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Electrically conductive silicon carbide with the addition of Ti–NbC

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Abstract

The work deals with the preparation of dense SiC based ceramics with high electrical conductivity. SiC samples with different content of conductive Ti–Nb–Si–C–O based phase were hot pressed at 1820 °C for 1 h in Ar atmosphere under mechanical pressure of 30 MPa. The conductive phase is a mixture of 50 wt% Ti–NbC (molar ratio of Ti/NbC is 1:1.8) and 50 wt% eutectic composition of Y_2O_3–SiO_2. Composite with 30% of conductive Ti–Nb–Si–C–O phase showed the highest electrical conductivity 28.4 S mm^{-1}, while the good mechanical properties of SiC matrix were preserved (fracture toughness K_{IC} = 5.4 MPa m$^{1/2}$ and Vickers hardness 17.8 GPa).

The obtained results show that the developed additive system is suitable for the preparation of SiC-based composite with sufficient electrical conductivity for electric discharge machining.

Keywords: Hot-pressing; Composites; Electrical conductivity; Hardness; Carbides; Silicides

1. Introduction

Silicon carbide (SiC) is a promising material for structural and electronic applications owing to its excellent oxidation resistance, high mechanical strength at elevated temperature, high hardness, high corrosion resistance, high thermal conductivity and high thermal shock resistance.[1–3]

SiC ceramics are known as very difficult to machine materials.[4] The main factors that cause SiC ceramics to be hard to shape are their high hardness, high strength and brittleness. Diamond grinding is one of the commonly used techniques for SiC ceramics, but it is a costly process with limitation on the complexity of the final shapes. One way to solve this problem was to add electroconductive phases, such as $MoSi_2$[5,6] and Ti–NbC[7] to extensively resistive SiC ceramics in large quantities for electric discharge machining (EDM). However, the addition of large amount of secondary phases leads to the degradation of high-temperature stability of SiC ceramics. EDM enables to machine extremely hard materials and complex shapes can be produced with high precision. Therefore, EDM is a potential and attractive technology for the machining of ceramics, providing that these materials have a sufficiently high electrical conductivity. A minimum electrical conductivity of 10^{-3} S mm^{-1} is considered as a limit for EDM.[8]

SiC is a semiconductor with a large bandgap ranging from 2.4 eV (β-SiC) to 3.4 eV (2H-SiC) according to the polytype.[9] However, a number of experimental results showed that impurity doping in SiC has led to the wide range of electrical conductivity (10^{-4}–10^{-16} S mm^{-1}) measured at the room temperature.

The main goal of this work was the preparation of dense SiC-based composite with high electrical conductivity and maintaining the good mechanical properties of the original SiC ceramics. Liquid phase sintering was selected for densification and the goals were achieved by two steps. First the Y_2O_3–SiO_2–NbC–Ti additive system was studied and characterized (details of preparation of the additive system is described in Ref. 7). In the second step the electroconductive SiC composite was prepared by addition of the electroconductive system developed in the first step to the SiC matrix. The present paper is devoted to the second step, i.e. to the fabrication of electroconductive SiC ceramics.

The successful preparation of such composite would extend the application potential of such a composite. The possible applications of electroconductive SiC ceramics could be widened, e.g.

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Table 1
Chemical composition of the electrically conductive N-phase.

	Composition (wt%)			
	SiO_2	Y_2O_3	Ti	NbC
N-phase	20	30	18	32

as heat exchangers, furnace heating elements, bearings without surface charging, aircraft engine parts, etc., and moreover allows the discharge machining of electrically conductive SiC.

2. Experimental

Commercially available powders of β-SiC (HSC-059, Superior Graphite, USA), SiO_2 (Aerosil OX-50, Degussa, Germany), Y_2O_3 (grade C, H.C. Starck, Germany), Ti (TOHO Titanium Co., Japan) and NbC (Japan New Metals Co., Japan) were used for the starting powders preparation. The SiC-based composites were prepared by the addition of different amount of electrically conductive Ti–Nb–Si–C–O phase (hereafter be cited as "N-phase"[7]) which is a mixture of 50 wt% Ti–NbC (molar ratio of Ti/NbC is 1:1.8) and 50 wt% eutectic composition of Y_2O_3–SiO_2. The chemical composition is listed in Table 1.

The compositions of studied composites and reference SiC materials are listed in Table 2. In the case of composites the ratio SiO_2:Y_2O_3 was 0.39, corresponding to the lowest eutectic temperature $T_E = 1660\,^{\circ}C$ in the binary diagram SiO_2–Y_2O_3, and the ratio Ti:NbC was 1:1.8.[7] The reference material (SiC_{ref}) was prepared for a comparison of the mechanical properties and the electrical conductivity.

The powder mixtures were ball milled in isopropyl alcohol with SiC balls for 24 h. The homogenized suspension was dried and subsequently screened through 71 μm sieve in order to avoid large hard agglomerates. The pre-pressed pellets were hot pressed according to the following regime: 1500 °C/1 h + 1820 °C/1 h in Ar atmosphere under 30 MPa pressure. The reference material was hot pressed at 1820 °C for 1 h in Ar atmosphere under 30 MPa. The densities of the samples were measured by Archimedes method in mercury. The theoretical densities were calculated according to the rule of mixtures. The microstructures were observed by scanning electron microscopy (Zeiss, EVO 40HV, Germany). The elemental analysis of crystalline phases was examined by EDX. For this purpose the sintered samples were cut and polished. The crystalline phases present in the ground samples were identified using X-ray diffraction (XRD) (STOE Stadi-P, Germany, Co Kα radiation). The electrical conductivity measurement was performed by four-probe method. The X-ray microtomography (Nanotom 180) was used to observe the distribution of Ti and Nb particles in the composite. Vickers hardness and fracture toughness were measured using Leco hardness tester (LV-100, Leco Co., USA) by indentation method with a load of 9.8 N and 98 N, respectively.

Table 2
Chemical composition of composites and reference material.

Sample	Composition (wt%)					
	SiC	SiO_2	Y_2O_3	Ti	NbC	AlN
SiC5	90	2	3	1.8	3.2	–
SiC10	80	4	6	3.6	6.4	–
SiC20	60	8	12	7.2	12.8	–
SiC30	40	12	18	10.2	19.8	–
SiC_{ref}	90.7	–	3.9	–	–	5.4

3. Result and discussion

3.1. XRD phase analysis of the samples

The phase composition of samples sintered at 1820 °C is summarized in Table 3 together with the weight loss data and their densities.

From the results listed in Table 3 it is obvious that the weight loss of the composites after sintering increases linearly with the addition of N-phase. It can be assumed that the weight loss is mainly related to the reduction of SiO_2 to gaseous products (e.g. SiO), because the portion of SiO_2 in the starting mixture is almost identical with the observed weight loss of the composites (Table 3). This assumption confirms the results of XRD phase analysis. In the composites with 5–20 wt% of N-phase (SiC5, SiC10, SiC20) yttrium silicate Y_2SiO_5 was identified, whereby the intensity of its diffractions gradually decreases with the increasing portion of N-phase. β-SiC was detected as a majority phase in the mentioned composites, together with the minority NbC and TiC phases. In the composite with 30 wt% of N-phase (SiC30) both β and α modifications of SiC have been detected as a majority phases, and neither yttrium silicate, nor SiO_2 were observed. The minority phases were the carbides of niobium and titanium (NbC, TiC) and their silicides (Nb_5Si_3, Ti_5Si_3). The silicides were not confirmed in the composites with 5–20 wt% of N-phase, but it does not exclude their presence, since their content may be below the detection limit of XRD analysis. The XRD analysis of SiC_{ref} shows the presence of β-SiC, α-SiC, $Y_2Si_2O_7$ and $Y_{10}Al_2Si_3O_{18}N_4$.

3.2. Microstructure

The results of SEM analysis of the polished surfaces of the composites with 5–30 wt% of the conductive N-phase are shown in Fig. 1.

The micrographs show that the amount of pores decreases with the increasing proportion of N-phase. This is in accordance with the observed increasing density (Table 3) with the rising N-phase content. However, we must keep in mind that also the theoretical density increases from SiC5 to SiC30 samples, because the amount of heavy elements (Ti, Nb) also increases and the measured density values do not reflect the real porosity. Moreover, the calculation of the theoretical density from the volume fraction of various phases in the starting mixture can be misleading, because the final phase composition after sintering is different. The porosity of the composites shown in Fig. 1 was estimated on the basis of the area of the pores in the microphotographs and is 47%, 34%, 28% and 16% for samples