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Liquid phase formation in the system SiC, Al_2O_3, Y_2O_3

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Abstract

The liquid phase formation in the system SiC–Al_2O_3–Y_2O_3 was investigated via differential thermal analysis (DTA) combined with thermogravimetry (TG). For this purpose mixtures of various alumina and yttria mol ratios and 10 and 20 mol% silicon carbide were densified and heat treated at different temperatures. It was shown that silicon carbide in the examined amounts has low influence on the melting temperature of the oxide phase. The compositions and microstructures formed were studied by SEM, EDX and XRD. The results were compared to thermodynamic calculations.

Keywords: SiC; Al_2O_3; Y_2O_3; Sintering; SPS/FAST

1. Introduction

Silicon carbide (SiC) is the most deployed non-oxide ceramic in the world.[1] Its high temperature stability, the high hardness and the excellent resistance against oxidation and corrosion are some of the advantages of silicon carbide ceramics in technical applications.

The classical way of solid phase sintering of SiC (SSiC) is performed at high temperatures up to 2200 °C where additions of small amounts of boron, aluminium and carbon make the production of dense SiC technically manageable.[2,3] SiC arising from this process is quasi single phase with all the above mentioned properties. Alternative sintering methods have been developed to lower the sintering temperatures and to improve fracture toughness and mechanical strength. The use of rare earths together with alumina and AlN, respectively, allows a liquid phase sintering (LPS) of SiC.[4] These additives form a liquid phase at temperatures above 1850 °C allowing the reduction of the sintering temperature. During cooling the liquid phase solidifies to crystallised phases such as rare earth aluminates or oxynitrides (in the case of AlN). These additives strongly change the mechanical properties of the material in comparison to the solid phase sintered ceramics. An increase of fracture toughness up to 100% and an increase of flexural strength up to 70% in comparison to SSiC can be achieved.[2] Also the electrical properties[5] and the chemical resistance[6] are influenced.

Thus for the liquid phase sintering of SiC the phase relations in the SiC–Al_2O_3–Y_2O_3 system and melting temperatures at different ratio of components are of interest. The publications addressing this system are rare and mostly deal with the interaction of the oxides and SiC with the sintering atmosphere.[7–9] No reliable data exist concerning the composition of the liquid phase and the eutectic or peritectic temperatures. The observed liquid phase sintering mechanism requires some dissolution of SiC in the liquid phase. The observed incorporation of small amounts of alumina into the SiC grains and the fast phase transformation from β- to α-SiC during liquid phase sintering are evidences of such a solution. In work of Hoffmann and Nader[10] it was estimated, that the solubility of the SiC at sintering temperatures should be in the range of 10 mass%. However no experimental data concerning the solubility and the liquidus formation in the system SiC–Al_2O_3–Y_2O_3 exists. Therefore, the aim of present work is a detailed investigation of phase equilibria in the system SiC–Al_2O_3–Y_2O_3 including melting behaviour.

The liquid phase formation in the system SiC–Al_2O_3–Y_2O_3 was investigated by simultaneous thermal analysis (STA), ceramographic and XRD methods. Additionally the experimental

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Table 1
Samples and corresponding compositions.

Sample	SiC [mol%]	Mol ratio Y_2O_3/Al_2O_3
YAlSiC-		
208000	0	20/80
208010	10	20/80
208020	20	20/80
YAlSiC-		
455500	0	45/55
455510	10	45/55
455520	20	45/55
YAlSiC-		
604000	0	60/40
604010	10	60/40
604020	20	60/40
YAlSiC-		
802000	0	80/20
802010	10	80/20
802050	50	80/20

data of this paper are compared with thermodynamic calculations of the quasi-ternary system $SiC–Al_2O_3–Y_2O_3$.[11]

2. Experimental

Specimen with silicon carbide contents of 10 mol%, 20 mol% and one with 50 mol% were produced (Table 1 and Fig. 1). The high oxide content leads to significant effects in the DTA and also the solubility of SiC in the liquid melt is assumed to be less than 10 mass%[10]. High SiC contents are assumed to have no effect on melting temperatures. Compositions without silicon carbide were additionally prepared to be able to compare the results to literature data and to study the effect of the SiC on the melting temperatures. The ratio of yttria/alumina was changed from 20/80 over 45/55 and 60/40 to 80/20, according to the eutectic- (and one intermediate, 60/40) compositions in the pseudo binary phase diagram $Al_2O_3–Y_2O_3$. All specimen and their corresponding compositions are shown in Table 1. The powders used to produce the mixtures were SiC (grade UF15, H.C. Starck Germany, oxygen concentration < 1.5%), α-Al_2O_3 (AKP 50, Sumitomo Chemical Co.) and Y_2O_3 (grade C, H.C. Starck Germany). The powders were mixed in isopropanol in a planetary ball mill (200 rpm, 2 h) and then dried in a rotary evaporator. Afterwards the silicon carbide containing powders were densified via spark plasma sintering (SPS, device: HP D 25/1 of FCT Systeme GmbH) for 5 min at 1400 °C in vacuum with a pressure of 50 MPa. The heating rate was 100 K/min. As a result the materials were compacted to dense samples with 40 mm diameter and 5 mm height. The achievement of full density at low temperatures ensures a strong reduction of the decomposition of the materials taking place at higher temperatures due to the interaction with the atmospheres (see e.g. [8]). These samples were the basis for all further heat treatments and the DTA/TG analysis.

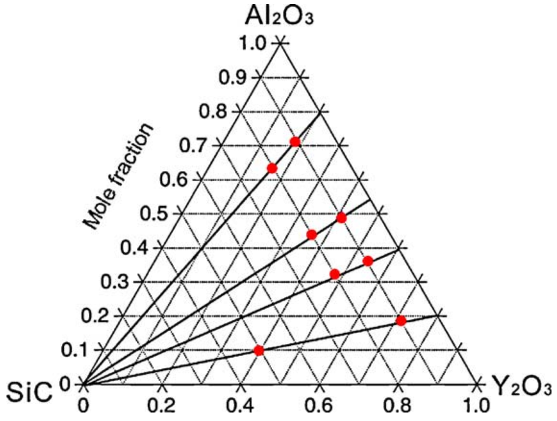

Fig. 1. Ternary system $SiC–Y_2O_3–Al_2O_3$. Lines assign the mol ratios yttria to alumina (20/80, 45/55, 60/40 and 80/20). Points mark the compositions of samples produced.

In order to check if the fast SPS process produces equilibrium phases an additional heat treatment of the materials containing 20 mol% SiC was carried out for 1 h at 1700 °C in Argon. This is below the expected melting temperatures. The experiments were done in a graphite heated furnace having the samples embedded in powder mixtures of the same composition as the samples to reduce reactions with atmosphere. In addition the silicon carbide containing samples were molten to reveal the phases and the microstructure after melting and solidification. This was necessary because the DTA samples had a mass of only some mg. The melting was carried out in a graphite heated furnace (Thermal Technologies GmbH) at 1850 °C for samples YAlSiC-2080x and at 1950 °C for samples YAlSiC-4555x, -6040x, -8020x for 5 min in preconditioned graphite crucibles. The heating and cooling rate was 20 K/min and the atmosphere was a mixture of Argon and CO. The preconditioning was done to minimise reactions of specimen with the graphite crucible in the subsequent experiment. For this conditioning the crucibles were filled with powder mixtures of the same composition as the samples and were heat treated in a graphite heated furnace up to 1950 °C in Argon atmosphere.

The powders without silicon carbide were heat treated in a muffle furnace up to 1400 °C in air with a dwelling time of 3 h. Here also the contained phases were checked. It was in agreement with the phases expected by the phase diagram. The heat treatment in air was used, because no decomposition of the materials is expected. In contrast the interaction with the graphite during SPS could change the composition slightly (formation of some carbides or formation of carbon inclusions).

Melting temperatures were determined using differential thermal analysis (DTA) combined with thermogravimetry (TG), also known as simultaneous thermal analysis (STA). Measurements were carried out in the device STA 429 of Netzsch Gerätebau GmbH Selb under static helium atmosphere with heating and cooling rates of 20 K/min in tungsten crucibles using no reference substance. A tungsten heating element and a thermocouple of WRe (3%) and WRe (25%) were used. The temperature was calibrated by the melting points of alumina (NIST SRM 742) and sampling was done from the bulk of the densified samples. The absolute uncertainty of measurement is estimated to be 16 K and the relative one to be 5 K. Since the specimen showed a mass loss when melting began, the maximum heating temperatures were set to a few degrees above the melting temperature.