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Electrochemical corrosion of silicon-infiltrated silicon carbide ceramics in aqueous solutions

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Abstract

Silicon carbide ceramics have found widespread use due to their high corrosion stability. Nevertheless, under certain conditions electrochemical corrosion is observed. Hence, in the present work a SiSiC ceramic and a composite material containing SiC as well as free carbon and Si were investigated in terms of microstructure and electrochemical corrosion behaviour. The SiC grains in the SiSiC exhibited a core-rim structure. The core and rim were formed from primary and secondary SiC, respectively, and had different corrosion stabilities due to the higher electrical conductivity of the rim. In contrast to the behaviour observed with pure chemical corrosion, under electrochemical conditions the Si showed a higher stability than the SiC in NaOH. Also, thicker protective SiO₂ layers were formed in H_2SO_4 on the SiC grains than on the Si grains.

Keywords: Silicon carbide; Corrosion; Microstructure

1. Introduction

Silicon carbide materials, and solid state-sintered silicon carbide materials (SSiC) in particular [1], have found widespread use as seals, bearings and valves in a variety of media in industrial wear applications. SiC materials are used on account of their good tribological properties [1] and high corrosion resistance [1-4]. Silicon-infiltrated SiC (SiSiC) ceramics are also used for wear applications. Especially large wear parts are produced from SiSiC because these components can be produced without shrinkage during the reaction sintering. The materials are produced by infiltrating a SiC preform, which also contains a small amount of free carbon, with liquid silicon at a temperature of 1500 °C to 1700 °C. Infiltration occurs by capillary action, with the Si partially reacting with the free carbon. Due to this reaction the silicon content can be reduced, but SiSiC ceramics usually contain 5-20 vol% of free silicon which is less stable than SiC at high temperatures and in solutions at high pH [1,5].

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Besides the classic SiSiC, a similar material can be produced by Si infiltration of carbon preforms [5–7]. These materials typically contain residual carbon as well as Si. A commercial material produced by this process is SiC 30 [7].

The SiC phase of the ceramic itself consists of a cubic phase (β -SiC) or hexagonal or rhombohedral polytypes (α -phase), which have the same structural units, but differ in terms of the sequence of layers along the body diagonal of the cubic lattice [1]. SiC is an intrinsic semiconductor and can have specific electrical resistivities in the Ω m to M Ω m range, depending on the additives and preparation method used [1].

SiC ceramics exhibit high chemical stability, but can undergo elecrochemical corrosion, depending on the preparation, phase content and electrical conductivity [8–13]. However, the corrosion rates of ceramics are generally very low compared with those of metals. Over the last few years the electrochemical corrosion behaviour of solid phase-sintered SiC ceramics and liquid phase-sintered SiC ceramics (LPS-SiC) has been investigated [8–14]. The investigations of the SSiC materials showed an inverse relationship between the corrosion rate and the resistivity of the material. The local corrosion rate of the grains was found to be controlled by the local resistivity, depending mainly on the

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resistivity of the grain boundaries [8,15]. No correlation between the corrosion rate and the polytype or the crystallographic orientation was found in acids or alkaline solutions [8,15]. In LPS-SiC materials, with grains exhibiting a core-rim structure, the rim exhibited a higher corrosion rate. This was caused by the higher conductivity of the rim than the core due to the higher doping level of the rim. These results demonstrate that differences in the intragranular resistivity also result in different corrosion rates.

Dissolution of the grains was found in alkaline solutions due to the formation of soluble silicates [12-15]. In contrast, formation of a SiO₂ layer was observed in acids. The results indicated surface passivation by formation of the SiO₂ layer according to the high-field mechanism [8].

SiC ceramics containing metallic Si are known to be chemically stable in acids, but have a lower chemical stability in alkaline solutions due to the preferential solution of silicon [1,5,9,10]. Very few investigations concerning the electrochemical stability of SiSiC have been carried out thus far. Divakar et al. [10] showed that the electrochemical corrosion of SiSiC is more pronounced than that of SiC in acids. The authors assumed that silicon was the reason for the stronger corrosion, but they did not proof this assumption by carrying out the associated microstructural investigations. For SiSiC ceramics, not only the described electrochemical dissolution of SiC [8,12,13,15], but also the electrochemical corrosion of Si in acid and alkaline solutions, has to be considered. The following half-reactions are involved:

$$Si + 2H_2O \rightleftharpoons SiO_2 + 4H^+ + 4e^-$$

$$Si + 6OH \rightarrow ZSiO_3^2 + 3H_2O + 4e^-$$

$$Si + 8OH \rightarrow ZSiO_4^{4-} + 4H_2O + 4e^{-}$$

These reactions are very similar to the reaction of silicon carbide, but the chemical potentials are shifted to more negative values. In basic solutions soluble silicates are formed and in acids SiO₂ passivating layers as for SiC materials.

The aim of the article is to determine the influence of residual Si on the electrochemical stability of SiC. Two materials (a commercial SiSiC material and the SiC 30 material containing SiC as well as Si and residual carbon) are analysed and compared with an SSiC material with a high conductivity.

2. Materials and methods

2.1. Materials and microstructural analysis

The properties of the silicon carbide materials used are given in Table 1. For the investigation of the microstructure and the

Table 1 Properties of the investigated materials.

Material	Phases	Density [g/cm ³]	Electrical resistivity [Ωcm]
SSiC	α-SiC (Al)	3.16	250
SiC 30	β-SiC, C, Si	2.65	1.2 10 ⁻²
SiSiC	α-SiC, Si	3.05	1000

electrochemical resistivity the materials were embedded in epoxy resin, ground and polished with diamond suspensions, cleaned with ethanol and dried. The microstructures of the SiSiC and the SiC 30 materials are given in Fig. 1.

The microstructures and compositions of the samples were analysed using a field emission scanning electron microscope (NVISION40; Zeiss, Germany). Energy-dispersive X-ray spectroscopy (EDX) was used to determine the chemical compositions of the microstructural constituents (INCA, Oxford Instruments). An electron back-scattered diffraction (EBSD) system (Channel 5, Oxford Instruments) was used to investigate the grain orientations and the polytypes.

The thickness of the formed corrosion layers was determined using the Oxford Instruments thin film measurement tool [14,16] allowing layers between 1 nm and 1 µm in thickness to be measured. For SiO₂ layers with relatively low electron densities the lowest thickness that could be detected is approximately 2–3 nm. Details are described elsewhere [14].

2.2. Electrochemical measurements

The electrochemical experiments were carried out at room temperature in a common electrochemical three-electrode cell housed in a Faraday cage without light. The potentiodynamic and chronoamperometric experiments were performed with a computer-controlled potentiostat (Autolab PGSTAT 30, Metrohm). A saturated calomel electrode (Sensortechnik Meinsberg GmbH)

Fig. 1. Light microscope image of the SiSiC material (a) and SiC 30 material (b). (Dark gray - Carbon; grey - SiC, white - Si).



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