研 究

Electrical Conductivity of MoSi_2 -SiC Ceramics Prepared by Reaction Sintering of Polysilazane with Molybdenum Metal

Masayoshi Miyamoto, Makoto Sasaki and Ken-ichi Mukaida

Muroran Institute of Technology, 27-1 Mizumoto, Muroran 050-8585.

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SYNOPSIS

To develop high-temperature heat elements with a small temperature-coefficient electrical conductivity, small-grained MoSi_2 -SiC ceramics were prepared by reaction sintering ceramic precursor with molybdenum powder. By second sintering at 1773 K for 10 h, two phases of MoSi_2 and β -SiC were formed. The average grain size of both MoSi_2 and SiC ranges several tens nanometers. Electrical conductivity measurement revealed that conductive behavior changed from semiconductive to metallic with increasing molybdenum disilicide content. 54.3 wt% MoSi_2/β -SiC composite showed an almost constant temperature coefficient in the temperature range at around to 600~850 K.

KEY WORDS

polysilazane, ceramic precursor, reaction sintering, MoSi_2 , β -SiC, electrical conductivity

1 Introduction

MoSi_2 and SiC are typical nonoxide ceramics used at high temperature atmospheric conditions^{1,2}. MoSi_2 has been studied to use as a high temperature structural material^{2,4}, a heat element and an infrared light source because of its excellent oxidation resistance. It is known, however, mechanical strength of MoSi_2 tends to decrease at high temperatures⁴. It follows, therefore, SiC-added MoSi_2 has more excellent high temperature strength than that of MoSi_2 ⁵.

Small-grained MoSi_2 -SiC ceramic composites are more preferable as heat element. A conventional sintering method may not give large enough sinterability; hence, a novel route may be examined. Organic-inorganic conversion method, so-called precursor route, is attractive to derive the ceramic composites by reaction sintering of polymers such as polysilazane with other elements^{6,7}. A polysilazane, one of organosilicon polymers, has an advantage of self-cross linking sites to derive nonoxide ceramics without oxygen⁸⁻¹⁰. Polymer-derived small-grained MoSi_2 -SiC ceramics has been expected as a heating element because of its excellent oxidation resistance, mechanical strength, and a small electrical conductivity coefficient vs. temperature.

The present work has focused on the Mo-Si-C-N ceramics by reaction sintering of polysilazane with molybdenum, and on the small-grained MoSi_2 -SiC ceramic composites, and their electrical conductivity.

2 Experimental

An infusible ceramic precursor was prepared by cross linking of polysilazane (Si-C-N-H) at 693 K for 6 h in an Ar atmosphere. After the milling and sieving (grain size less than $75\mu\text{m}$) of the cross-linked polysilazane, molybdenum powder (grain size less than $3.0\mu\text{m}$) was mixed in a dry process. And then, mixed powder samples were CIPed (pressure of 625 MPa, and pressing times of 60 sec.) as a cylindrical shape (ca. 6.5 mm in diameter, and ca. 8.0 mm in height). The molybdenum composition was 15 wt % or 30 wt% against polysilazane.

Mo-Si-C-N amorphous ceramics were derived by reaction sintering at 1273 K for 4 h in Ar (flow rate: 500 SCCM for 1st sintering). Furthermore, the Mo-Si-C-N ceramics were tried to crystallize at 1623 K, 1673 K and 1773 K for 10 h in Ar (flow rate: 100 SCCM for 2nd Sintering).

The weight change of the CIPed specimens during 1st and 2nd sinterings were examined by TGA (Shinku-Riko, TGD-9800A, carrier gas: Ar, flow rate: 100 SCCM, heating rate: 250 K h^{-1}). Chemical composition of the polymer and the derivatives were measured by combustion method (N, O: Horiba Oxygen/ Nitrogen Analyzer 550 650 series, C, S: Carbon Sulfur Analyzer 510, 511, 512). Crystallization of Mo-Si-C-N ceramics was evaluated by XRD (Rigaku-Denki, RV-200). Furthermore, the MoSi_2 and β -SiC contents were calibrated by comparing of (110) of MoSi_2 with (111) of β -SiC. Electrical conductivity measurement was achieved by

direct-current two terminal method.

3 Results and Discussion

3.1 Preparation of the Mo-Si-C-N amorphous ceramics

A TG curve of a first sintering is shown in Fig.1. The rapid weight decrease was observed in the temperature range from 500 K to 1073 K. The weight loss may be caused by hydrogen or hydrocarbon gas exhaust^{9,11}. Organic-inorganic conversion, so-called ceramization, has mainly done in the temperature range from 500 K to 1073 K. A gentle weight decrease on holding process has progressed in the following temperature region which may concern with the reaction sintering and the Mo-Si-C-N ceramic formation.

Fig.1 TG curve of ceramics (15 wt% Mo) obtained by heating at 1273 K for 56 h in Ar.

Fig.2 XRD patterns of ceramics (15 wt% Mo) obtained by heating at 1273 K for various holding time in Ar.

Figure 2 shows XRD patterns of each periods of holding processes at 1273 K for 4 h, 24 h and 48 h. Molybdenum remained can find in 4 h and 24 h heating samples, however, 48 h condition is long enough to achieve reaction sintering to obtain the Mo-Si-C-N ceramics.

3.2 MoSi₂-SiC ceramics formation by second sintering

TG curves of second sintering at 1773 K are shown in Fig.3. The 1st sintered samples were used for 2nd sintering. No weight change occurred up to around 1300 K, and the following temperature above 1600 K showed a gentle weight decrease. XRD patterns of 2nd sintered samples (30 wt% Mo) heated at 1623 K, 1673 K and 1773 K for 10

Fig.3 TG curves of the MoSi₂-SiC ceramics derived in Ar.

Fig.4 XRD patterns of ceramics (30 wt% Mo) obtained by heating at various temperatures in Ar.

h in Ar are shown in Fig.4. The temperature of 1623 K in Fig.4 shows a beginning of crystallization to prepare MoSi₂ and β-SiC. The higher temperatures above 1673 K are high enough to obtain MoSi₂-SiC ceramic composites. More suitable sintering condition to form MoSi₂-SiC composite is 1773 K for 4 h. Figure 5 shows a sintering time effect on the MoSi₂-SiC formation. Molybdenum free specimen in Fig.5 is almost still amorphous after heating at 1773 K for 10 h, however, Mo-containing ceramics have a tendency to crystallize in both cases, and resulted in the formation of MoSi₂ and SiC phases.

The particle sizes given by the Scherrer's expression are shown in Table 1 (CuK_{α1}, 0.1541 nm) by using a (110) of MoSi₂ and a (111) of β-SiC. The Scherrer's expression is well known to give a relative average particle size as follows;

$$D_{hkl} = (K \cdot \lambda) (\beta \cos \theta)^{-1},$$

where, K; constant, λ; wave length, β; width of angle of diffraction, θ; angle of diffraction, D_{hkl}; particle size.

The particle sizes of MoSi₂ and β-SiC were in the several tens nanometers. By the calibration of XRD, the weight ratio of MoSi₂ and β-SiC are given as follows;

- 15 wt% Mo → 44.7 wt% MoSi₂/β-SiC,
- 30 wt% Mo → 54.3 wt% MoSi₂/β-SiC.

The chemical composition of each samples are shown

in Table 2. Almost no hydrogen remains in the 1st sintered specimen independently molybdenum content. The ceramization may completely progress during heating at 1273 K. The lower nitrogen content was observed in the 2nd sintering specimen obtained at 1773 K, and the greater molybdenum results in less the nitrogen.

3.3 Electrical conductivity of MoSi₂-SiC ceramics composites

The specimens obtained at 1773 K as shown in Fig.5 were used as electrical conductivity measurement. The results are shown in Figs.6 and 7. Molybdenum free sample was in a small electrical conductivity range of 10⁻³ Sm⁻¹, and shows a typical semiconductive property such that conductivity increases with increasing temperature. 44.7 wt% MoSi₂/β-SiC obtained from 15 wt% Mo addition also shows a semiconductive property, but almost linear conductivity vs. temperatures. On the other hand, 54.3 wt% MoSi₂/β-SiC obtained from 30 wt% Mo addition demonstrates a metallic property with a negative conductivity coefficient vs. temperatures, with almost constant conductivity in the temperature measured.

Table 1 Particle size of MoSi₂/β-SiC ceramics (44.7 wt% MoSi₂/β-SiC derived from 15 wt% Mo, 54.1 wt% MoSi₂/β-SiC derived from 30 wt% Mo).

	44.7 wt% MoSi ₂ (nm)	54.3 wt% MoSi ₂ (nm)
β-SiC (111)	19.41	28.78
MoSi ₂ (110)	35.19	42.23

Table 2 Chemical compositions of polysilazane, ceramic precursor, the derived Mo-containing ceramics and MoSi₂/β-SiC ceramics.

	Si (wt%)	C (wt%)	N (wt%)	H (wt%)	O (wt%)	Mo (wt%)
Polysilazane	37.8	23.3	13.6	7.5	1.3	
Ceramics Precursor	37.6	21.6	18.1	7.6	1.8	
0 wt% Mo 1273 K	41.1	14.6	25.0	0.01	2.2	
0 wt% Mo 1773 K		13.4	23.2		4.5	
15 wt% Mo 1273 K	40.6	11.1	19.4	0.2	2.6	
15 wt% Mo 1773 K	47.3	12.7	5.7		1.2	23.1
30 wt% Mo 1273 K	34.0	9.1	15.2	0.2	2.3	
30 wt% Mo 1773 K	31.3	7.9	0.2		1.0	46.1

Fig.5 Powder XRD patterns of ceramics obtained by heating at 1773 K for 10 h in Ar.

Fig. 6 Electrical conductivity of ceramics (0 wt% Mo) obtained by heating at 1773 K for 10 h in Ar.

Fig. 7 Electrical conductivities of ceramics (15 wt% Mo, 30 wt% Mo) obtained by heating at 1773 K for 10 h in Ar.

4 Conclusions

A ceramic precursor composed of Si-C-N-H was used as a self-cross linked preform for the organic-inorganic conversion process to prepare Mo-Si-C-N ceramics, by reaction sintering. The Mo-Si-C-N amorphous ceramics obtained at 1273 K resulted in MoSi₂-SiC ceramic composites.

44.7 wt% MoSi₂/β-SiC and 54.3 wt% MoSi₂/β-SiC were formed from additional molybdenum of 15 wt% Mo, and 30 wt% Mo, respectively, by 2nd sintering at 1773 K for 4 h in Ar.

44.7 wt% MoSi₂/β-SiC was semiconductive and 54.3 wt% MoSi₂/β-SiC was metallic with an almost constant temperature coefficient of electrical conductivity, desirable as a heat element used at high temperatures.

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