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Journal of the European Ceramic Society 31 (2011) 2393–2400

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Anomalous oxidation behaviour of pressureless liquid-phase-sintered SiC

F. Rodríguez-Rojas [a], A.L. Ortiz [a,*], F. Guiberteau [a], M. Nygren [b]

[a] *Departamento de Ingeniería Mecánica, Energética y de los Materiales, Universidad de Extremadura, 06071 Badajoz, Spain*
[b] *Department of Materials and Environmental Chemistry, University of Stockholm, 10691 Stockholm, Sweden*

Received 31 January 2011; received in revised form 29 April 2011; accepted 13 May 2011
Available online 14 June 2011

Abstract

The oxidation behaviour of pressureless liquid-phase-sintered (PLPS) SiC, an important non-oxide engineering ceramic, was investigated, and was found to be universally anomalous. Thermogravimetry oxidation tests performed in oxygen in the temperature range 1000–1225 °C on three PLPS SiC ceramics fabricated with different combinations of Al_2O_3–RE_2O_3 (RE = Gd, Sc, or Sm) as sintering aids indicated that the oxidation is in all cases passive and protective, but unexpectedly anomalous in the sense that the oxidation resistance does not scale inversely with temperature. In particular, in all cases it was observed that there is less oxidation above 1100 °C than below, in clear contradiction to the expectation for a diffusional process. Exhaustive characterization of the oxide scales by scanning electron microscopy, X-ray energy dispersive spectrometry, and X-ray diffractometry, together with detailed modeling of the oxidation curves, showed that the origin of this universal anomalous oxidation behaviour lies in the marked crystallization within the oxide scale of rare-earth silicates that act as effective barriers against the inward diffusion of oxygen thus improving notably the oxidation resistance. A strategy is proposed to provide PLPS SiC, and probably other SiO_2-scale-forming ceramics that are sintered using rare-earth oxides, with the superior oxidation resistance at moderate temperatures (i.e., <1100 °C) that they do not currently have.

Keywords: D. SiC; Liquid-phase sintering; Oxidation

1. Introduction

Non-oxide advanced ceramics are increasingly being used in engineering applications at high temperature in air or other oxidizing atmospheres.[1] Oxidation is thus a major cause of their degradation in service,[2,3] and the oxidation behaviour of non-oxide engineering ceramics is currently a topic of intensive research and a critical aspect of design. Pressureless liquid-phase-sintered (PLPS) SiC is one of these non-oxide engineering ceramics with great potential for high-temperature structural and functional applications because it combines a very attractive set of physicochemical properties with the economy and ease of the pressureless processing for the fabrication of large components with complex geometries. Current opinion is that PLPS SiC can operate safely in oxidizing environments below ~1300 °C because up to that temperature the oxide scales that form are protective, and the oxidation is passive and is controlled by diffusion.[4] In addition, because the diffusion coefficients obey an Arrhenius-type law, the conventional wisdom within the ceramic community and among design engineers is that the oxidation resistance of PLPS SiC decreases with increasing temperature in the temperature range 25–1300 °C. Indeed, the history of literature on the oxidation of LPS SiC ceramics, pressureless processed or not, long presented no evidence against this wisdom,[4–17 *and references therein*]. However, an oxidation study by Jensen et al.[18] on a PLPS SiC fabricated with 20 vol% Y_2O_3–Al_2O_3 (henceforth, PLPS SiC–Y) showed clear evidence, although the only case published so far, contradicting the common belief that the oxidation resistance scales inversely with temperature. In particular, they oxidized their PLPS SiC–Y ceramic in ambient air between 1000 and 1350 °C, observing surprisingly greater oxidation at 1000 °C than at 1100, 1150, 1200, and 1250 °C, an unexpected phenomenon that they confirmed by repeated oxidation tests. This oxidation behaviour is highly anomalous not only because the oxygen diffusivity

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[*] Corresponding author. Tel.: +34 924289600×86726; fax: +34 924289601.
E-mail addresses: alortiz@materiales.unex.es, alortiz@unex.es (A.L. Ortiz).

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doi:10.1016/j.jeurceramsoc.2011.05.015

increases by two or more orders of magnitude in 250 °C, but also because they found no signs of formation of non-protective oxide scales. Indeed, the origin of such anomalous oxidation behaviour has yet to be elucidated. Furthermore, while the study of Jensen et al. does not necessarily imply universality, the fact that the microstructural ingredients are essentially the same in all PLPS SiC ceramics[4] suggests that the anomalous oxidation behaviour observed in the PLPS SiC–Y ceramic might not be exclusive to that type but may also occur in all other PLPS SiC ceramics fabricated with other rare-earth oxides. Whether or not this anomalous oxidation is universal in PLPS SiC's is a fundamental question requiring an answer, as it may have important consequences for the use of these ceramics in high-temperature applications in oxidizing atmospheres. If the phenomenon indeed turned out to be universal, then there arise two fundamental questions: What is its origin, and how can it be prevented?

The present study seeks to address these issues. To this end, we fabricated three PLPS SiC ceramics with Al_2O_3–RE_2O_3 (RE = Gd, Sc, or Sm; henceforth, PLPS SiC–RE) as sintering additives, and oxidized them at different temperatures. We also observed in these three PLPS SiC ceramics the anomalous oxidation of the PLPS SiC–Y ceramic. We next went a step further and identified in the PLPS SiC–Gd ceramic the origin of the anomalous oxidation by an exhaustive characterization of the oxide scales through scanning electron microscopy (SEM), X-ray energy dispersive spectrometry (XEDS), and X-ray diffractometry (XRD), together with a detailed analytical modeling of the oxidation curves, and then validated the findings in the PLPS SiC–Sc and –Sm ceramics. Based on the experimental results and analyses, we propose a strategy to provide PLPS SiC with superior oxidation resistance at moderate temperatures (i.e., <1100 °C), which can have important implications for its use in applications requiring oxidation-resistance.

2. Experimental procedure

The processing procedure used is that employed conventionally to fabricate PLPS SiC ceramics. Commercially available α-SiC (UF-15, H.C. Starck, Goslar, Germany), Al_2O_3 (AKP-30, Sumitomo Chemical Company, Japan), and RE_2O_3 (Gd_2O_3, Sc_2O_3, and Sm_2O_3; Strem Chemicals, France) powders were used as starting materials. The choice of these rare-earth oxides is because they allow one to investigate the fundamental questions of the universality of the anomalous oxidation observed in the PLPS SiC–Y ceramic and its origin if such universality is indeed the case, while contributing new data to the PLPS SiC oxidation literature. Three powder batches were individually prepared by combining the SiC, Al_2O_3, and RE_2O_3 (RE = Gd, Sc, or Sm) powders in appropriate amounts to result in PLPS SiC ceramics with 90 vol.% SiC and 10 vol.% $RE_3Al_5O_{12}$ after sintering (henceforth abbreviated as PLPS SiC–RE). The powder mixtures were then blended intimately by wet ball milling in ethanol for 24 h in polyethylene bottles using Si_3N_4 balls as milling media. The resulting slurries were dried carefully in Teflon beakers on hot-plates while being continuously stirred, and subsequently in an oven at 100 °C for 24 h. The dried powders were next crushed and sieved to remove the hard agglomerates. Compacts were then made from each of the powder batches by uniaxial pressing (C, Carver Inc., Wabash, IN, USA) at 50 MPa, followed by cold-isostatic pressing (CP360, AIP, Columbus, OH, USA) at 350 MPa. Finally, the individual pellets were embedded in powder beds inside graphite crucibles and were pressureless sintered in a graphite furnace (1000-3560-FP20, Thermal Technology Inc., Santa Rosa, CA, USA) at 1950 °C for 1 h in a flowing Ar-gas atmosphere of 99.999% purity. The sintered materials were ground down 1 mm and polished to a 1-μm finish, and their microstructure was examined by SEM (S-3600N, Hitachi, Japan) after plasma etching with $CF_4 + 4\%O_2$ gas for 2 h.

Parallelepiped specimens of size 8 mm × 5 mm × 2 mm were machined out of the sintered discs and all their faces were diamond-polished to a 1-μm finish. The oxidation tests were carried out with a thermobalance (TAG 24, Setaram, France) whose resolution is better than 2 μg and whose baseline drift is lower than 5 μg per 24 h. The oxidation tests were performed at different temperatures (1000, 1150 and 1225 °C for PLPS SiC–Gd, 1075 and 1225 °C for PLPS SiC–Sc, and 1075 and 1150 °C for PLPS SiC–Sm), in an atmosphere of flowing (50 mL/min) dry oxygen of 99.999% purity, for times in the range 0–22 h, and with the specimens suspended on the thermobalance by Pt wires. The oxidized samples were characterized as extracted from the thermobalance by SEM, XEDS (XFLASH Detector 3001, Röntec GmbH, Germany), and XRD (X'pert PRO MPD, PANalytical, The Netherlands) to determine the microstructure and chemical composition (elemental and crystalline phases) of the oxide scales. The surface coverage of the oxide scales by crystals was also measured, by image analysis of the SEM micrographs.

3. Results and discussion

Fig. 1 shows representative SEM micrographs of the three PLPS SiC–RE ceramics in the as-processed condition. As can be seen, they all have the microstructure typical of PLPS SiC ceramics, with submicrometre SiC grains (∼0.8 μm) embedded in a continuous oxide matrix. The aspect ratio of the SiC grains is 1.4, which is the equilibrium morphology of α-SiC.[19] It can also be seen that the three ceramics are fully dense because there is no evidence of residual porosity in the SEM images.

Fig. 2 shows the specific mass-change curves measured experimentally for the three PLPS SiC–RE ceramics oxidized at different temperatures. As can be observed, in the three cases there is always mass gain throughout the oxidation period, which indicates that the oxidation is passive due to the formation of oxide scales. This is consistent with the fact that the active oxidation of PLPS SiC occurs at lower oxygen partial pressure and higher temperatures than used in the present study[2]. A detailed inspection of the oxidation curves in Fig. 2 reveals nevertheless that the oxidation behaviour of the three PLPS SiC–RE ceramics is highly anomalous, as will be described in the following. As can be seen in Fig. 2A for the PLPS SiC–Gd ceramic, initially both the rate of specific mass gain and the total specific mass gain at 1000 °C are lower than at 1150 and 1225 °C. After ∼0.5 h of oxidation this scenario changes partly, so that the rate of spe-