LIQUID PHASE SINTERING OF SiC WITH RARE-EARTH OXIDES

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A variety of sintering additives Y_2O_3/Yb_2O_3/Sm_2O_3 together with AlN have been used for liquid phase sintering of silicon carbide. The hot pressed samples were further annealed to emphasize the effect of sintering additives on microstructural development. Remarkable influence of sintering additives on the microstructure was observed. Dependences of mechanical properties on microstructure and grain boundary chemistry were evaluated in more details. The hardness of SiC ceramics increased with decreasing ionic radius of the rare-earth elements, and contrary, the fracture toughness decreased.

INTRODUCTION

Polycrystalline silicon carbide is a perspective material for many extreme applications owing to its good mechanical properties at room and elevated temperatures. Solid state sintering was the common method for the densification of polycrystalline SiC [1]. Carbon and boron are frequently used as sintering aids. The main disadvantage of the solid state sintered SiC is the relatively low fracture toughness of the prepared ceramic materials. The liquid phase sintered SiC (LPS SiC) ceramics partially overcame this problem. Due to the platelet like shape of LPS SiC and the various chemistry of grain boundary phase the fracture toughness increased depending on the sintering additives and densification method used [2,3]. Most frequently Al_2O_3 and Y_2O_3 were used as sintering additives [4-7].

Densification of polycrystalline SiC with oxide additives is accompanied by a weight loss [8]. The detailed study showed that SiO_2 and Al_2O_3 react at the sintering temperature with SiC or with free carbon, present in SiC starting powder as an impurity. The reaction products are gaseous species like SiO and Al_2O, respectively. It was shown that by replacement of Al_2O_3 with AlN the weight loss decreased during sintering [8,9].

Similarities of chemical and physical properties of rare-earth oxides with Y_2O_3 lead to the idea to replace Y_2O_3 with the other rare-earth oxides. This processing method is commonly used for preparation of Si_3N_4--based materials with tailored microstructure.

Present paper deals with the characterization of SiC samples prepared by the addition of mixed rare-earth oxides (Y_2O_3, Yb_2O_3, Sm_2O_3) and AlN. Fracture toughness and macro-hardness of these materials will be correlated with the microstructure and composition of the sintering additives.

EXPERIMENTAL

β-SiC powder (grade HSC-059s, Superior Graphite, USA) was mixed with rare-earth oxides Y_2O_33, Yb_2O_3 (both H.C. Starck, Germany), Sm_2O_3 (Meldform Rare Earth Ltd., U.K.), and AlN (H.C. Starck, Germany) in compositions listed in table 1. The amount of the sintering additives was kept constant, 10 wt.% in total, with the molar ratio 1:1 of particular oxides (table 1). The powder mixtures were ball milled in isopropanol with SiC balls for 24 hours. The homogenized suspensions were dried, subsequently sieved through 75 μm sieve screen. Uniaxially pressed samples (12 mm in diameter and 10 mm high) were embedded in BN and located into graphite die. The samples were hot pressed

Table 1. Chemical composition of samples.

Sample	Composition (wt.%)				
	SiC	AlN	Y_2O_3	Yb_2O_3	Sm_2O_3
SC-YYb	87	3	4.6	5.4	-
SC- YSm	87	3	3.9	-	6.1
SC-YbSm	87	3	-	5.3	4.7

at 1850°C for 1 h under mechanical load of 30 MPa in mixed Ar+N_2 atmosphere. The hot pressed samples were further annealed at 1900°C for 10 hours in the same atmosphere. Densities of cooled samples were measured by Archimedes method in mercury. The theoretical densities were calculated according to the rule of mixtures. The microstructures of polished and plasma etched samples were observed by scanning electron microscopy (SEM, JEOL, Japan). Vickers hardness and fracture toughness were measured using LECO Hardness tester (Model LV-100AT, LECO, USA) by indentation method with a loads of 9.8 N and 98 N respectively.

RESULTS AND DISCUSION

Sintering additives were selected on the base of the thermodynamic stability calculations [10]. The results for the sintering additives investigated are shown in figure 1. The thermodynamic stability of the rare-earth oxides compared with silicon carbide oxidation is significantly higher (figure 1). Theoretically decomposition of SiC by rare-earth oxides therefore cannot occur in the investigated systems. Thermodynamic calculations confirmed the stability of SiC in the presence of studied RE_2O_3 during thermal treatment. Hence, the proposed oxide sintering aids are probably suitable for densification of SiC. Aluminium nitride was also used as sintering additive together with oxides. To restrain the decomposition of AlN nitrogen + argon atmosphere was used during sintering. All samples were densified by hot pressing to the densities > 94 % of theoretical density. Relatively high obtained densities of sintered SiC samples indicate that the investigated additives are suitable for liquid phase sintering of SiC. However, further optimization is necessary to achieve fully dense ceramics body. The densities of hot pressed samples decreased during annealing treatment (> 93 % TD) due to the decomposition of sintering additives [11]. Densities of hot pressed and annealed samples are summarized in table 2. The highest residual porosity was observed near a samples surface. The middle parts of the samples were relatively dense with smaller pores distribution.

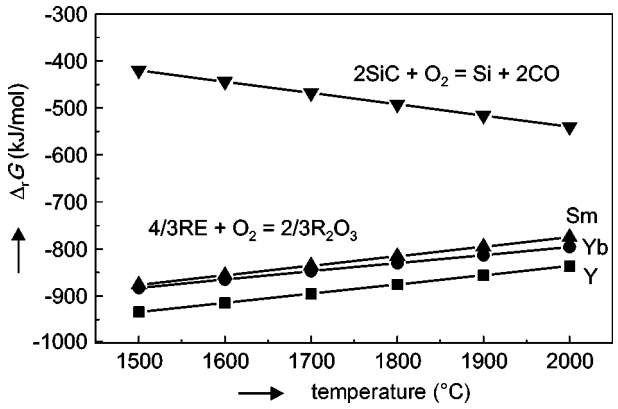
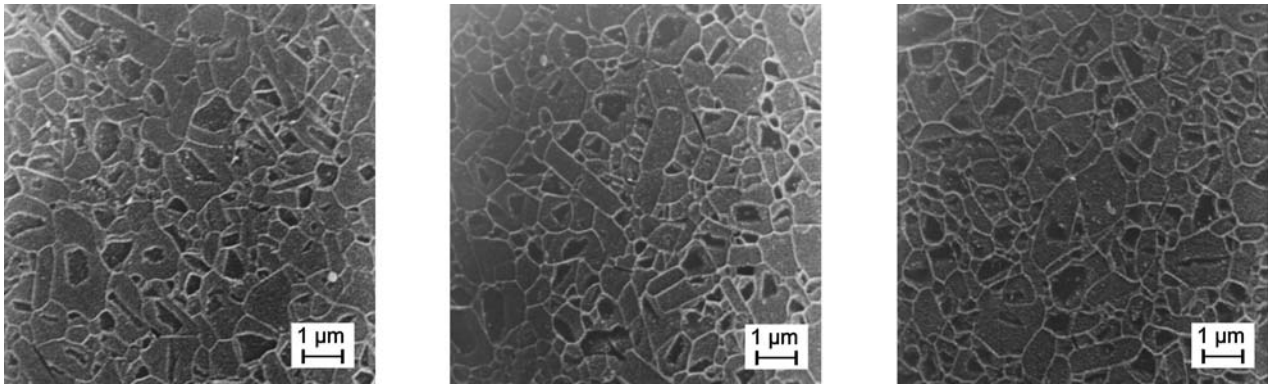


Figure 1. Thermodynamic stability calculation.

The characteristic microstructures of hot pressed SiC samples are shown in figure 2. Generally, all samples exhibit homogeneous equiaxed microstructure containing a small amount of elongated platelet-like grains. Sintering additives did not show a strong influence on the microstructure after sintering for a short time at relatively low temperature (1850°C, 1 h). The microstructure of the annealed samples compared with the hot pressed samples was significantly different. Grain growth was observed after annealing for all composi-

Table 2. Relative densities of hot pressed and annealed samples.

Sample	Relative density (%)	
	HP	AN 10
SC-YYb	96.5	94.3
SC- YSm	95.8	93.8
SC-YbSm	94.5	93

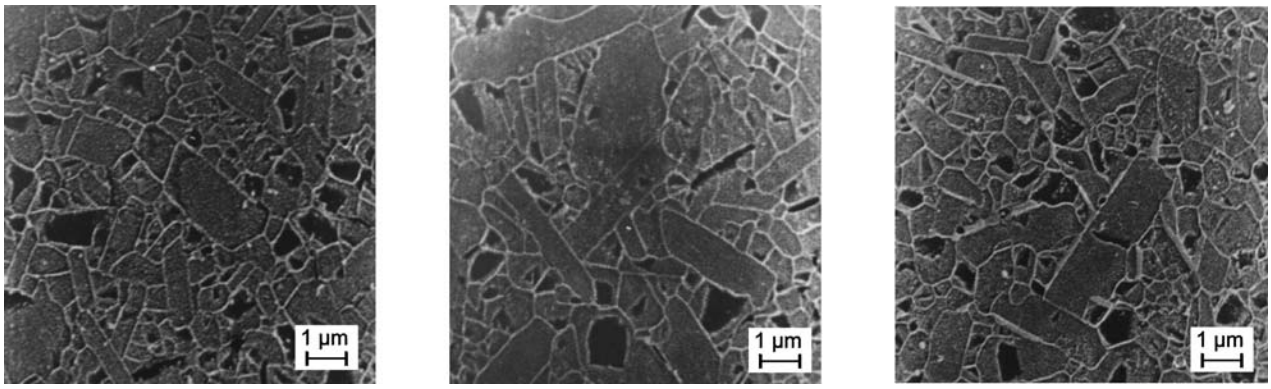


SC-YYb SC-YSm SC-YbSm.

Figure 2. Characteristic microstructures of the hot pressed samples.

tions (figure 3). The grain growth depends on the composition of grain boundary phase. The highest aspect ratio was observed for the samples SC-YSm. The microstructural differences between annealed samples are owing to the different viscosity and chemical composition of the grain boundary phase. The results indicate that different sintering additives in conjunction with appropriate post heat- treatment evocate different microstructural development.

Mechanical properties (hardness and fracture toughness) were measured at middle part of the SiC samples with the relatively low porosity. The Vickers hardness and fracture toughness of SiC ceramics are shown in figures 4 and 5, respectively. It can be seen that the microstructure has an influence on the studied mechanical properties. Generally, annealing improved the mechanical properties of samples compared with hot pressed samples. The hardness and fracture toughness of both kind of samples (hot pressed and annealed) are in correlation with the observed microstructure. Samples with high content of elongated grains exhibit higher fracture toughness, and *vice versa* samples with finer microstructure have higher hardness. The residual porosity and the presence of inhomogenities from starting powders negatively influenced the mechanical properties of the SiC ceramics. Except of the grain size and residual porosity the mechanical properties are also dependent on the composition of grain boundary phase. The analysis of measured data shows a partial correlation between the ionic radius of rare-earth dopant and the mechanical properties. The ionic radius increases in the order: $r(Yb^{3+})$ = 0.0858 nm, $r(Yb^{3+})$ = 0.0893 nm, and $r(Sm^{3+})$ = 0.0964 nm, respectively. In this work the sintering additives contain two different rare earth elements. Therefore, the direct correlation of ionic radius with mechanical properties is more difficult. Comparison of samples with one identical rare earth element (e.g. Y in samples SC-YYb and SC-YSm) shows a general trend that with increasing ionic radius the fracture toughness increases and the hardness decreases. However, small rule exceptions were observed for hardness. A similar correlation between the ionic radius of rare-



SC-YYb SC-YSm SC-YbSm.

Figure 3. Characteristic microstructures of the annealed samples.

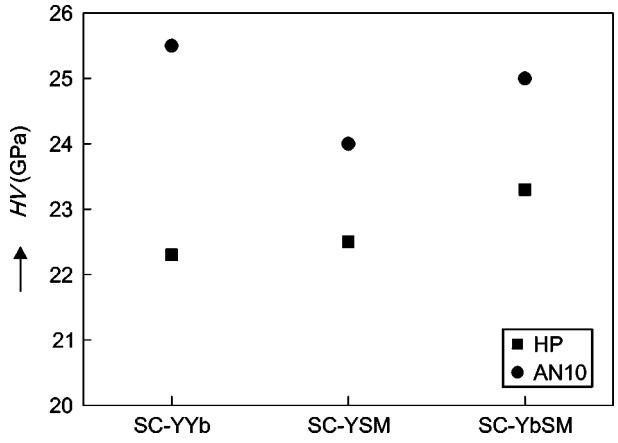


Figure 4. Hardness of the samples.

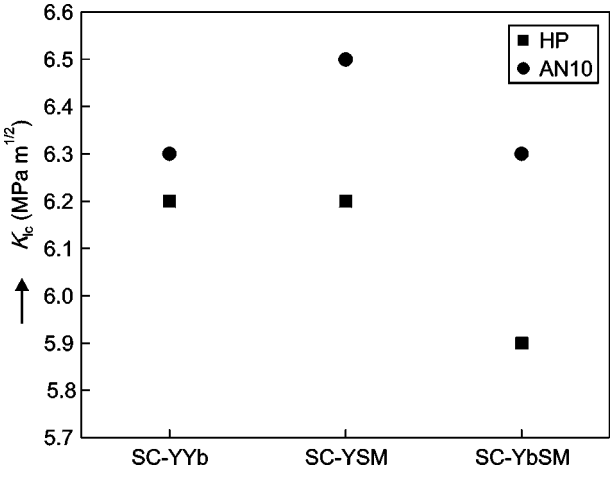


Figure 5. Fracture toughness of the samples.

earth oxide additives and mechanical properties of liquid phase sintered SiC was observed also by Zhou et al [12]. Generally, it can be concluded that the control of grain boundary chemical composition is an important technological aspect for tailoring the properties of LPS SiC.

CONCLUSIONS

The microstructure of SiC sintered in the presence of the liquid phase formed from the mixture of oxide (Y_2O_3/Yb_2O_3/Sm_2O_3), and nonoxide (AlN) sintering additives depends on the kind of sintering additives and also on the sintering and annealing conditions. Hot pressed samples exhibit more or less equiaxed microstructure that was changed after annealing. Significant grain growth was observed after annealing especially for sample SC-YSm (oxide additives Y_2O_3 and Sm_2O_3). The mechanical properties are in correlation with the obtained microstructure. Samples with finer microstructure have higher hardness, while contrary samples with elongated grains have higher fracture toughness.

In general it was observed that with decreasing ionic radius of rare-earth additive the hardness of SiC ceramics increases and the fracture toughness decreases. This trend of mechanical properties was attributed to the difference in the chemical composition of the intergranular phase. These results suggest that the mechanical properties of liquid phase sintered SiC can be improved by the optimization of the intergranular phase.

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SPEKANIE SIC V PRÍTOMNOSTI KVAPALNEJ FÁZY TVORENEJ Z OXIDOV VZÁCNYCH ZEMÍN

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Karbid kremíka bol spekaný v prítomnosti kvapalnej fázy tvorenej z oxidov vzácnych zemín Y_2O_3/Yb_2O_3/Sm_2O_3 a AlN. Z dôvodu zvýraznenia vplyvu spekacích prísad na vývoj mikroštruktúry boli žiarovo lisované vzorky podrobené následnej dlhodobej tepelnej výdrži. Bol pozorovaný zaujímavý vplyv spekacích prísad na vývoj mikroštruktúry. Detailne je hodnotená závislosť mechanických vlastností od mikroštruktúry a zloženia fáz na hraniciach zŕn. Tvrdosť SiC keramiky narastá s klesajúcim iónovým priemerom lantanoidov a naopak lomová húževnatosť klesá.