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The Influence of α- and β-Si_3N_4 Precursors on Formation of α-SiAlON Ceramics

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Abstract

During the formation of α-SiAlON from a powder mixture wet-milled in isopropyl alcohol at a temperature of 1500–1600°C there appears considerable amount of β-SiAlON. β-SiAlON is formed in high α- as well as in high β-Si_3N_4 starting powders. The β-SiAlON is dissolved at higher temperatures. The rate of dissolution of α-Si_3N_4 was observed to be higher than that of β-Si_3N_4 and the densification and rate of α-SiAlON formation is higher in high α-Si_3N_4 powder.

1 Introduction

SiAlON ceramics have attracted the attention of materials scientists during last two decades. At the very beginning of their development there was a belief that the reaction of 'transient' liquids resulting in incorporation of sintering additives into the α- or β-SiAlON structure and thus giving less or no grain boundary phase would improve the high temperature properties.[1,2] For many years this expectation was not fulfilled and the mechanical properties of Si_3N_4-based materials were superior to SiAlONs. The advantage of SiAlONs was in their different chemical properties, resulting in different corrosion resistance and ease of fabrication. The second main point focusing interest on SiAlON materials was the fact that they allowed us to have stable α-phase in the system. The α-phase is considerably harder,[5,6] which is of interest in cutting and wear applications.[3,4,7] Recent results of carefully prepared α/β-SiAlON composite materials with exceptional high temperature properties[8] are confirming early expectations.

α-SiAlON can be characterized by the formula $Me_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$ where Me is Li, Ca, Mg, Y and rare-earth metals except La, Ce, Pr and Eu[2,9] and $m = 3x$ when x represents the valence of the Me atom. Yttrium α-SiAlON is among the α-SiAlONs most widely investigated.[2,7,9,10] The triangle Si_3N_4–$Y_2O_3 \cdot 9AlN$–$YN \cdot 3AlN$ has a stability area of α-SiAlON, as shown in Fig. 1.

β-SiAlON has the formula $Si_{6-z}Al_zO_zN_{8-z}$ where $0 < z < 4{\cdot}2$.[1] α- as well as β-SiAlONs are isostructural with α- and β-Si_3N_4, respectively. The influence of different starting Si_3N_4 powders, mixing techniques, temperature and rate of temperature increase on phase composition and relative density is reported in this paper.

2 Experimental Procedure

In the present work, three starting silicon nitride powders were used. Two of them, labelled as A and B were prepared by nitridation of silicon powder in-house.[11] They were extracted from the different parts of the nitrided powder compact and due to the different thermal conditions they consisted of various α/β-Si_3N_4 proportions. The specification of the powders is shown in Table 1.

The appropriate powder mixtures, expected to produce α-SiAlON with an x-value of 0·4 were attrition milled for 4 h with Si_3N_4 balls in isopropyl alcohol. Abrasion of the milling balls (β-Si_3N_4) resulted in a 5% increase of β-Si_3N_4 in the starting powder. Alternatively, one powder mixture (C) was mixed in a rotating polyethylene bottle in isopropyl alcohol with agate balls as mixing media. This was labelled as D. The abrasion of the balls was not detected. The mixing time was 48 h. The isopropyl alcohol was dried prior to all experiments. The composition of the powder mixtures is shown in Table 2.

The powders were dried and isostatically pressed to solid bodies approximately 60% of theoretical density under a pressure of 200 MPa. The firing was performed at 1300–1900°C for 1 h under 1 MPa of static nitrogen in a graphite resistance furnace, which was evacuated before heating to 1000°C. A powder bed prepared from Si_3N_4 (86 wt%),

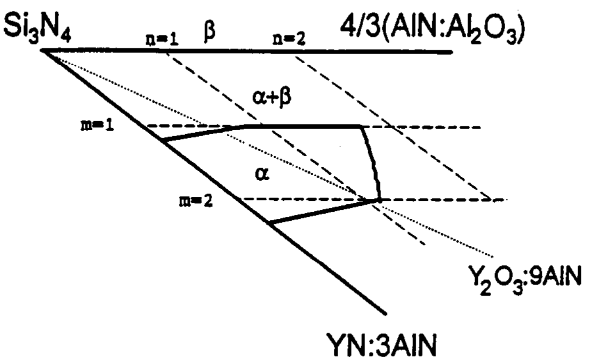

Fig. 1. Detail from the triangle Si_3N_4–4/3Y_2O_3·9AlN–YN·3AlN, showing composition area of α-SiAlONs, according to Ref. 9.

Table 1. Specification of the powders used

Material	*Specification*
Si_3N_4-A	Prepared in house, median grain size 0·3 μm, 85% α-phase, 15% β-phase, oxygen content 1·8 wt%
Si_3N_4-B	ditto, 10% α-phase, 90% β-phase
Si_3N_4-C	H. C. Starck Grade H1, median grain size 0·66 μm, >> 90% α-phase, oxygen content 1·6% (LECO), specific surface 9·87 m^2 g^{-1} (BET)
AlN	Fluka, No. 06280, oxygen content 1·4 wt%, median grain size 1 μm
Y_2O_3	Techsnabexport, Russia, 99·99% pure, median grain size 4 μm

Table 2. Composition of the powder mixtures (wt%)

Powder mixture	Si_3N_4	Y_2O_3	AlN
A, B and C	80·04	7·58	12·38

Al_2O_3 (7 wt%) and Y_2O_3 (7 wt%) powders were used in all experiments. Dilatometry experiments were performed in a high-temperature dilatometer heated by graphite resistance furnace. The sample was isolated from the graphite assembly by thin (0·5 mm) BN disks. Densities of the fired samples were determined by mercury immersion method. X-ray diffraction patterns were collected on the powdered samples with primary beam monochromatized CoK_{α} radiation ($CoK_{\alpha 1}$ = 1·788965 A) using a STOE Stadi P transmission diffractometer configured with a linear position sensitive detector. The α/β ratio in the samples was determined from the X-ray intensities of planes 102 and 210 for the α-phase and 101 and 210 for the β-phase.[12] To reveal the microstructure, polished samples were plasma etched (Fisons Instruments, model Polaron PT 7150).

3 Results and Discussion

The phase composition of powder mixtures prepared from Si_3N_4 powders A, B and C (materials A, B and C) fired at various temperatures (1300–1900°C) for 1 h is shown in Figs 2–4 (only Si_3N_4-based phases are shown). In all three powder mixtures α-SiAlON starts to form at approximately 1300°C and its formation is at the expense of α- as well as β-Si_3N_4. At approximately 1500°C there is in all powder mixtures, an increase in the β-phase. Above 1600°C the β-phase is converted to α-SiAlON. The composition of secondary β-phase (z-value) was, with the help of X-ray unit cell determination established in the range of $0{\cdot}2 < z < 0{\cdot}3$. These results are not in full accordance with recent work of Sheu,[8] who concluded that, while using 100% α-Si_3N_4 as the starting powder, α-SiAlON and β-Si_3N_4 phases evolved. While using 100% β-Si_3N_4 as the starting powder, only α-SiAlON evolved but the original β-Si_3N_4 decreased. The difference between these two observations can be explained by the use of various starting materials. While in the present work the difference between the pow-

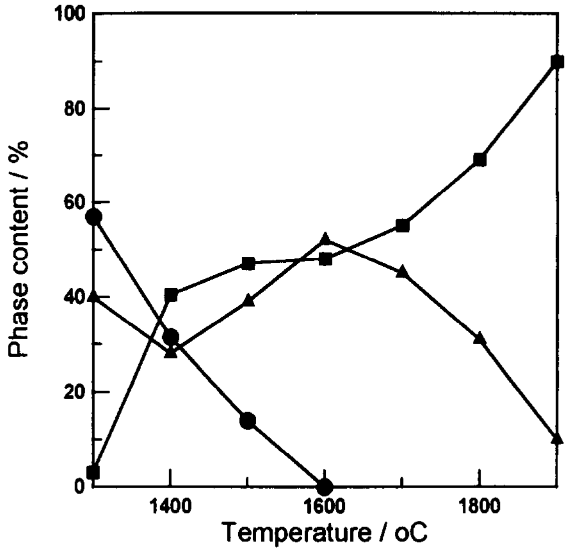

Fig. 2. Phase composition of the powder mixture A fired at various temperatures for 1 h in nitrogen. ● α-Si_3N_4, ■ α-SiAlON, ▲ β-phase.

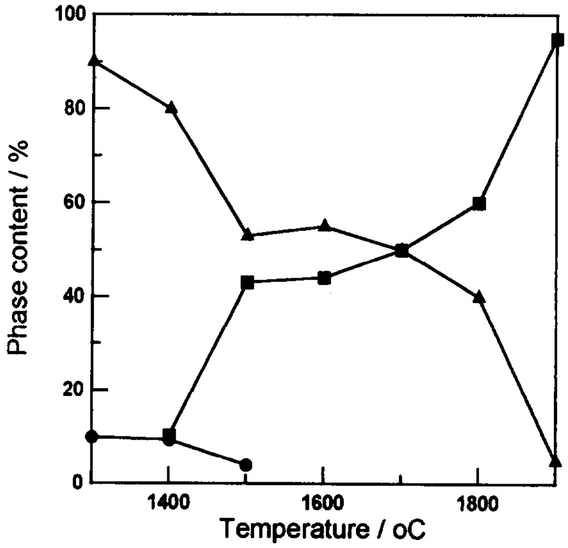

Fig. 3. Phase composition of the powder mixture B fired at various temperatures for 1 h in nitrogen. ● α-Si_3N_4, ■ α-SiAlON, ▲ β-phase.

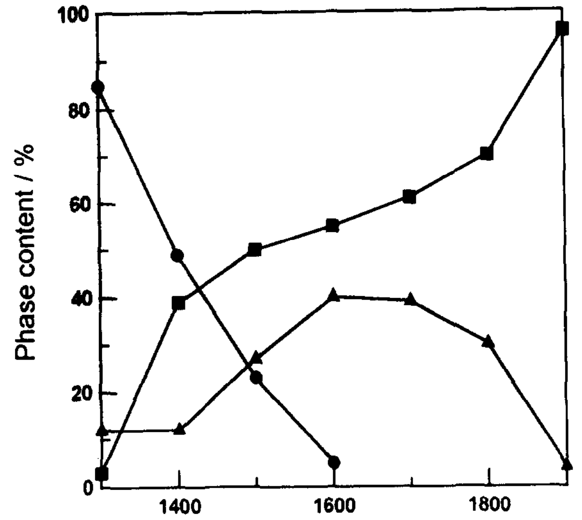

Fig. 4. Phase composition of the powder mixture C fired at various temperatures for 1 h in nitrogen. ● α-Si_3N_4, ■ α-SiAlON, ▲ β-phase.

ders A and B, as they stem from the same nitridation batch, is only in their phase composition, Sheu[8] used commercial high α-Si_3N_4 powder, which was heat treated in order to convert it to β-Si_3N_4. This treatment could result also in some change of its chemical composition. It is also possible, that the reason that Sheu[8] did not observe cooperative formation of α-SiAlON and the β-phase may have kinetic reasons, as his results represent the phase composition during heating up of the sample and not after some time lapse (1 h in present paper) at given temperature.

The phase composition of the powder mixture D, where wet milling was substituted by mixing in plastic bottle is shown in Fig. 5. Here the formation of α-SiAlON starts at lower temperatures than in attrition-milled sample, and the formation of secondary β-SiAlON is absent. The temporary formation of β-SiAlON is in agreement with the results in Ref. 13. This paper confirms this observation also in the case of the high β-Si_3N_4 starting powder. The decomposition of β-SiAlON above 1600°C suggests that the region of stability of α-SiAlON is better at higher temperatures.

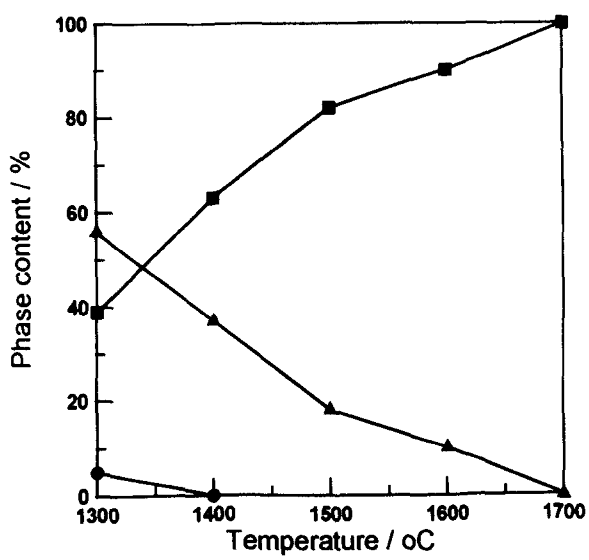

Fig. 5. Phase composition of the powder mixture D fired at various temperatures for 1 h in nitrogen. ● α-Si_3N_4, ■ α-SiAlON, ▲ β-phase.

The densification kinetics of powder mixtures A and B was studied in a dilatometer using various heating rates. The results are shown in Figs 6 and 7. At both heating rates, 50 and 500°C/min, the powder mixture B (consisting of 85% of β-Si_3N_4) exhibits lower densification. The densification process in the system of α-SiAlON is a very complex one. The classical sintering consisting of neck growth and pore elimination is accompanied by phase transformation, where the morphology of dissolving as well as emerging phases plays an important role. According to Hendry[14] the difference in free energies of formation of α- and β-Si_3N_4 at 1100°C is about 10%, when α modification is a more stable one. According to these data,

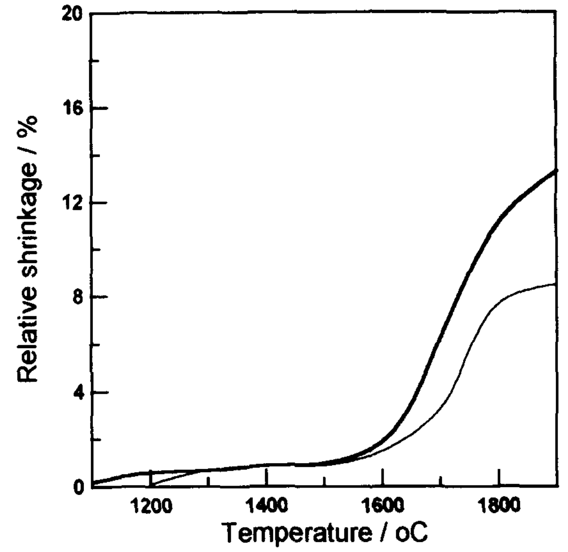

Fig. 6. Relative shrinkage versus temperature of the powder mixtures A (bold line) and B (thin line). Heating rate 50°C/min.

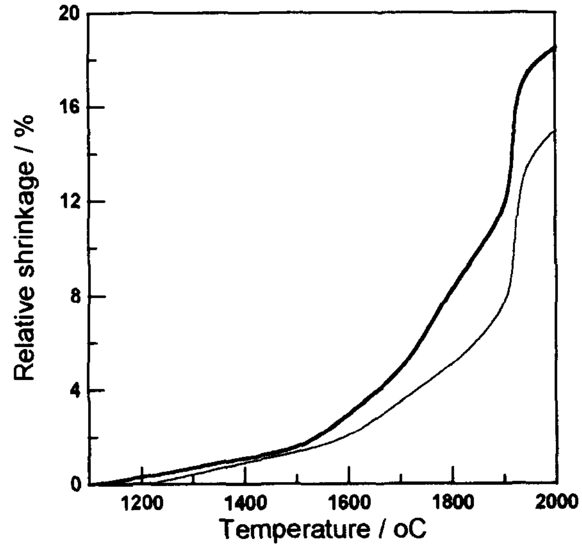

Fig. 7. Relative shrinkage versus temperature of the powder mixtures A (bold line) and B (thin line). Heating rate 500°C/min.

β-modification is supposed to become more stable above 1330°C. However, according to the recent data for β-Si_3N_4 by Pánek,[15] β-Si_3N_4 is more stable above 950°C. The earlier onset of densification of the powder mixture A is probably caused by higher dissolution rate of α-Si_3N_4. This is also in agreement with the similar observation of Šajgalík and Galusek[16] and it is the reason for higher rate of formation of α-SiAlON, specially at lower temperatures, *cf* Figs 2 and 3.

The higher heating rate (500°C/min) leads to higher relative shrinkage in the studied systems. The difference is probably caused by the amount and composition of transient liquid present in the densifying α-SiAlON system. With the ongoing phase transformation and formation of α-SiAlON (above 1300°C), this liquid is consumed. At higher heating rates the transient liquid remains, due to the kinetic reasons, in the system up to higher temperatures, influencing positively the densification. The phase composition (only major, Si_3N_4 phases are shown) of the samples after dilatometric experiments is shown in Fig. 8. At the heating rate of 50°C/min in the sample A, there is more α-SiAlON formed (61 versus 56%) compared to the sample B. This also confirms that α-Si_3N_4 from the starting powder dissolves faster than β-Si_3N_4. At the heating rate of 500°C/min the former α- and probably also β-Si_3N_4 powders did not react completely. (The resolution of X-ray diffraction analysis did not allow us, due to the close values of unit cell dimensions, to distinguish between β-Si_3N_4 and β-SiAlON quantitatively). Also in this case, the amount of α-SiAlON is higher in the sample A.

The microstructure of samples from dilatometry is shown in Fig. 9. The samples were polished and plasma etched. By plasma etching 'pure' Si_3N_4 is attacked more intensively, followed by β-SiAlON, α-SiAlON and the grain-boundary phase. Thus, the Si_3N_4 is darkest, the β-SiAlON is lighter, etc. (*cf.* Fig. 9(a)). In sample A, heated at the rate of 50°C/min (Fig. 9(a)), there is relatively low amount of original Si_3N_4 grains. The microstructure of the sample A heated with the rate of 500°C/min (Fig. 9(b)) contains a higher amount of the original Si_3N_4 grains and is considerably finer. In sample B heated at the rate of 500°C/min (Fig. 9(c)), the former Si_3N_4 grains are bigger than in sample A. This observation confirms that the rate of dissolution of β-Si_3N_4 during formation of α-SiAlON is lower in comparison with α-Si_3N_4.

4 Conclusions

The results of this study show that in the powder system expected to form α-SiAlON, in the temperature region 1500–1600°C β-SiAlON is formed, regardless of the α/β-Si_3N_4 starting powder composition. During the reaction producing α-SiAlON the rate of dissolution of α-Si_3N_4 is faster than that of β-Si_3N_4. The high α-Si_3N_4 starting powders thus exhibit higher densification and α-SiAlON formation.

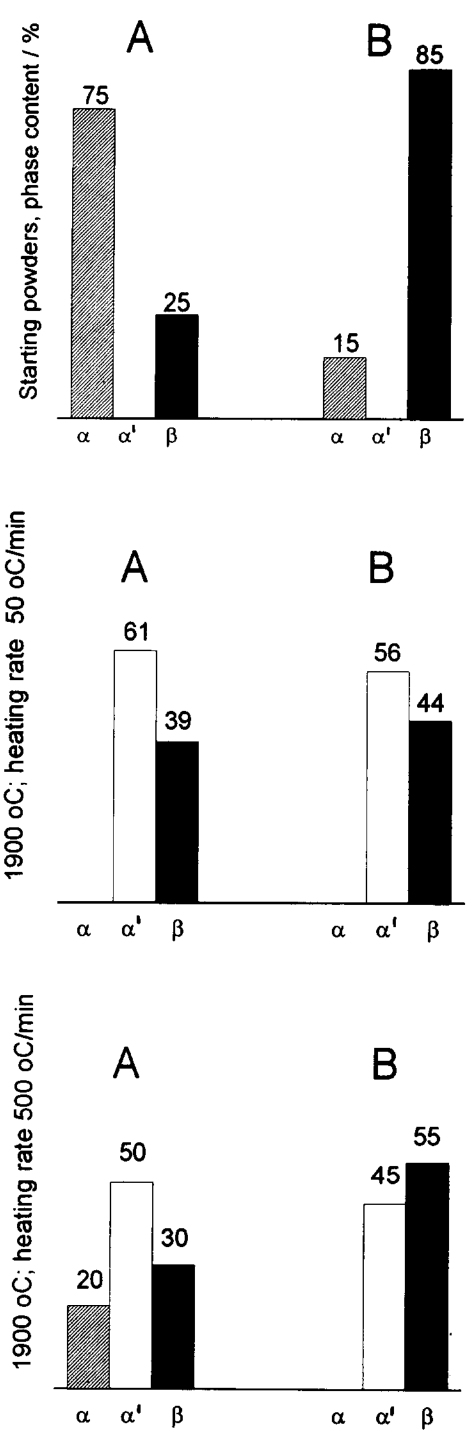

Fig. 8. Phase composition of the starting powders and samples after dilatometry.

Acknowledgement

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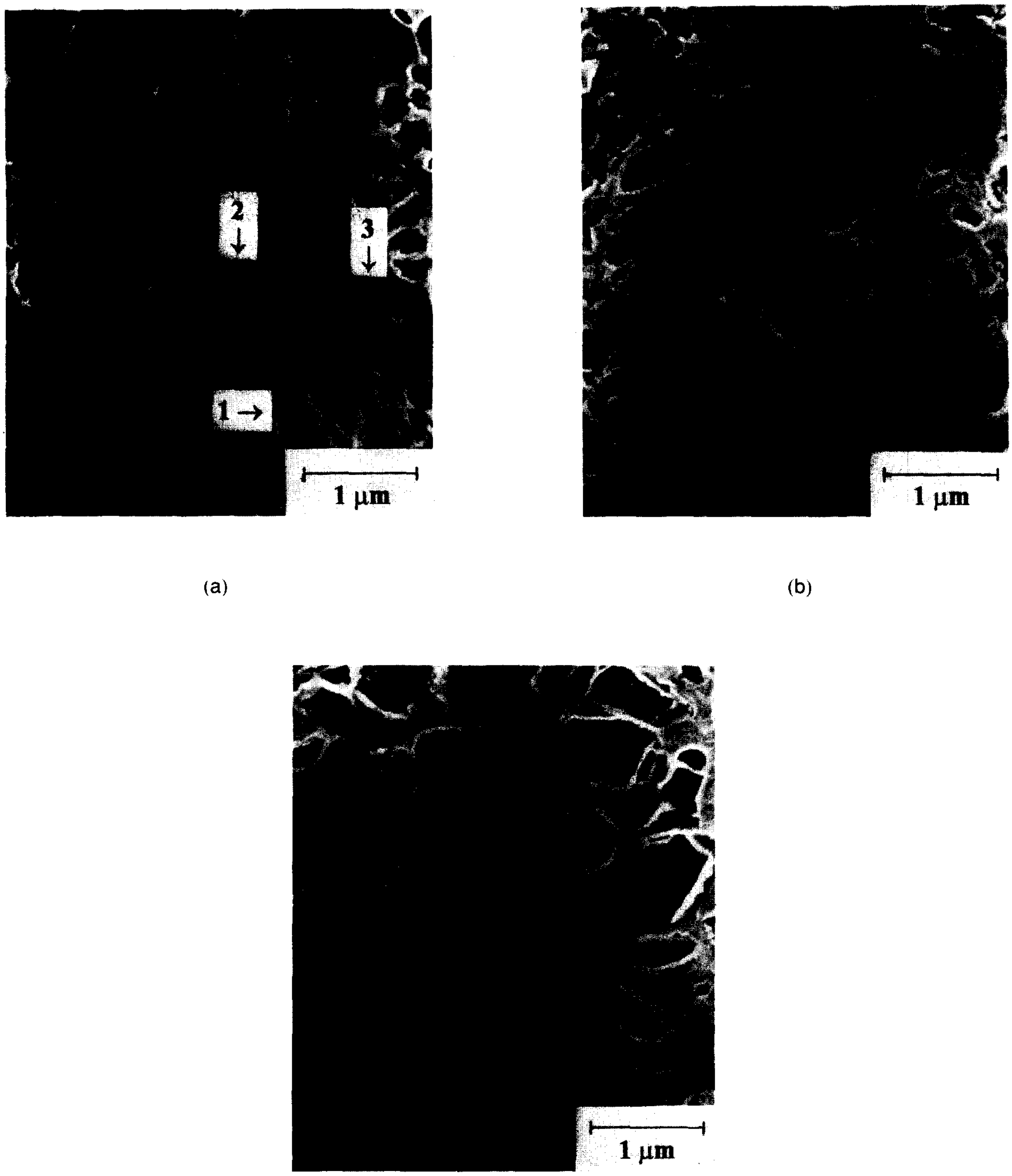

(a) (b)

(c)

Fig. 9. Microstructure of the samples after dilatometry. (a) Powder mixture A, heating rate 50°C/min. (b) Powder mixture A, heating rate 500°C/min. (c) Powder mixture B, heating rate 500°C/min.

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