Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of the European Ceramic Society 25 (2005) 997–1003

www.elsevier.com/locate/jeurceramsoc

Phase formation in porous liquid phase sintered silicon carbide: Part II: Interaction between Y_2O_3 and SiC

J. Ihle*, M. Herrmann, J. Adler

Fraunhofer-Institute for Ceramic Technologies and Sintered Materials, Winterbergstr. 28, 01277 Dresden, Germany

Received 10 December 2003; received in revised form 6 April 2004; accepted 22 April 2004
Available online 17 July 2004

Abstract

During the sintering of porous liquid phase sintered silicon carbide (porous LPS-SiC) a strong interaction with the atmosphere takes place, influencing the composition and stability of porous LPS-SiC components. The present paper is focused on the interaction of Y_2O_3 with SiC, which is part of the common used sintering additives for LPS-SiC (Y_2O_3–Al_2O_3–SiC). The interaction of Al_2O_3 and SiC has been studied in a previous paper [J. Eur. Ceram. Soc. (in press)].

The reaction products of the interaction of Y_2O_3 with SiC and the resulting microstructures were analysed using model experiments. The effects of the influence of different sintering atmospheres, namely Argon and Ar/CO, as well as vacuum and different temperatures have been investigated. The phase formation was determined by X-ray diffraction (XRD) and can be explained on the basis of thermodynamic calculations. Depending on the sintering conditions, silicides or yttrium carbides can be formed in addition to stable oxides, which can result in the decomposition of the samples after sintering. Reactions between SiC and Y_2O_3 during sintering can be suppressed successfully if an Ar/CO atmosphere is used.

Keywords: SiC; Liquid phase sintering; Phase development; Additives; Y_2O_3

1. Introduction

The solid state sintering of SiC (S-SiC) can be performed at very high temperatures up to 2200 °C with small additions of boron and carbon or boron, aluminium and carbon. In the case of LPS-SiC there is liquid phase formation due to Al_2O_3 and Y_2O_3 or other rare earth oxide additions, which subsequently accelerate the sintering in comparison to S-SiC. The sintering temperature can be decreased to 1800–2000 °C if the composition of the additives is close to the eutectic.[2,3]

The sintering conditions and the presence of a liquid phase during sintering have an essential influence on structure and phase composition, and subsequently the properties of the material. Beside the formation of yttrium–aluminium–garnet (YAG) as intergranular phase between the SiC grains, a reduction of the oxides by the silicon carbide can occur. Reactions between oxides and silicon carbide that result in the evolution of gases are associated with mass loss.

The properties of LPS-SiC have been observed and presented by several authors.[2–8] Groebner[9] has provided a thermodynamic assessment of the Gibbs energy functions for the phases in the system Y–Al–Si–C–O. A complete Gibbs energy data set was established for thermodynamic calculations in this quinary system.[9]

The decomposition of SiC during sintering by Al_2O_3 and Al_2O_3/Y_2O_3 mixtures was analysed by numerous authors.[1,2,5,6,10] The weight losses during sintering of SiC with Al_2O_3–Y_2O_3 additives result mostly from the evaporation of Al and Si suboxides. The sintering atmosphere influences the composition of the gas phase and consequently the extent of weight losses.[1,2,5,6] A common practice is the use of powder beds containing Al_2O_3 and SiC for minimising the mass loss by gas forming reactions during sintering of LPS-SiC.[3,4,6]

Baud et al.[6] described the evaporation of a SiC–Al_2O_3/Y_2O_3 mixture. They suggest a very similar behaviour in comparison to a pure SiC–Al_2O_3 mixture. In their thermodynamic calculations gaseous CO, SiO, Al_2O and Al are the main gas species. Additionally, there is a minor presence of gaseous Y and YO. Al_2O_3 and Y_2O_3 would react during

---

* Corresponding author. Tel.: +49 351 2553 682;
fax: +49 351 2554 128.
E-mail address: Jan.Ihle@ikts.fraunhofer.de (J. Ihle).

0955-2219/$ – see front matter. © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2004.04.016

sintering to form either aluminates or a liquid oxide phase. In both cases the activity of Y_2O_3 would be less than one resulting in even smaller partial pressures of gaseous Y and YO.[6]

Cordrey et al.[4] investigated the sintering behaviour of silicon carbide with an yttrium oxide addition of 2 and 5 wt.%. During sintering the samples were surrounded in a coarse alumina and silicon carbide powder bed and contained within a carbon crucible. The authors observed that aluminium containing gas species react with the yttria to form a reactive liquid phase. The XRD analysis was inconclusive for identifying the resulting phases due to the small amount of additives. They concluded with the aid of energy dispersive spectroscopy (EDS) that Al, Y, Si and O are present in the secondary phase after sintering. The ratio of Al:Y:O in the secondary phase was determined by scanning Auger spectroscopy. In addition to the detected different ratios of Al:Y:O they assumed that an Al–Y–C–O compound and a Y–C–O compound may have formed.

The presence of yttrium silicates was detected by Hermanutz et al.[11] for hot-pressed SiC sintered with yttria. Y_2SiO_5, $Y_{4.67}(SiO_4)_3O$ and $Y_2Si_2O_7$ were formed in the bulk. Falk[7] observed a formation of $Y_2Si_2O_7$ as well as Si-O-rich glass pockets and graphite in capsulated hot isostatic pressed SiC samples with 1 wt.% Y_2O_3. The SiO_2 and carbon are likely constituents of the starting SiC powder and do not decompose due to the reduced decomposition rate under these conditions in comparison to normal sintering. Grande et al.[2] and Nagano et al.[12] concluded reaction (1)

$$SiC(s) + Y_2O_3(s) \rightarrow Y_2O(g) + SiO(g) + CO(g) \qquad (1)$$

as a decomposition reaction of Y_2O_3 beside the main decomposition during sintering involving Al_2O_3. Because of a lack of data the thermodynamics of reaction (1) could not be appraised by Grande et al.[2] They did not measure a significantly reduced yttrium content in the secondary phase in LPS-SiC samples, and therefore have proposed that reaction (1) is not important for the weight loss.

Groebner[9] investigated the system Y–Si–C and has shown the silicides YSi_2 and Y_3Si_5 to be stable phases after synthesis at 1200 and 1500 °C. The carbon solubility of the silicides is low enough so that no alteration of the lattice constants was observed with an increase of carbon.[9]

In addition to the SiC lines, Grande et al.[2] found several weak diffraction lines in LPS-SiC samples maintained for 6 h at 1820 °C, which could not be attributed to a known phase. They proposed that a reduction of Y_2O_3 occurred after evaporation of Al_2O_3 resulting in carbide or oxy-carbide formation. By using EDS, the authors detected lower oxygen content in heat treated samples than that expected, by considering the amount of Y_2O_3 in the green samples. They considered the formation of oxy-carbides as the most probable reaction, due to the indicated release of gaseous SiO and CO after Al_2O_3 evaporation.[2]

Consequently, no conclusive information is available for the interaction of SiC and Y_2O_3 and therefore thermodynamical and experimental investigations are necessary for the understanding of the interactions during sintering.

The present paper is a study of the phase formation due to the dependence of the interaction of SiC and Y_2O_3 on temperature and gas atmosphere, and a comparison of the results with thermodynamic calculations.

2. Experimental

Samples with a higher content of oxides than the usual compositions of porous LPS-SiC were produced to enable a better detection of minor phases. A composition of 50 wt.% α-SiC (ESK F1200 green) and 50 wt.% Y_2O_3 (H.C. Starck grade C) was chosen. The samples were green pressed into tablets with a thickness of 5 mm and a diameter of 25 mm or bending bars with dimensions of 6 mm × 8 mm × 60 mm. All samples were sintered at 1 bar gas pressure or under vacuum (4×10^{-5} bar) in a graphite-heater furnace. The sintering conditions are shown in Table 1.

All samples were sintered in graphite crucibles. Graphite foil was placed between the crucibles and the samples in order to prevent adhesion of the samples to the crucible bottom by liquid formation during sintering. It was not possible to measure exactly the mass loss after sintering because some graphite foil was bonded to the samples after sintering. No mass loss results are therefore presented.

The phase composition of the samples was determined by X-ray diffraction analysis (XRD 7; Seifert-FPM; Cu Kα), using JCPDS standards.[13] Rietveld analysis (AutoQuan software) was used for the determination of the $Y_3Si_2C_2$ phase from XRD measurements. Optical microscopy and scanning electron microscopy with attached EDX (Leica Stereoscan 260) were used for an analysis of the microstructure of polished surfaces.

The FactSage® software package was used for thermodynamic calculations.[14] The necessary thermodynamic data for calculations were taken from the SGTE (Scientific Group

Table 1
Sintering temperatures, dwell time, atmospheres and resulting phase composition

Temperature (°C)	Dwell time (h)	Atmosphere	Phase composition of sintered samples
1850	1, 3, 5	Argon	Y_2O_3, α-SiC, $Y_3Si_2C_2$, YSi, (Y_xC_x)
1925	1	Vacuum	$Y_3Si_2C_2$, YC_2, α-SiC
1925	1	Argon + CO	Y_2O_3, α-SiC
1950	1	Argon	Y_2O_3, α-SiC, $Y_3Si_2C_2$, YSi, (YC_2)