T. Hicks, J. Chem. Phys. 38 (1963) 1873–1880.
[13] N.N. Greenwood, A. Earnshaw, Chemistry Of The Elements, Pergamon Press, 1984.
[14] M.A. Bredig, J.W. Johnson, W.T. Smith Jr., J. Am. Chem. Soc. 77 (1955) 307–312.
[15] M.E. Straumanis, J. Appl. Phys. 23 (1952) 330–334.
[16] B. Girault, F. Chevrier, A. Joullié, G. Bougnont, J. Cryst. Growth 37 (1977) 169–177.
[17] W. Scott, R.J. Hager, J. Electron. Mater. 8 (1979) 581–602.
[18] K. Ito, K. Kojima, Jpn. J. Appl. Phys. 19–2 (Suppl.) (1979) 37–41.
[19] T. Yoshikawa, K. Morita, ISIJ Int. 45 (2005) 967–971.
[20] J.O. McCaldin, M.J. Little, A.E. Widmer, J. Phys. Chem. Solids 26 (1965) 1119–1123.