JOURNAL OF MATERIALS SCIENCE 21 (1986) 2254–2256

The formation of β-SiC fibres with SiO_2–C–NaF(AlF_3) components

M. KAJIWARA
Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Nagoya 464, Japan

The formation of β-SiC fibres with SiO_2–C–NaF(AlF_3) components was investigated. It was found that the formation of a longer β-SiC fibre was governed by the mole ratio of C/SiO_2 or C/NaF. Using a mole ratio for C/SiO_2 or C/NaF of 3 or more, β-SiC fibres of length 3 mm were prepared in a closed system. On the other hand, short β-SiC fibres were obtained in an open system. β-SiC fibres prepared under the various experimental conditions were stable when heated in a high-concentration acidic solution such as HCl or H_2SO_4, and in an alkaline solution such as NaOH.

1. Introduction

Silicon carbide (SiC) has recently been attracting interest as a high-temperature material because of its high resistance to oxidation, corrosion and thermal shock. In 1975, Yajima and co-workers described the use of polysilanes as precursors for β-SiC [1–3]; polycarbosilanes were spun into fibres, cured and then heated at a high temperature under a non-oxidizing atmosphere to give SiC fibres with a high tensile strength. Also, Achson described how SiC could be prepared from silicon dioxide and carbon. This report describes the formation of SiC fibres using SiO_2–C–NaF(AlF_3) components in both open and closed systems.

2. Experimental details

After given amounts of SiO_2, carbon and NaF or AlF_3 were mixed with an agate mortar and pestle, the mixture was placed on a boat. After the boat was kept at 1200, 1300 and 1400° C for one to four hours under a flow of 200 ml min^{-1} of argon gas, the temperature was lowered to 900° C at a rate of 200° C h^{-1}. Argon gas flow was turned off when the temperature went up to 900° C. The boat was a murite tube made by Niphon Kagaku Togyo Co. The length and outside or inside diameter of the tube were 100 cm and 3.6 cm, respectively, and it was cut into a round slice. The boat when used as a container was the "open" system and the tube was the "closed" system as shown in Fig. 1. The mole ratio of SiO_2 : C : NaF or SiO_2 : C : NaF : AlF_3 was changed in the case of the open system. The grain size of SiO_2, carbon, NaF or AlF_3 was about 200 mesh. 100 or 325 mesh carbon was also used in the closed system.

The main crystalline products prepared under various experimental conditions were investigated by X-ray diffraction analysis and by optical and electron microscopy. The lengths of the fibres were determined with a micrometer.

3. Results and discussion

3.1. Thermodynamic study of the formation of SiC

Achson reported that the formation of SiC from SiO_2–C components occurred at 2000° C or over. Using SiO_2–C–NaF components, SiC will be prepared by the reaction

$$(3 + x)\,SiO_2 + 3xC + 4NaF = xSiC + 2xCO + SiF_4 + 2Na_2SiO_3 \quad (1)$$

The free energy of formation of SiC is then calculated by substituting various x values; the results are shown in Fig. 2.

It was found that SiC was easily prepared with increasing x values at a low temperature.

3.2. Open system

3.2.1. SiO_2–C–NaF:

After the sample containing SiO_2, carbon and NaF was heated at 1200, 1300 and 1400° C for one hour or four hours, the substance remaining in the boat was determined by X-ray diffraction analysis; the results are shown in Table I. Furthermore, the average length

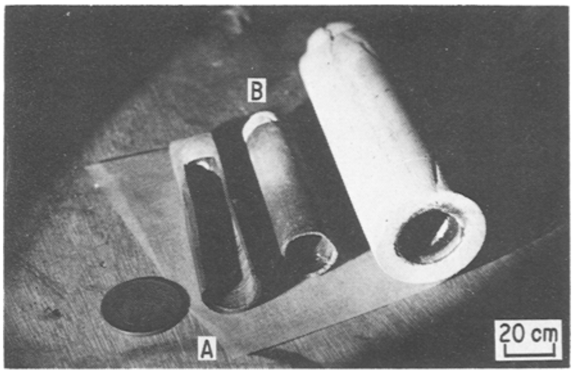

Figure 1 Boat used as a container for (A) open and (B) closed system.

0022–2461/86 $03.00 + .12

TABLE I Length of fibres and main crystalline products under various experimental conditions in an open system

Experiment No.	Reaction		Mass (g)			Mole ratio $SiO_2:C:NaF$			Main crystalline products and fibre length
	Temperature (°C)	Time (h)	SiO_2	C	NaF				
1	1200	2	0.48	0.288	0.336	1	3	1	β-SiC, α-crystobalite, 50 μm
2	1300	2	0.48	0.288	0.336	1	3	1	β-SiC, 50 μm, α-crystobalite
3	1400	1	0.48	0.288	0.336	1	3	1	β-SiC, 100 μm
4	1400	2	0.48	0.288	0.336	1	3	1	β-SiC, 50 μm
5	1400	4	0.48	0.288	0.336	1	3	1	β-SiC, short
6	1400	1	0.48	0.072	0.336	4	3	4	β-SiC, 50 μm, α-crystobalite
7	1400	2	0.72	0.108	0.504	4	3	4	β-SiC, short, α-crystobalite
8	1400	1	0.27	0.432	0.210	9	72	10	β-SiC, 50 μm
9	1400	2	0.27	0.432	0.210	9	72	10	β-SiC, 50 μm
10	1400	4	0.27	0.432	0.210	9	72	10	β-SiC, 100 μm

TABLE II Length of fibres and main crystalline products prepared under various experimental conditions in an open system using SiO_2–C–NaF–AlF_3

Experiment No.	Reaction		Mass (g)				Mole ratio $SiO_2:C:NaF:AlF_3$				Main crystalline products and fibre length
	Temperature (°C)	Time (h)	SiO_2	C	NaF	AlF_3					
11	1400	2	0.216	0.303	0.504	0.336	9	63	30	10	β-SiC, 50 μm
12	1400	4	0.216	0.303	0.504	0.336	9	63	30	10	β-SiC, 50 μm
13	1400	2	0.216	0.303	0.336	0.168	9	63	20	5	β-SiC, 50 μm
14	1400	2	0.216	0.303	0.168	0.366	9	63	10	10	β-SiC, Very short
15	1400	2	0.216	0.303	0.168	0.168	9	63	10	5	β-SiC, 100 μm, α-Al_2O_3

of β-SiC fibres was measured by a micrometer, and the results are summarized in Table I.

It is found from the data that the main crystalline products are β-SiC and α-crystobalite. However, α-crystobalite is not formed when using a mole ratio of SiO_2 : C : NaF = 1 : 3 : 1 or 9 : 72 : 10 when the reaction temperature is 1400° C. On the other hand, the longest fibres are formed using a mole ratio of SiO_2 : C : NaF = 9 : 72 : 10. The longest β-SiC fibres seen in the electron microscopic are shown in Fig. 3. Calculations based on the thermochemical data indicate that the mole ratio of SiO_2 : C : Na = 4 : 3 : 4 is a more suitable condition for the formation of SiC than other mole ratios in this experiment. However, the mole ratio 4 : 3 : 4 is not a good condition is that α-crystobalite and short β-SiC fibres are formed.

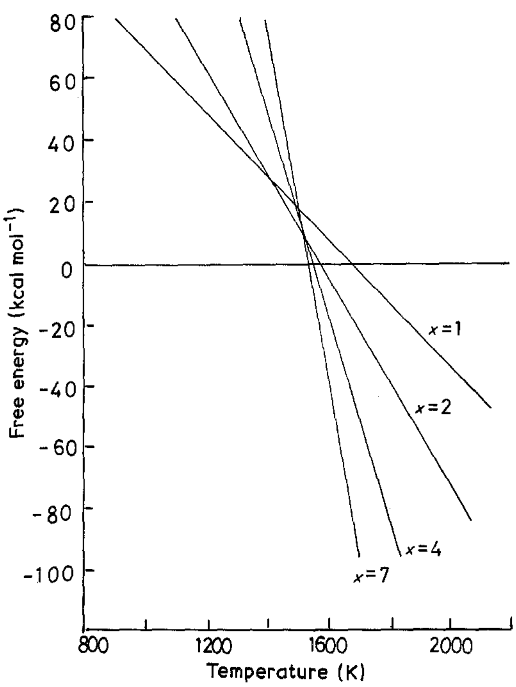

Figure 2 Free energy of formation of SiC, calculated for various values of x. 1 kcal = 4186.8 J.

3.2.2. SiO_2–C–NaF–AlF_3

After the reaction mixture was heated at 1400° C for two or four hours, the substances remaining in the boat were determined by X-ray diffraction analysis and the main crystalline products detected are summarized in Table II. It is found from Table II that the longest β-SiC fibres are formed under the conditions of Experiment No. 15, but this is not suitable since α-Al_2O_3 appears.

3.3. Closed system

The formation of SiC from SiO_2–C–NaF is determined by vapour-phase components such as CO or SiF_4 as shown in by Yajima *et al.* [1]. That is, the vapour phase is the important factor for the formation and growth of SiC fibres. The reaction was carried out in a closed system because a considerable growth of

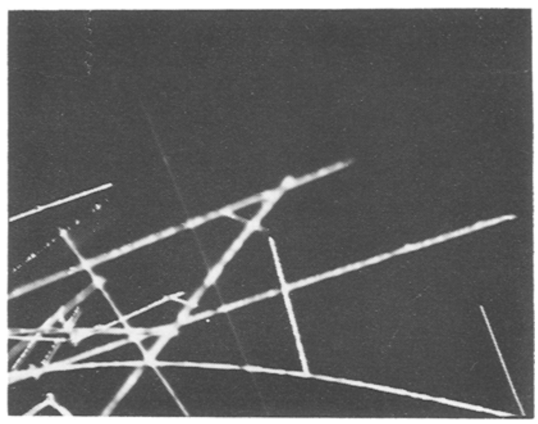

Figure 3 Electron micrograph of β-SiC fibres formed in an open system at 1400° C for 4 h with a mole ratio SiO_2 : C : NaF = 9 : 72 : 10. × 5800.

TABLE III Length of fibres and main crystalline products under various experimental conditions in a closed system using SiO_2–C–NaF

Experiment No.	Reaction		Grain size (mesh)	Mass (g)			Mole ratio SiO_2:C:NaF			Main crystalline product and fibre length
	Temperature (° C)	Time (h)		SiO_2	C	NaF				
16	1400	2	200	0.27	0.432	0.21	9	72	10	β-SiC, 1 mm
17	1400	1	200	0.27	0.432	0.21	9	72	10	β-SiC, 3 mm
18	1400	1	325	0.27	0.432	0.21	9	72	10	β-SiC, 1 mm
19	1400	1	200	0.48	0.288	0.366	1	3	1	β-SiC, 1 mm
20	1400	1	325	0.48	0.288	0.366	1	3	1	β-SiC, 3 mm
21	1400	1	100	0.24	0.480	0.168	1	10	1	β-SiC, 3 mm
22	1400	1	200	0.24	0.480	0.168	1	10	1	β-SiC, 3 mm
23	1400	1	325	0.24	0.480	0.168	1	10	1	β-SiC, 0.5 mm
24	1400	1	200	0.600	0.360		1	3		β-SiC, 50 μm

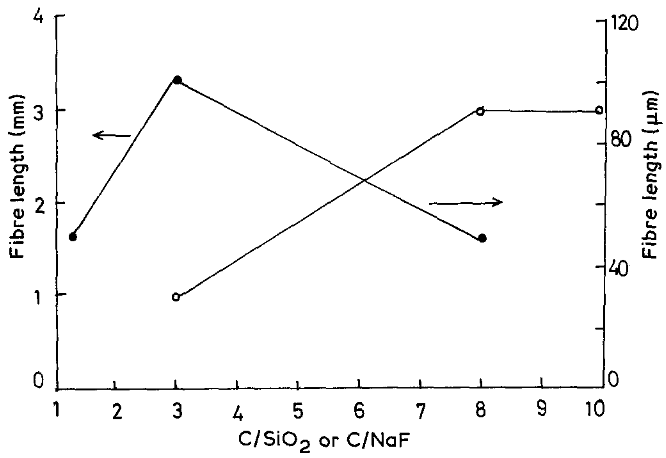

Figure 4 Relation between β-SiC fibre length prepared at 1400° C for 1 h in (●) open and (○) closed system, and the mole ratio C/SiO_2 or C/NaF.

β-SiC fibres was not produced in the open system. The influence on the formation of β-SiC of the grain size of carbon was also studied at the various mole ratios of SiO_2 : C : NaF. The results are shown in Table III.

It is found that the main crystalline product is β-SiC, and the grain size of carbon is not related to the growth of β-SiC fibres. However, short β-SiC fibres are produced without NaF. Using 200 mesh carbon and heating at 1400° C for one hour, the relation between β-SiC fibre length prepared in an open or a closed system and the mole ratio of C/SiO_2 or C/NaF is given in Fig. 4.

It is found that the ratio of C/SiO_2 or C/NaF is related to β-SiC fibre growth, and the most suitable mole ratio is three or more. The mole ratio obtained from the thermodynamic study is 3/4; however, in both open or closed systems, the best mole ratio for long β-SiC fibres is not consistent with this value. A typical electron micrograph is given in Fig. 5. In addition, gas eliminated during the experiment was analysed with a mass spectrometer. The results show that CO and SiF_4 gas are detected.

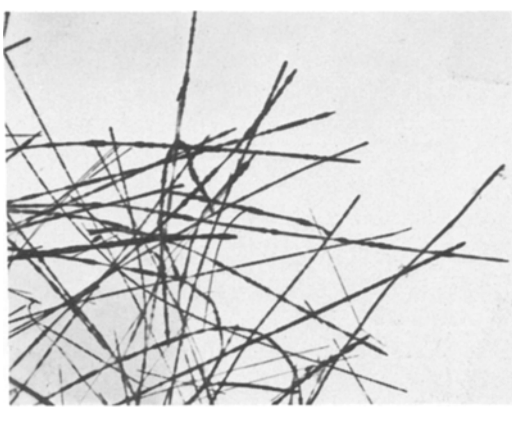

Figure 5 Electron micrograph of β-SiC fibres found in a closed system at 1400° C for 1 h with a mole ratio SiO_2 : C : NaF = 1 : 10 : 1. × 5800.

3.4. Analysis of β-SiC fibres

Thermal analyses of β-SiC fibres prepared under various experimental conditions were performed with a Shimazu thermal analyser DT–20B. Weight loss, exo- and endothermic peaks did not appear at 1200° C in air or a nitrogen atmosphere. After β-SiC fibres were immersed in boiling aqueons solutions of 20 or 40% HCl, 80% H_2SO_4 or 20 or 40% NaOH for one or two hours, no change in morphology of β-SiC fibres was observed under the microscope. Consequently, β-SiC fibres prepared in this study are stable to heating and chemical agents.

References

1. S. YAJIMA, K. OKAMOTO, J. HAYASHI and M. OMORI, *J. Amer. Ceram. Soc.* **59** (1976) 324.
2. S. YAJIMA, K. OKAMURA, T. MATSUZAWA, Y. HASEGAWA and T. SHISHIDO, *Nature* **279** (1979) 706.
3. S. YAJIMA, J. HAYASHI and M. OMORI, US Patent, 4 100 233 (1978).

Received 22 April and accepted 4 July 1985