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Micro-segregations in liquid phase sintered silicon carbide ceramics

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Abstract

The densification behaviour of LPSSiC ceramics with different amount of secondary phases was investigated during Field Assisted Sintering (FAST). In the densified materials micro-segregations were found with dimensions of several 100 μm. Sometimes such segregations were found in gas pressure sintered materials. The investigation of the state of crystallisation by EBSD and XRD revealed that these micro-segregations are connected with the formation of large YAG (Yttrium aluminium garnet) crystals. The mobility of yttrium in the grain boundaries was investigated by measuring concentration profiles in diffusion couples. The high diffusion coefficient determined at 1850 °C (10^{-6} cm/s) indicates that the observed segregations are caused by the crystallisation kinetics of the secondary phases during cooling.

Keywords: SiC; Silicon carbide; Diffusion; Sintering

1. Introduction

Silicon carbide is a prevalent ceramic material for many applications in harsh environmental conditions because of its resistance to high temperatures, aggressive chemicals and abrasion.[1] The sintering of SiC (SSiC) is usually performed at very high temperatures up to 2200 °C in the solid state, with small amounts of boron, carbon, or aluminium as additives. In the recent years liquid phase sintered silicon carbide (LPSSiC) has been developed as a material with higher fracture toughness than SSiC ceramics but a similar hardness. The use of yttria or other rare earth oxides and Al_2O_3 or AlN as sintering additives, which form, together with the SiO_2 existing on the surface of the starting SiC-powder, a liquid phase during the sintering, reduce the sintering temperature to values less than 1900 °C,[1,2] in comparison to 2100–2200 °C for solid phase sintered SiC (SSiC).

The formation of the grain boundaries has different consequences for the properties:

- it increases the fracture toughness and strength,[3–13]
- it influences the electrical properties of the materials,[14–17]
- it reduces the chemical stability.[18]

Investigations concerning the tailoring of the microstructure were carried out to optimize the properties of the LPSSiC ceramics. This includes grain growth dependence of the SiC grains on starting powder composition (α- or β-SiC), composition and amount of the additives and the sintering conditions.[3–13] The distribution of the secondary phases was not taken into account in these investigations. Only a few researchers mention segregations in LPSSiC[13] similar to the so-called snow flake structures in Si_3N_4-materials.[19]

The present paper investigates the distribution of the secondary phase depending on the processing conditions. To make the effect more pronounced a high additive content (10 vol.%) was used.

2. Experimental

The samples were prepared starting from α-SiC (H.C. Starck, UF15, $d_{50} = 0.55$ μm) and 10 vol.% mixed Al_2O_3 (Sumitomo, AKP 50) and Y_2O_3 (H.C. Starck, grade C, $d_{50} < 0.9$ μm) as

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Table 1
Composition, densifications and densities of the materials (the ratio of the additives was: 80 mol% Al_2O_3/20 mol% Y_2O_3).

Name	Composition	Isothermal temp. (°C)	Holding time (min)	Density (g/cm^3)	Theoretical density
Y1a	10 vol.%	1700	5	2.93 ± 00.1	3.32
Y1b	″	1750	5	3.03 ± 00.1	3.32
Y1c	″	1800	5	3.24 ± 00.1	3.32
Y1d	″	1900	5	3.23 ± 00.1	3.32
Y1cT1[a]	″	1900	30	3.246 (1.97)[b]	3.32
Y1cT1[a]	″	1900	90	3.285 (2.7)[b]	3.32
Y1Ti[c]	″	1800	5	3.25 ± 0.01	3.33
Yb1[d]	10 vol.% Yb_2O_3	1800	5	3.32 ± 0.01	3.44
Y2	7 vol.%	1800	5	3.23 ± 0.01	3.28
Y3_1	3 vol.%	1800	5	2.87 ± 0.01	3.25
Y3_1	3 vol.%	1900	5	3.22 ± 0.01	3.25

[a] Heat treatment after SPS.

[b] Weight loss in percent during heat treatment in brackets.

[c] Contain 1 vol.% TiC.

[d] Y_2O_3 is replaced by Yb_2O_3.

additives. The SiO_2 content in the starting powder was 1.7 wt%. The composition of additives had a mol ratio 4 Al_2O_3/1 Y_2O_3 (Table 1).

The powders were first mixed in Isopropanol in a planetary ball mill for 2 h and afterwards dried, sieve granulated and densified by the FAST/SPS method.

The development of SPS (Spark Plasma Sintering; Sumitomo, Japan) or FAST (Field Assisted Sintering Technology; FCT Company, Germany) allows the fast densification of materials. Both names describe the same technology, i.e., the use of pulsed direct current for direct heating of the dies and/or the samples. Typical sintering cycles last only a few minutes versus hours for standard hot pressing or gas pressure sintering cycles. This offers new possibilities for effective densification of the material with minimal decomposition. The densification was carried out with a heating rate of 100 K/min and a pressure of 50 MPa. The isothermal dwelling time was 5 min.

The final dimensions of the samples were 40 mm in diameter and 6 mm in height. After densification the samples were grinded and cut for further investigations. All investigations were made on cross-sectional faces. Some of these samples additionally were heat treated at 1850–1900 °C in Ar.

To get an idea of the mobility of the cations in the liquid phase during sintering a material with 1 wt% of TiC and a material in which Y_2O_3 was replaced by Yb_2O_3 was produced. These samples were densified, and cut into pieces of 10 mm × 10 mm × 3 mm. A diffusion couple consisting of material Yb1 and Y1Ti was compressed in the SPS at 1600 °C and a pressure of 15 MPa. Thus in the initial state one part of the SiC material contained Y_2O_3/Al_2O_3 additives and the other side Yb_2O_3/Al_2O_3 both of the same molar composition. These samples were then heat treated in the gas pressure sintering furnace at 1850 °C for 4 h.

The distribution of Y and Yb through the cross-section in the initial state and after the heat treatment was determined by EDX measurements. The species' concentration of a rectangular area of 1.7 mm × 0.1 mm was averaged. Yb and Y oxide as additives were used, because they have very similar ionic radis[21] and therefore similar diffusion constants can be expected.

The phase composition of the samples was determined by X-ray diffraction analysis (XRD 7; Seifert-FPM; CuK$_\alpha$), using JCPDS standards.[20] The theoretical density was determined using the density of the starting components, while the SiO_2 on the surface of the SiC was not taken into account.

The SEM investigations were carried out using LEO 985, with an attached EDX (INCAx-sight, Oxford Instruments) and NVISION 40 (Company Zeiss) with an EBSD (HKL, Nordlys).

3. Results

The densification curves of the materials are given in Fig. 1. Table 1 shows, that the densification is finished at 1800 °C for the material with the higher additive content. Increasing temperatures do not increase the density. These data are very similar to the values observed in hot pressed materials before. The XRD analysis of the samples after SPS confirm beside SiC, $Y_3Al_5O_{12}$ and Al_2O_3. No silicates were determined. Also SEM analysis revealed no silicates at the grain boundaries of these samples.

The microstructures of the densified materials at different magnifications are given in Figs. 2 and 3. From the low magnification it is obvious that some segregations took place. These

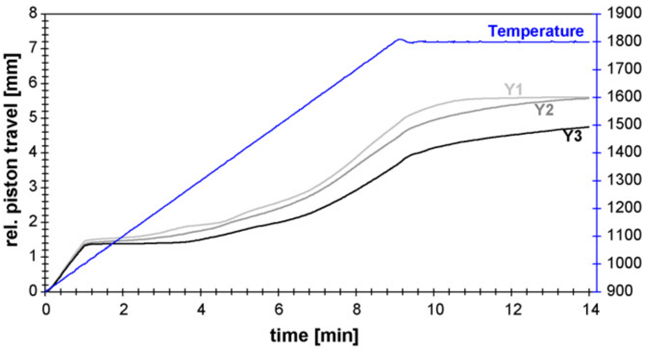

Fig. 1. Densification curves of the material Y1, Y2 and Y3.

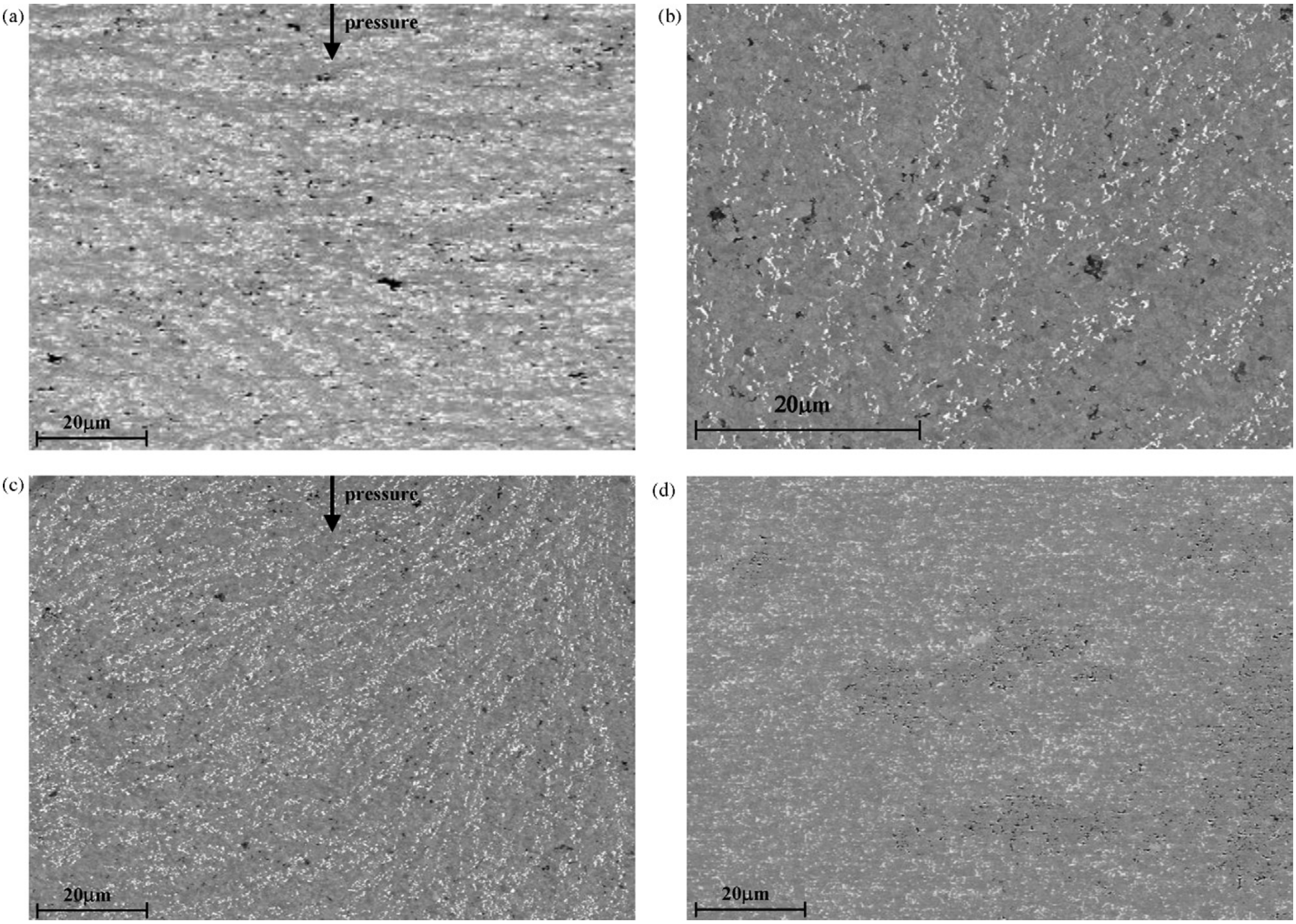

Fig. 2. SEM micrographs of polished sections of the densified materials Y1 (a) Y1a, (b) and (c) Y1c, (d) Y1cT1. Arrows mark the direction of the applied pressure during FAST/SPS process.

segregations of elongated shape are not perpendicular to the direction of the applied load. After heat treatment these segregations are still visible (Fig. 2d). Only their shape has changed into a more ball like form.

A more detailed analysis of the segregated areas showed that the darker area consists of grain boundaries free of Y_2O_3 whereas in the brighter areas a constant Y_2O_3/Al_2O_3 ratio was observed. This is crystallised $Y_3Al_5O_{12}$ (YAG) (Fig. 3).

On the sample Y1Ti heat treated at 1875 °C an EBSD analysis of the surface was carried out. The analysis (Fig. 4) showed clearly the distribution of SiC and the YAG phase. The analysis of the orientation of the YAG phase showed that they have the same orientation in different triple junctions. These areas with a constant orientation were larger than 20–50 μm.

The formation of these large YAG crystals can be derived indirectly from the XRD results of the samples showing a large scattering of the intensity of the different YAG peaks depending on the area which was analysed (Fig. 5). Both methods reveal the large sizes (>20–50 μm) of the YAG crystals.

To exclude that these segregations are connected with a bad mixing of the additives the homogeneity of the starting powder was analysed by EDX, showing no agglomerates of the additives larger than 10 μm. The segregations would therefore take place during the sintering and imply a high mobility of the ions in the secondary phases. No data concerning the mobility of Y and Al in the liquid phase are available therefore the diffusion couple experiments were carried out. The results are given in Fig. 6. After compressing the diffusion couple only in a very narrow region the concentration of Y and Yb is changed. The boundary between both samples is visible due to some residual porosity (Fig. 6a). After 4 h heat treatment a very broad diffusion profile was observed (Fig. 6d). In the sample after heat treatment the interface is marked by some residual pores (Fig. 6c). Thus the TiC which was added for marking the Y side of the diffusion couple was not necessary. A comparison of the distribution of the TiC-particles showed that in a region near the interface (50 μm) these particles disappear. This indicates that also Ti must have certain solubility in the liquid phase during sintering at the chosen conditions.

4. Discussion

The densification of the LPSSiC by the FAST (SPS) method is very similar to what was observed for the hot pressing of LPSSiC. The densification strongly depends on the amount of liquid phase. The materials with higher additive content densi-

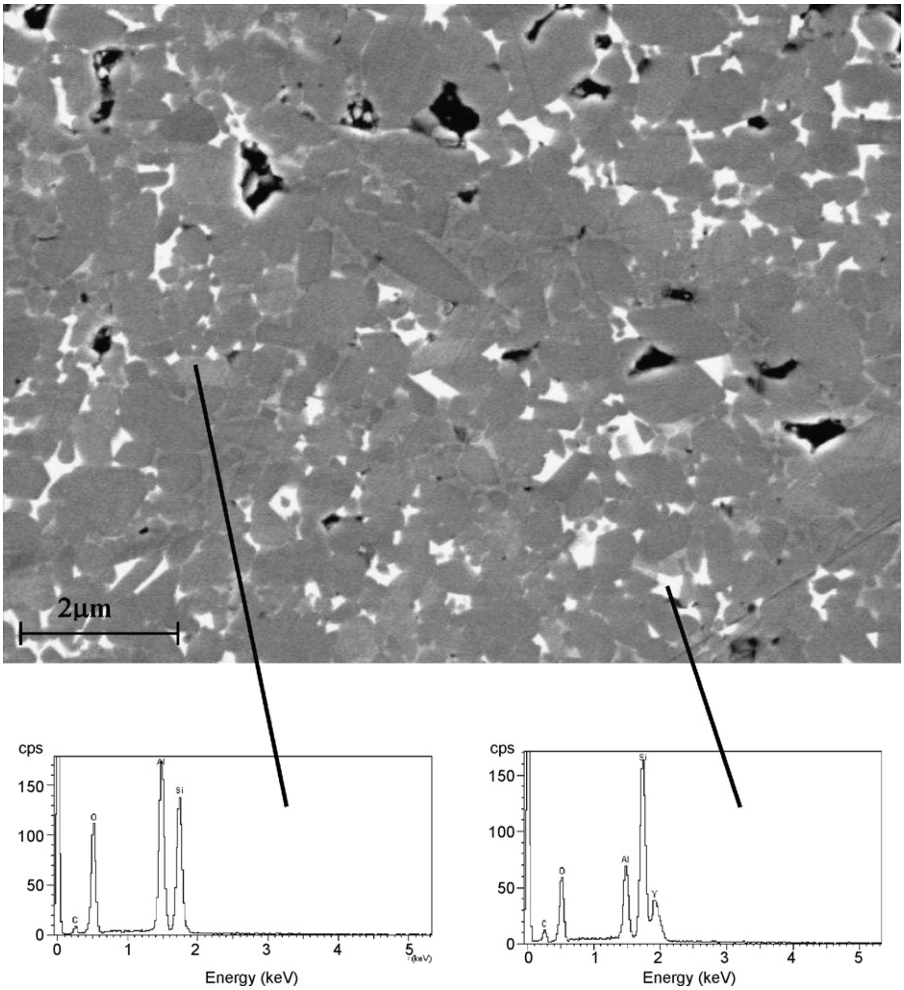

Fig. 3. SEM micrographs of polished sections of the densified materials Y1 and corresponding EDX measurements.

fied faster than samples with lower additive content. Due to the slower densification rate of the materials with low additive content open porosity exists up to high temperatures and therefore the reduction of the residual SiO_2 is stronger in materials with lower additive content and lesser amount of the amorphous grain boundary phase is formed.

The density increases strongly during heat treatment without applied load. This is mainly connected with the loss of SiO_2 (weight loss given in Table 1). For hot pressed materials this was observed as well and is explained in detail.[13] The polished cross-sections of the materials with higher additive content show some higher porosity which contributes to the lower density. This is surprising because the samples were densified under a pressure of 50 MPa. The pores are segregated in the same way as the secondary phases are. Therefore it is very likely, that they are caused by the separation of the secondary phases during cooling.

The diffusion experiments showed that the mobility of the ions in the liquid during sintering is high. An estimation of the diffusion coefficient from these data results in values of 10^{-6} cm^2/s. Additional experiments with less diffusion time are under way to determine the diffusion coefficient more accurately. Jiménez-Melendo und Haneda[21] have determined the diffusion coefficient of Yb in YAG. The extrapolation of the value to 1850 °C result in $D \approx 10^{-11}$ cm^2/s which is much lower than the observed one. This is in agreement with the formation of a melt in the system. The diffusion of Si in glassy SiO_2 at 1800 °C has a similar value.[22]

This value results in a characteristic length of the diffusion of $\sqrt{Dt} = 10\,\mu$m for $t = 1$ s. This indicates that initial in homogeneities must equilibrate very fast. There are no reasons known, why the segregations have to take place in the liquid during isothermal sintering. Therefore they have to be formed during cooling.

During the isothermal heating the oxide additives form a liquid phase, which partially can contain SiO_2 in the case of the FAST densified samples. In the case of the heat treated samples the temperature is still high enough for the complete melting even if all SiO_2 is evaporated.

It has to be taken into account that neighbouring triple junctions which do not look connected in the polished cross-section are connected to each other out of the plane of the cross-section. This can be derived from the fact, that the oxide liquid will wet the SiC (wetting is a precondition for liquid phase sintering).[23]

During cooling the liquid phase starts to crystallise. The main observed crystalline compound in the investigated materials is YAG. If the nucleation rate of the YAG is low, only few nuclei

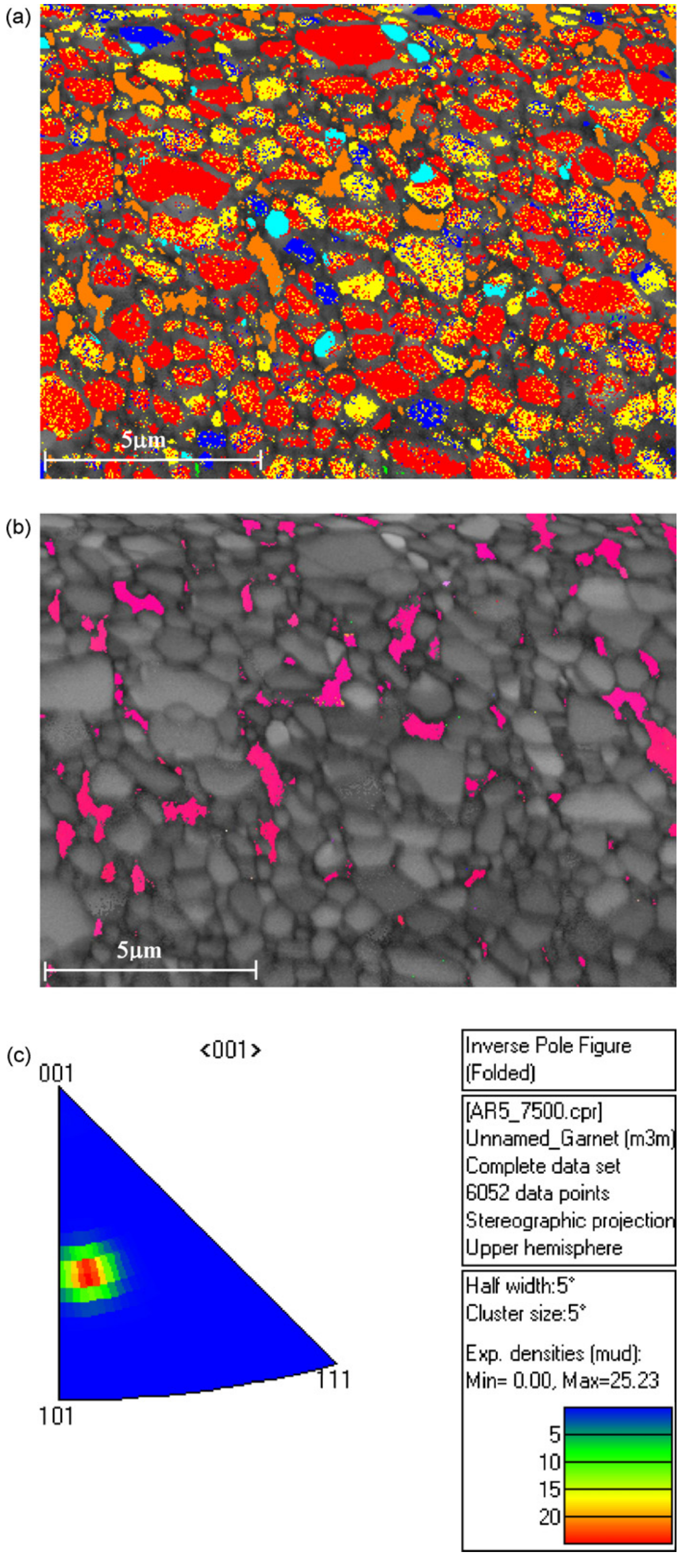

Fig. 4. Phase distribution in the material Y1Ti after heat treatment at 1875 °C using EBSD detector (a: phase mapping (red - 6h-SiC, blue - 4h-SiC, yellow - 15-RSiC, orange - YAG, green - Corundum, aqua TiC), (b: distribution of the YAG phase (the color corresponds to the crystallographic orientation), (c: the corresponding pole figure showing the single orientation of the YAG crystals in all triple junctions). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

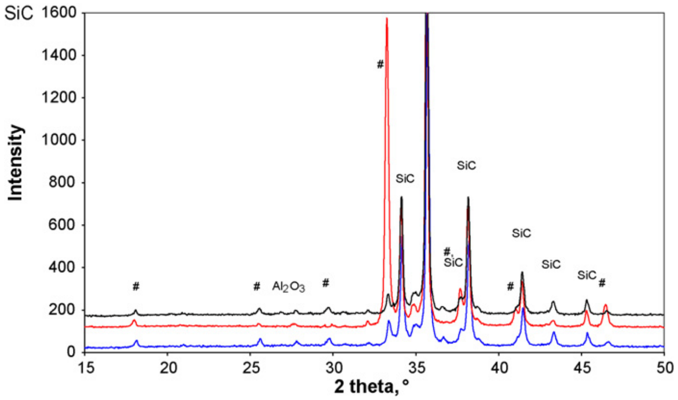

Fig. 5. Diffractograms of the material Y1c at different positions. # YAG.

will form, i.e., not every triple junction visible on the micrograph contains a nucleus. The nucleus grows around the SiC grains and includes them into the YAG crystals. Locally two interpenetrating networks of the SiC polycrystals and the YAG single crystal area form. The composition of the liquid phase differs from the stoichiometric YAG composition (in the investigated materials it is more rich on Al_2O_3). Hence the melt becomes with increasing YAG crystallisation more and more Al_2O_3 rich. At a certain Al_2O_3 concentration in the melt (at least higher than 80 mol%, eutectic composition YAG/Al_2O_3) the crystallisation of Al_2O_3 around the YAG crystals starts and thus stops their growth. Therefore the resulting microstructure shows the segregations. During crystallisation a volume change takes place. If small crystals are formed in the liquid, then most of the internal stresses resulting from the crystallisation can relax by viscous flow of the remaining liquid. The fast crystallisation of only few nuclei hinders this relaxation. The relaxation can take place by pore formation. This process results in the observed pore cluster at the interfaces between the segregated phases. A low nucleation rate of YAG was also observed in SiAlON materials which is an additional indirect evidence for the explanation.[24] This is shown schematically in Fig. 7. From the explanation the following conclusions can be drawn:

- The segregation will be less if the composition of the melt is close to the composition of the primary crystallizing phase. Due to the partial evaporation of Al during sintering and due to the incorporation of Al into the SiC grains the ratio of Y_2O_3/Al_2O_3 is difficult to control precisely.
- With high nucleation rate and lower growth rate the segregation would be minimized. This means fast cooling helps to avoid the segregation.
- With decreasing amount of the additives the segregation reduces (evaporation of more Al or incorporation of a higher percentage into SiC grains). Additionally this is caused by the lower flow ability of the liquid through the connections between the triple junctions which become narrower with reducing additive content or can be completely blocked.

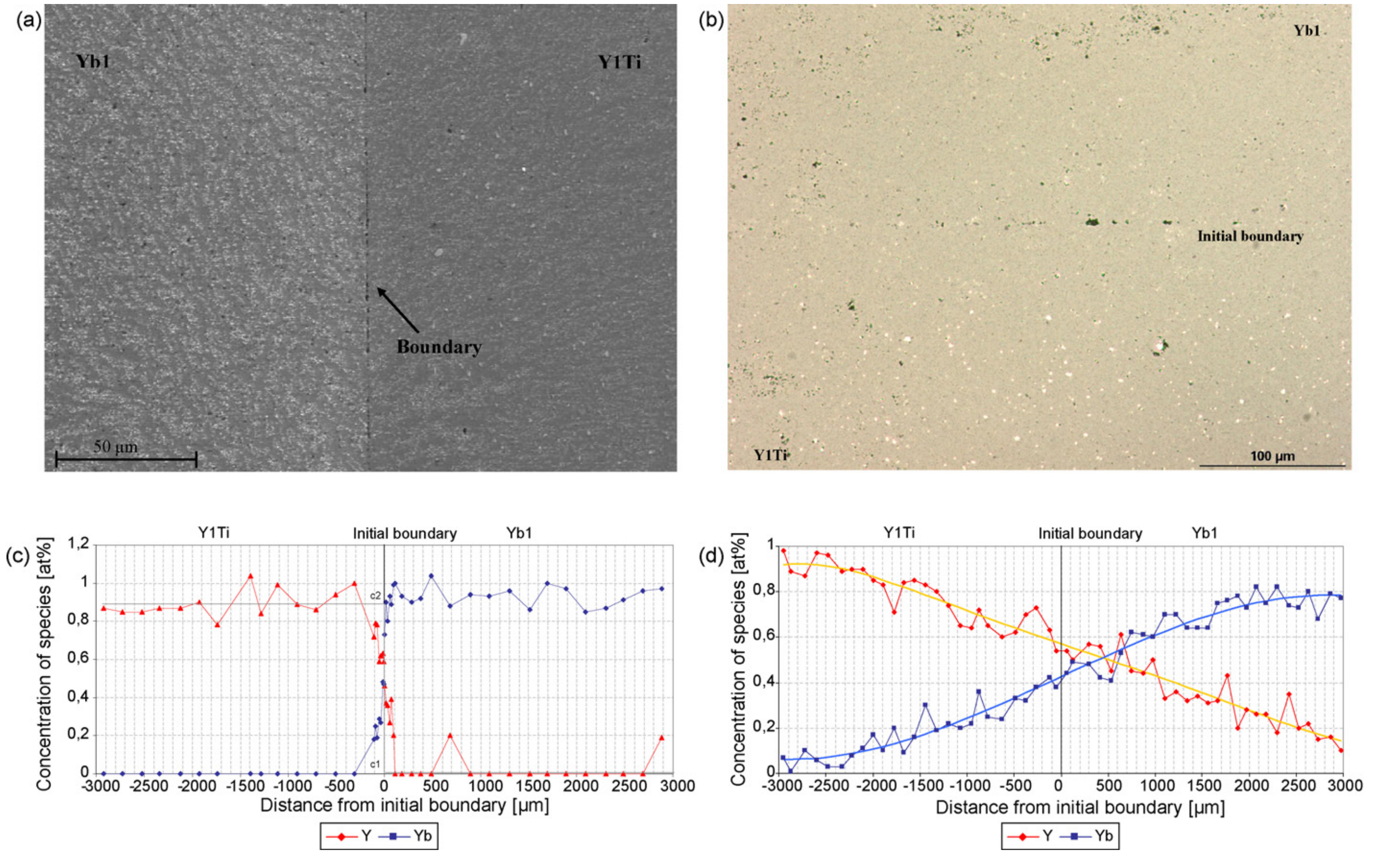

Fig. 6. SEM and optical micrographs and results of the EDX analysis of the diffusion couple after preparation of the material Y1c (a and b) and after heat treatment at 1850 °C for 4 h (c and d).

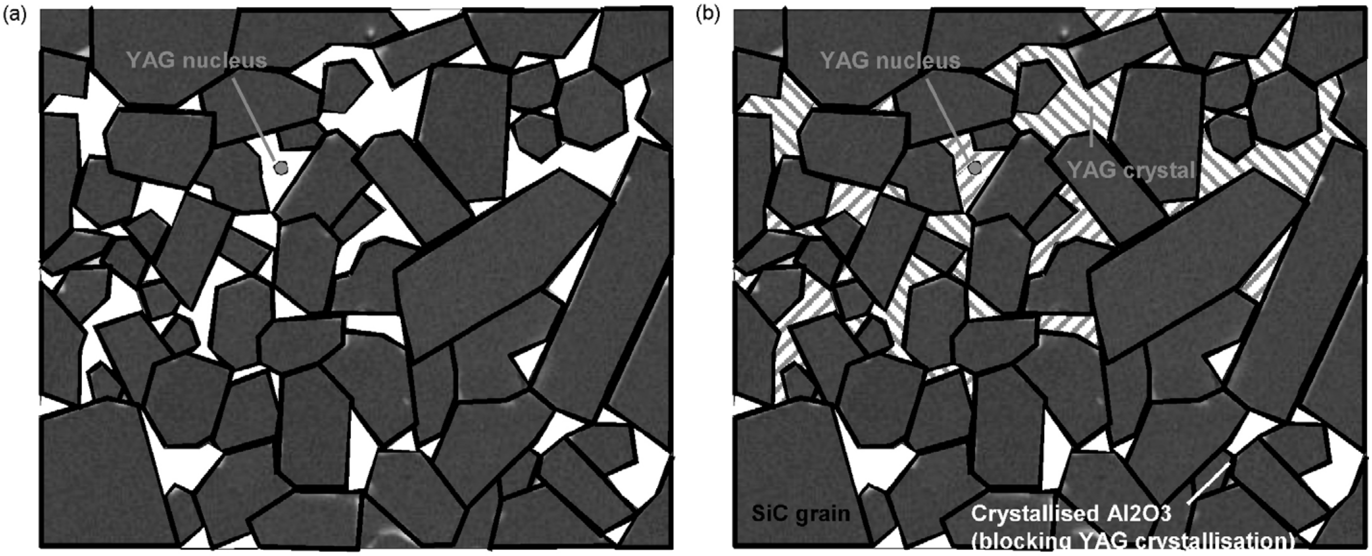

Fig. 7. Scheme of YAG crystallisation. (a) Beginning of YAG crystallisation around nucleus; (b) YAG crystallised in SiC network, crystallisation of Al_2O_3 blocks further YAG crystallisation.

5. Conclusions

The results show that the LPSSiC can be densified by FAST process in a few minutes. The densification strongly depends on the amount of additives. Diffusion couple experiments have shown, that the mobility of Y ions in the liquid phase at sintering temperature is very high (diffusion coefficient 10^{-6} cm^2/s). This will result in a fast local equalisation of the composition at sintering temperatures. In the materials with 10 vol.% liquid phase a pronounced local segregation (100–500 µm) was observed after

FAST densification and after heat treatment. Taking into account the high mobility of the ions in the liquid it can be concluded, that the segregations are caused by processes taking place during cooling. The reason of the segregation is the low nucleation rate of the YAG crystals in the triple junctions.

Acknowledgement

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References

1. Schwetz KA. Silicon carbide based hard materials. In: Riedel R, editor. *Handbook of ceramic hard materials*. Weinheim: Wiley-VCH; 2000. p. 683–748.
2. Omori M, Takei H. Pressureless sintering of SiC. *J Am Ceram Soc* 1982;**65**:C-92.
3. She JH, Ueno K. Effect of additive content on liquid-phase sintering on silicon carbide. *Mater Res Bull* 1999;**34**:1629–36.
4. Pujar VV, Jensen RP, Padture NP. Densification of liquid-phase-sintered silicon carbide. *J Mater Sci Lett* 2000;**19**:1011–4.
5. Winn EJ, Clegg WJ. Role of the powder bed in the densification of silicon carbide sintered with yttria and alumina additives. *J Am Ceram Soc* 1999;**82**:3466–70.
6. Padture NP, Lawn BR. Toughness properties of a silicon carbide with an *in situ* induced heterogeneous grain structure. *J Am Ceram Soc* 1994;**77**:2518–22.
7. Zhan G-D, Mitomo M, Kim Y-W. Microstructural control for strengthening of silicon carbide ceramics. *J Am Ceram Soc* 1999;**82**:2924–6.
8. Kim Y-W, Kim J-Y, Rhee S-H, Kim D-Y. Effect of initial particle size on microstructure of liquid-phase sintered silicon carbide. *J Eur Ceram Soc* 2000;**20**:945–9.
9. Sciti D, Guicciardi S, Bellosi A. Effect of annealing treatments on microstructure and mechanical properties of liquid-phase sintered silicon carbide. *J Eur Ceram Soc* 2001;**21**:621–32.
10. Cheong DI, Kim J, Kang S-JL. Effects of isothermal annealing on the microstructure and mechanical properties of SiC ceramics hot-pressed with Y_2O_3 and Al_2O_3 additions. *J Eur Ceram Soc* 2002;**22**:1321–7.
11. Rixecker G, Wiedmann I, Rosinus A, Aldinger F. High-temperature effects in the fracture mechanical behaviour of silicon carbide liquid -phase sintered with AlN-Y_2O_3 additives. *J Eur Ceram Soc* 2001;**21**:1013–9.
12. Biswas K, Rixecker G, Wiedmann I, Scweizer M, Upadhyaya GS, Aldinger F. Liquid phase sintering and microstructure–property relationships of silicon carbide ceramics with oxynitride additives. *Mater Chem Phys* 2001;**67**:180–91.
13. Can A, Herrmann M, McLachlan DS, Sigalas I, Adler J. Densification of liquid phase sintered silicon carbide. *J Eur Ceram Soc* 2006;**26**:1707–13.
14. Sauti G, Can A, McLachlan DS, Herrmann M. The AC conductivity of liquid-phase-sintered silicon carbide. *J Am Ceram Soc* 2007;**90**(8):2446–53.
15. Siegelin F, Kleebe H-J, Sigl S. Interface characteristics affecting electrical properties of Y-doped SiC. *J Mater Res* 2003;**18**(11):2608.
16. Volz E, Roosen A, Hartung W, Winnacker A. Electrical and thermal conductivity of liquid phase sintered SiC. *J Eur Ceram Soc* 2001;**21**:2089–93.
17. Ihle J, Martin HP, Herrmann M, Obenaus P, Adler J, Hermel W, et al. The influence of porosity on the electrical properties of liquid phase sintered silicon carbide. *Int J Mater Res (Z Metallkunde)* 2006;**97**(5):649–56.
18. Herrmann M, Schilm J, Michael G. Corrosion behaviour of different technical ceramics in acids, basic solutions and under hydrothermal condition. *CFI* 2003;**80**(4):E27–33.
19. Herrmann M, Schulz I, Bales A, Sempf K, Hoehn S. “Snow flake” structures in silicon nitride ceramics—reasons for large scale optical inhomogeneities. *J Eur Ceram Soc* 2008;**28**:1049–56.
20. Joint Committee on Powder Diffraction Standards (JCPDS). ASTM, Swartmore, 2001.
21. Jiménez-Melendo M, Haneda H. Ytterbium cation diffusion in yttrium aluminum garnet (YAG)—implications for creep mechanisms. *J Am Ceram Soc* 2001;**84**(10):2356–60.
22. Kiefer J, Borchardt G. A kinetic model of silicate melts. *Chem Geol* 1987;**62**:93–101.
23. German RH. *Sintering theory and practice*. New York: John Wiley and Sons Inc.; 1996.
24. Bressiani JS. Dissertation, University of Stuttgart (1984).