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Oxidation behavior of electrically conductive α/β SiAlON composites with segregated network of TiCN

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Abstract

The oxidation behavior of novel electrically conductive α/β SiAlON composites with a continuous network of 2.5–10 vol% TiCN particulates was investigated. Composites, produced by coating spray dried granules with nano TiCN particles by a simple blending method, were gas pressure sintered at 1990 °C for 1 h under 10 MPa N_2 pressure. Oxidation tests were carried out between 800 °C and 1200 °C in air for 2 and 48 h in atmosphere of dry air. Below 1000 °C, the formation of TiO_2 crystals on the surfaces of TiCN particles was observed. Before the glass transition temperature of intergranular phase (T_g < 1000 °C), it was revealed that oxidation is controlled by the diffusion of oxygen into pre-formed TiO_2 particles. Above T_g, liquid glass dissolves the intergranular phase elements such as Ti, Y, and Si at the interface between TiCN and SiAlON particles. Migration of Ti towards the (opening point of the TiCN network) surface was found to be the main reason for the formation of subsurface porosity that slows down Ti diffusion through the surface. Moreover, it was detected that at high temperatures surface porosity filled by the intergranular glassy phase. Consequently, the oxidation rate was found to be decreased due to the slower oxygen diffusion.

Keywords: Composites; SiAlON; TiCN; Electrical conductivity; Oxidation

1. Introduction

Si_3N_4 and SiAlON ceramics are important structural materials due to their superior mechanical, thermal and chemical properties both at room and high temperatures. While wear resistance, hardness, toughness and creep resistance of Si_3N_4/SiAlON can be improved considerably by the dispersion of the secondary carbides, nitrides or borides,[1–7] electrical properties can also be improved by the addition of some functional phases.[8–13] Conductive Si_3N_4/SiAlON based composites are candidate materials for the applications such as heat exchangers, heaters, ignitiors that operates at high temperatures containing oxygen and/or oxidant substances (water vapor and carbon dioxide oxygen atmosphere). Therefore, the behavior of these composites against to oxygen at high temperatures is critical and has been subjected to a series of studies.[14–20]

TiN and TiCN particulates are the most preferred reinforcing phases to make Si_3N_4/SiAlON ceramics electrically conductive due to not only low electrical resistivity but also unique combination of mechanical properties. There are various approaches to produce such composites. The most common method is the direct dispersion of TiN/TiCN particles in Si_3N_4 matrix by conventional powder processing routes.[7–9] In these types of composites, homogeneous dispersion of minimum amount of secondary phase without degrading densification and mechanical features is very critical, since it affects the electrical conductivity. However, the dispersion of a secondary phase is a difficult task to achieve. Therefore, in situ formation of homogeneously distributed nano conductive particles is an alternative method to this approach.[21–23] Obtaining good electrical conduction by this method is also challenging, since process parameters must be controlled precisely to avoid the grain growth and accordingly separation of conductive particles from each other. A new method to obtain a continuous network in these types of composites has been developed by Ayas and Kara.[24] In this method, spray dried SiAlON granules with an average diameter of 100 μm were coated with nano-TiCN particles by dry mixing of these two components. Consequently, low resistivity values ($\approx 10^{-2}$ Ω m) were achieved with the incorporation of as low as 5 vol% of TiCN after gas pressure sintering.

For such ceramics, it is important to evaluate the thermal stability and degradation of mechanical and functional properties of such composites at high temperatures. In the present work, oxidation behavior of α/β SiAlON composites with different

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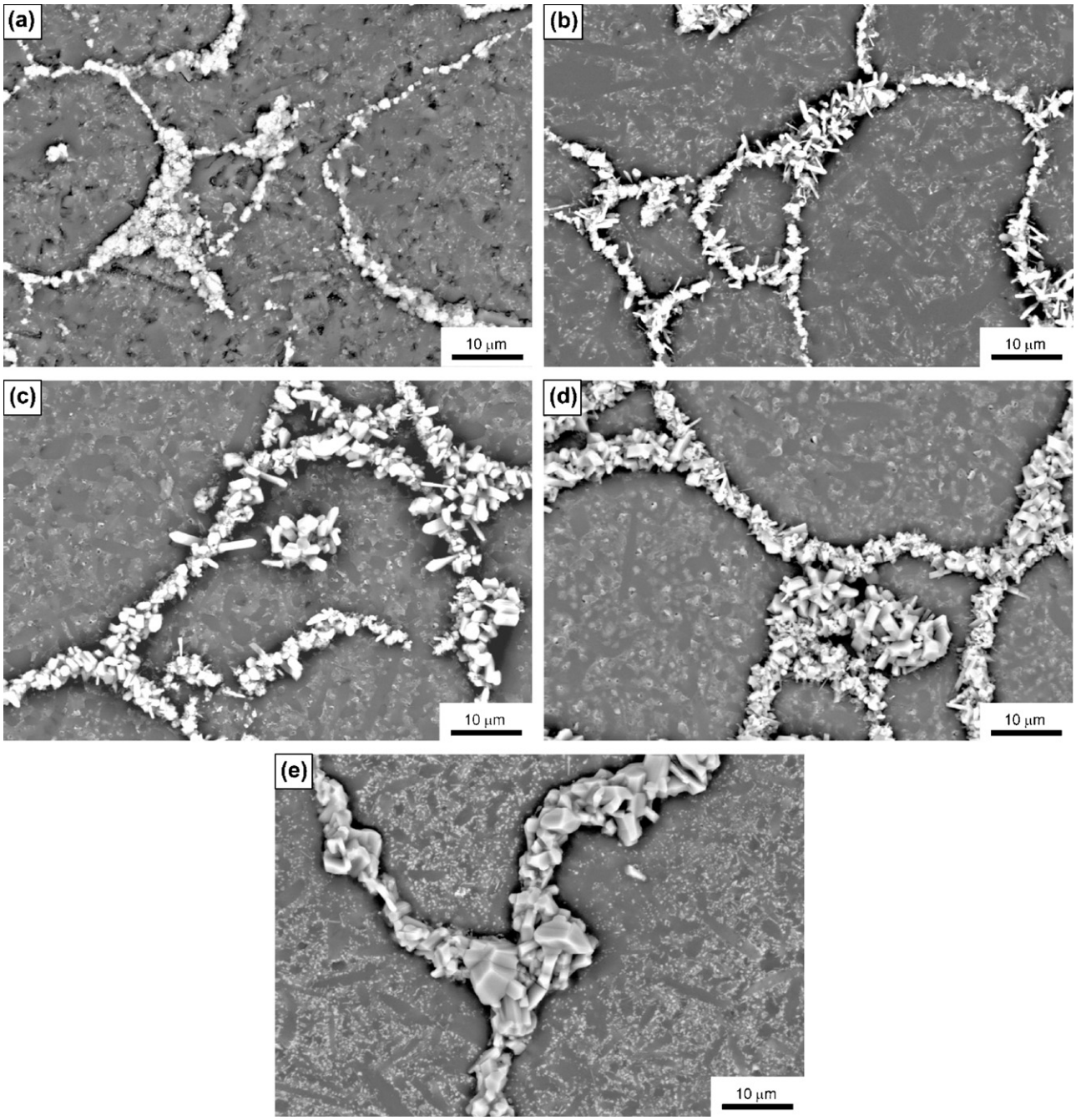

Fig. 1. Back-scattered SEM images of the composite containing 5 vol% TiCN oxidized at (a) 800 °C, (b) 900 °C, (c) 1000 °C, (d) 1100 °C and (e) 1200 °C for 2 h.

amounts of segregated network of TiCN particles was investigated by soaking the materials in air at different temperatures for short and long terms. The results are based on the thickness measurement of oxide scale from the surface and mass gain per unit area as a function of oxidation temperature.

2. Materials and methods

2.1. Production of composites

α/β SiAlON–TiCN composites were prepared by following a process[24] which is based on the dry mixing of different amounts of nano TiCN particles ranging from 2.5 to 10 vol% (60 nm APS, Merck) with spray dried SiAlON based granules of around 100 μm in diameter in a rotary plastic container. Coated granules were then uniaxial pressed in hardened steel die (50 mm × 50 mm × 4 mm) under ~220 MPa pressure. Sintering of the pellets was carried out in a BN crucible using a GPS furnace (FCT Anlagenbau GmbH, Germany), capable of operating at temperatures of up to 2000 °C in an inert atmosphere of up to 10 MPa pressure. A two-stage sintering schedule was employed, which included a first stage at a sintering temperature of 1940 °C for 60 min under a low nitrogen gas pressure of 0.2–0.5 MPa and a second stage at a sintering temperature