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Sintering and oxidation resistance of compositions in the $SiC–La_2O_3–Al_2O_3–Cr_2O_3$ system

I. Pressureless sintering of compositions in the $SiC–La_2O_3–Al_2O_3–Cr_2O_3$ system at low temperatures

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Abstract

Sintering of materials, which were prepared from β-SiC and $LaCrO_3$ with Al_2O_3, β-SiC and $LaAlO_3$, β-SiC and $LaAlO_3$ with Cr_2O_3 and Al_2O_3 via heating at 1700°C in graphite powder, was studied. Significant densification of material was achieved in $SiC–LaCrO_3–Al_2O_3$ composition due to a formation of liquid phase. The formation of liquid phase is considered to be promoted by a reaction of chromium oxide with starting components. $SiC–LaCrO_3–Al_2O_3$ compositions were sintered to about 90% of theoretical density at 1700°C. The material had a structure comprising a matrix made up of SiC grain with tiny $LaAlO_3$ crystals and 2–4 μm inclusions of chromium carbide. As result, the material showed improved fracture toughness of 5 MPa $m^{1/2}$ compared to that of SiC. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

Silicon carbide is known to be a material with high-temperature strength and oxidation resistance. However, SiC covalent bonding of silicon carbide results in its brittle nature and in poor sintering at temperature lower than 2000°C under normal pressure. Dense ceramic bodies without use of HIP can be obtained only at about 2100–2200°C and with sintering aids of C, B, Al [1,2]. Recently, ceramic compositions prepared on the basis of silicon carbide with additions of some oxides became under investigation of a number of researchers [3–6]. The oxide component of these compositions is usually an oxide, which is not reacting or weakly reacting to silicon carbide during heating up to high temperatures. The sintering mechanism of these compositions is considered to be a liquid phase sintering [6]. The groups of oxides, which could be probable candidates for SiC sintering additives, were theoretically defined by Negita [7] on the base of thermodynamic considerations for reactions of oxides with SiC. They include Al_2O_3, almost all rare earth elements and yttria, magnesium and beryllium oxides. The sintering of SiC ceramics with additions of alumina up to 30 wt% was studied by Mulla and Krstic [3]. The authors found that alumina has a tendency to react with SiC at temperature higher than 1900°C, giving volatile products such as CO and SiO gases. This reaction could be suppressed by applying an excessive pressure of CO gas or conducting the heating of samples in a tightly sealed graphite crucible.

The sintering of silicon carbide with another sintering addition, combination of aluminum and yttrium oxides, was studied by Omori et al. [4]. It was shown that compositions, which contained an oxide component up to 60 wt%, could be sintered to a dense ceramic body at 1900–1950°C. However, compositions containing only 30 wt% of oxides, required heating at 2050°C. The use of yttria–alumina combination as reported by Padture [5] gives not only facilitating of sintering but

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improving of fracture toughness of the material up to 7–8 MPa m$^{1/2}$. This occurs due to deflection of cracks on in-situ synthesized yttrium aluminum garnet crystals. Regarding a favorable effect of in-situ synthesized yttrium aluminate on the fracture toughness and sintering of silicon carbide, we were interested to study sintering of SiC-containing ceramic materials with incorporated lanthanum aluminate, since this compound is also formed by La_2O_3 and Al_2O_3 which play a role of sintering additives for SiC-containing materials as defined by Negita [7]. The $LaAlO_3$ was also considered to contribute to an improvement of material fracture toughness similar to yttrium aluminate effect. Since use of La_2O_3 as an addition in sintering is impossible due to strong hydration of the oxide in air, we used its stable compound — $LaCrO_3$, which reacting with additions of Al_2O_3 gives $LaAlO_3$. Cr_2O_3, which can be formed due to the substitution of Al_2O_3 in $LaCrO_3$, is believed to react with SiC giving SiO_2 what will promote the formation of a liquid phase. As reported by Ho [8], this reaction also gives chromium carbides. Since there is a difference in thermal expansion of SiC ($\sim 4.2\times 10^{-6}$/°C) and chromium carbides ($\sim 11.4\times 10^{-6}$/°C), a large residual compressive stress can be built up at the phase interface what would effect positively on SiC mechanical properties [9].

2. Experimental procedure

2.1. Materials

Ultrafine β-SiC (Betarundum by Ibiden Co., Ltd) with mean particle size of 0.28 μm and containing about 0.8 wt% free carbon and about 0.43 wt% free silica was used.

Al_2O_3 (Taimicron by Taimei Chemicals Co., Ltd) of 99.99% purity and mean particle size of 0.1 μm was used.

Reagent grade Cr_2O_3 and La_2O_3 (Kishida Chemicals Co., Ltd) with 99.9% and 99.99% purity grades, respectively, was used.

2.2. Synthesis of $LaCrO_3$ and $LaAlO_3$

$LaCrO_3$ and $LaAlO_3$ were synthesized to find out the effect of different ways for formation of $LaAlO_3$ into compacts. La_2O_3 and Cr_2O_3 or Al_2O_3 taken in equimolar ratios were wet mixed with ethanol and the resultant powder mixtures were calcined at 1400°C for 4 h. For $LaAlO_3$, the calcined powder was additionally treated with a 1 M HCL water solution to remove unreacted lanthanum oxide. The completion of the synthesis was determined by XRD analysis. The mean particle sizes of synthesized compounds determined with the aid of scanning electronic microscope (SEM) were 1.8 μm for $LaCrO_3$ and 1.0 μm for $LaAlO_3$.

2.3. Fabrication of ceramics

The $LaCrO_3$, $LaAlO_3$, Al_2O_3, Cr_2O_3 and SiC of ceramic compositions shown in Table 1 were first thoroughly mixed in ethanol, dried and again mixed with an aqueous solution containing 2–3 wt% of polyethylene glycol. The resultant mixtures were dried, passed through a 250 μm sieve and pressed at 100 MPa to form compacts of 20×20×4–5 mm. The compacts were buried in graphite powder enclosed in an alumina crucible fitted with a tight alumina lid and heated at 1000°C to 1700°C for 2 h.

2.4. Measurements

The phases in the as-prepared ceramic compositions after sintering were identified by X-ray diffraction (XRD) analysis. The degree of densification was determined by Archimedes' method with a nonaqueous fluid. Microstructures of compacts after sintering were observed with an optical microscope and with aid of scanning electromicroscope on samples polished with 0.5 μm diamond and slightly etched in a 1M HF aqueous solution for 30–40 min. The study of sintering was performed via phase composition analysis of samples heated at 1000–1700°C.

The polished samples sintered at 1700°C were tested for fracture toughness via applying Vicker's pyramid indentation technique.

3. Results and discussion

The phase composition and relative density of the compacts prepared from different starting materials ($SiC+LaAlO_3$, $SiC+LaCrO_3+Al_2O_3$, $SiC+LaAlO_3+Cr_2O_3+Al_2O_3$) and sintered at 1700°C for 2 h in graphite are summarized in Table 1. As can be seen the compacts showed the presence of SiC and lanthanum aluminates ($LaAlO_3$ or $LaAl_{11}O_{18}$) only, except for the 55:40:5 composition, in which SiO_2 was also identified. $LaAl_{11}O_{18}$, which forms in the La_2O_3–Al_2O_3 system at the Al_2O_3/La_2O_3 molar ratio of 11–12 [10], was observed only in compositions with big Al_2O_3/La_2O_3 molar ratio (70:15:15 and 65:20:15 compositions). The best sintering of compacts was achieved for a combination of $LaCrO_3$ and Al_2O_3 as compared with a use of $LaAlO_3$. Especially, high densification was shown by the compositions at 25–35 wt% $LaCrO_3$ and 10–15 wt% Al_2O_3. Thus, the 60 SiC–30 $LaCrO_3$–10 Al_2O_3 composition had 90% of theoretical density.

Better densification in the case of $LaCrO_3$ and Al_2O_3 additions as compared with $LaAlO_3$ required more study on a sintering mechanism of the compacts.

The changes of volume shrinkage and densities of the 60:30:10 composition over temperature range 1000–1700°C

Table 1
Physicochemical properties of the compacts prepared from SiC with oxide component and sintered in graphite at 1700°C for 2 h

SiC	Oxide component composition (wt%)				Relative density[b] (%)	Phases as identified by X-ray
(wt%)	$LaCrO_3$	Al_2O_3	Cr_2O_3	$LaAlO_3$		
100	–	–	–	–	57.9	SiC
70	–	–	–	30	75.7	$SiC + LaAlO_3$
	25	5	–	–	80.9	$SiC + LaAlO_3$
	20	10	–	–	84.3	$SiC + LaAlO_3$
	15	15	–	–	80.2	$SiC + LaAl_{11}O_{18}$
	–	5.7[a]	6.4[a]	17.9[a]	84.8	$SiC + LaAlO_3$
65	30	5	–	–	77.4	$SiC + LaAlO_3$
	25	10	–	–	87.8	$SiC + LaAlO_3$
	20	15	–	–	85.3	$SiC + LaAl_{11}O_{18}$
	–	4.7[a]	7.9[a]	22.4[a]	85.6	$SiC + LaAlO_3$
60	–	–	–	40	79.8	
	35	5	–	–	83.7	
	30	10	–	–	89.9	$SiC + LaAlO_3$
	25	15	–	–	88.3	
	–	3.6[a]	9.5[a]	26.9[a]	85.7	
55	40	5	–	–	80.9	$SiC + LaAlO_3 + SiO_2$
	35	10	–	–	87.8	$SiC + LaAlO_3$
	30	15	–	–	87.4	$SiC + LaAlO_3$
	–	2.5[a]	11.2[a]	31.3[a]	86.9	$SiC + LaAlO_3$

[a] Compositions simulating the material prepared with 10 wt% Al_2O_3 and 20–35 wt% $LaCrO_3$.

[b] Values of relative density were calculated on the basis of measurements for apparent and true densities of the compacts.

are shown in Fig. 1. The phase composition as determined by XRD analysis is presented in Fig. 2. As seen a start of shrinkage at 1200°C is accompanied with a drop of true density from 3.85 g/cm^3 to 3.33 g/cm^3. At 1200°C the starting $LaCrO_3$ and Al_2O_3 are not found in the compact and two new phases, SiO_2 and Cr_3C_2, are identified as it can be understood by XRD data. Such changes of physicochemical properties can be explained by a reaction of $LaCrO_3$, Al_2O_3 with SiC and the formation of a liquid phase. The presence of the liquid phase is also confirmed by change of the compact microstructure showing at 1200°C the areas of a solidified melt compared to a structure of unconsolidated grains at 1100°C (see Fig. 3). XRD data suggest that the liquid phase be likely comprised of SiO_2, Al_2O_3 and La_2O_3. Karlsson [11] also reported a phase with melting temperature as low as 1280°C in the SiO_2–Al_2O_3–La_2O_3 system. Since heating environment is considered to include CO gas due to a reaction between a graphite powder and O_2 of residual air at temperature higher 1000°C [12], there are two possible reactions for the formation of free silica in the compact as presented in Fig. 4. The first one is a reaction of chromium oxide with SiC, giving a chromium carbides and silica. The second reaction is an oxidation of SiC by CO gas. As it can be deduced from Fig. 4, both reaction (1) and (2) are probable to proceed during heating over 1000–1700°C. However, the reaction (1) is preferential at higher 1100°C that is confirmed by the formation of chromium carbide and silica namely at 1200°C (see Fig. 2). In materials without chromium oxide the free silica could form mainly by the reaction (2). Nevertheless, better effect on the liquid phase formation was produced by the reaction (1), since worse densification was observed for compacts containing $LaAlO_3$ only.

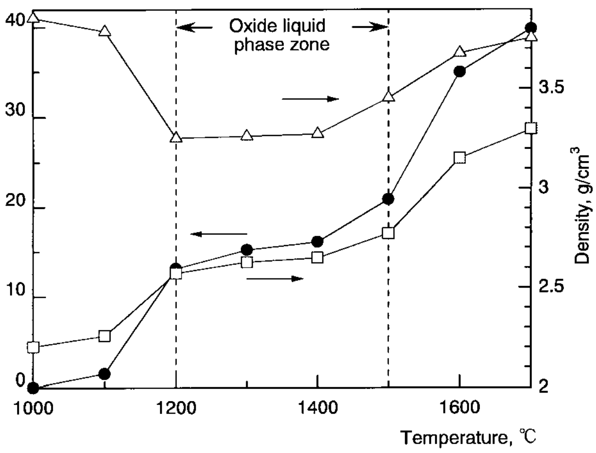

Fig. 1. Temperature dependencies of: ●, volume shrinkage; △, true; and □, apparent densities for 60:30:10 composition sintered in graphite for 2 h.

Over 1200–1500°C significant changes of the shrinkage, true density and phase composition are not observed. Thus, the liquid phase is supposed to be stable in presence of SiC till 1500°C. The next pronounced

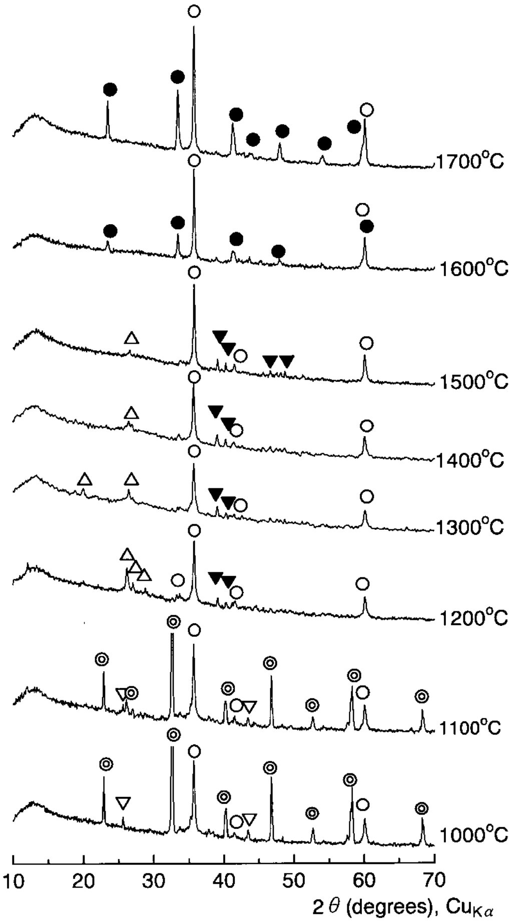

Fig. 2. XRD patterns of 60:30:10 composition heated at 1000–1700°C for 2 h in graphite: ○, SiC; ●, $LaAlO_3$; ⊙, $LaCrO_3$; ▼, Cr_3C_2; △, SiO_2; ▽, Al_2O_3.

growth of volume shrinkage and further densification continue from 1600°C. It is accompanied with an increase in the true density due to the formation of a new phase $LaAlO_3$ and disappearance of Cr_3C_2 and free SiO_2 previously observed (Fig. 2). The measurements of $LaAlO_3$ lattice parameters that confirmed no partial substitution of aluminum oxide with chromium oxide, allowed us to consider $LaAlO_3$ as crystallized out from the liquid phase. Crystallization of the liquid phase at high temperatures is considered to occur due to the effect of partial dissolution of SiC what was also observed by D. N. Coon in case of a magnesia-lithia-alumina-silica glass [14].

Microstructure of the compact sintered at 1700°C is presented in Fig. 5. An optical microscopic photograph at low magnification reveals uniformly distributed white inclusions of 2–4 μm. SEM observations at high magnification show the dark grains surrounded by areas of light tiny grains of less than 0.2 μm. Regarding the crystallization of $LaAlO_3$ from the liquid phase, the tiny grains can be recognized as crystals of $LaAlO_3$. The

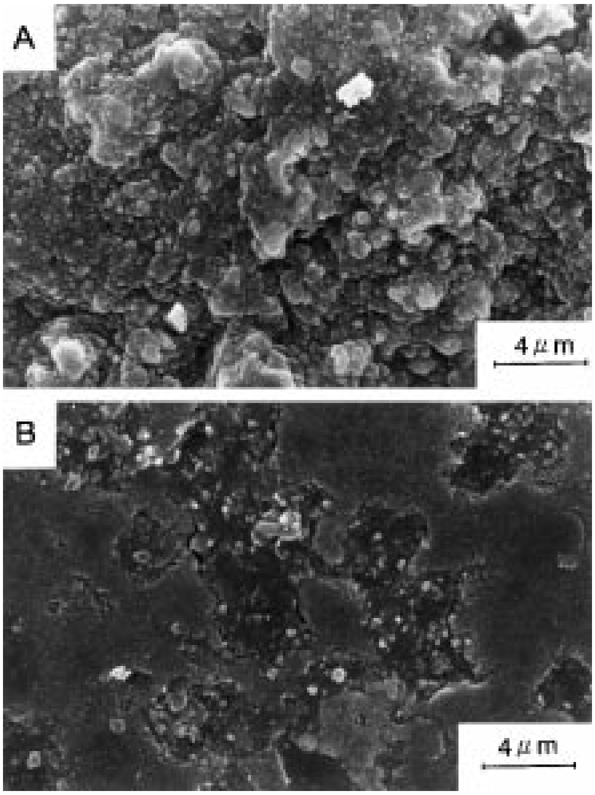

Fig. 3. SEM micrographs of the microstructures of $60SiC–30LaCrO_3–10Al_2O_3$ compacts heated at (A) 1100°C and at (B) 1200°C in graphite for 2 h.

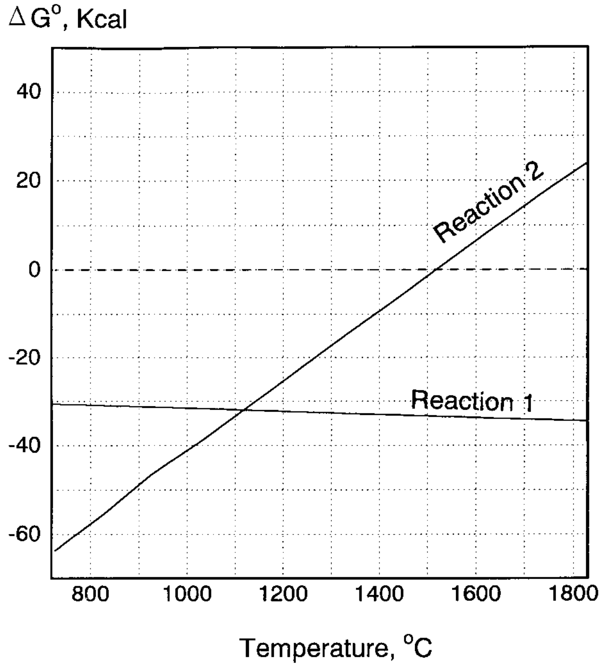

Fig. 4. Reaction equilibria for reactions within $SiC–Cr_2O_3–CO$ system [13].

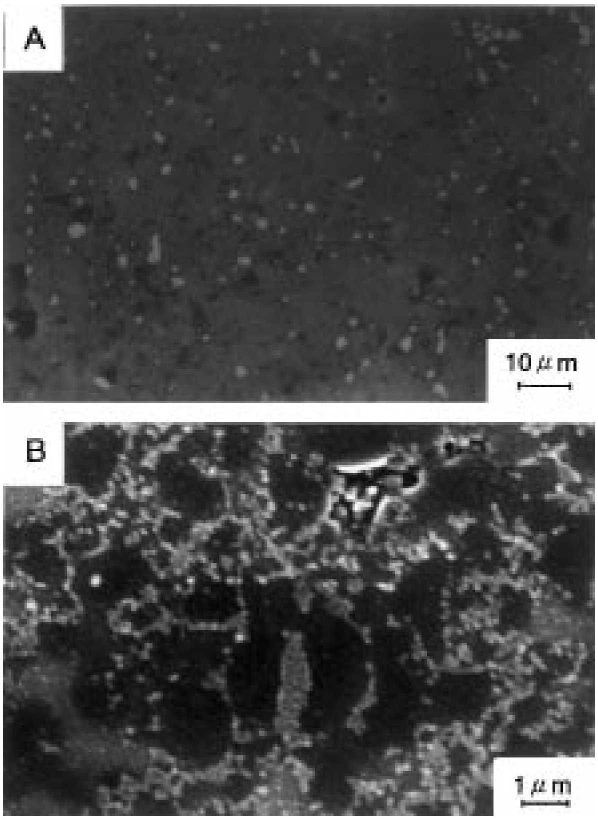

Fig. 5. (A) Optical photograph and (B) SEM micrograph of microstructure of 60SiC–30LaCrO$_3$–10Al$_2$O$_3$ compact as sintered at 1700°C for 2 h in graphite.

white inclusions observed in optical photograph have size similar to that of LaCrO$_3$, chromium oxide of which reacted with SiC to form the chromium carbide phase identified in the compacts from 1200°C till 1500°C. Thus, the inclusions are likely to be some kind of chromium carbide, the presence of which on XRD patterns might become hidden due to the crystallization of LaAlO$_3$.

The results of fracture toughness measurement of some samples are shown in Fig. 6. It can be understood that LaCrO$_3$ and Al$_2$O$_3$ addition, which resulted in incorporation of LaAlO$_3$ and chromium carbides in the compacts, improved the material fracture toughness from 3.4 MPa m$^{1/2}$ at 30 wt% LaCrO$_3$ + Al$_2$O$_3$ up to 5.1 MPa·m$^{1/2}$ for 35 wt% LaCrO$_3$ + Al$_2$O$_3$. However, fracture toughness didn't show a tendency to grow with an increase in LaCrO$_3$ + Al$_2$O$_3$ content after 35 wt% and remained in a range of 4.7–4.9 MPa m$^{1/2}$.

As it was shown above, the chromium oxide had played a significant role in formation of the liquid phase. However, compacts prepared with use of free chromium oxide instead of LaCrO$_3$, showed also good densification (see Table 1), the reaction of free chromium oxide with SiC resulted in a microstructure with pore sizes bigger than that of compacts made with use of LaCrO$_3$ as shown in Fig. 7.

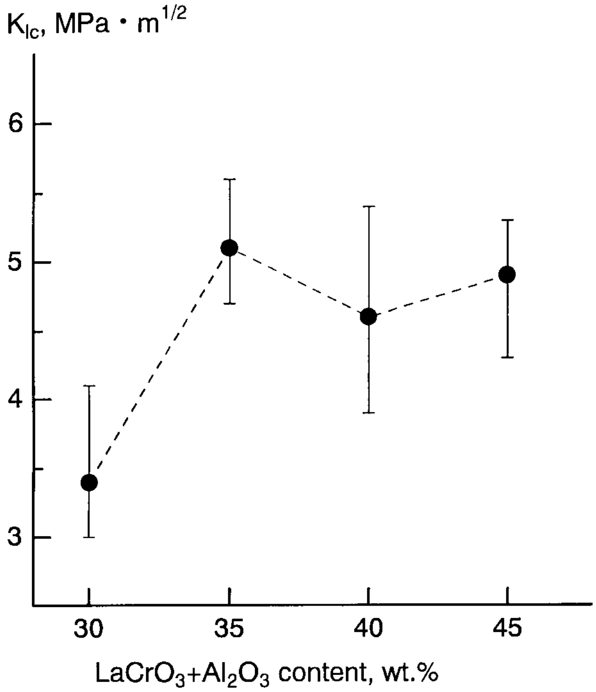

Fig. 6. Fracture toughness of SiC–LaCrO$_3$–Al$_2$O$_3$ material sintered in graphite at 1700°C for 2 h at 10 wt% Al$_2$O$_3$. The error bars indicate the standard deviation of measured values.

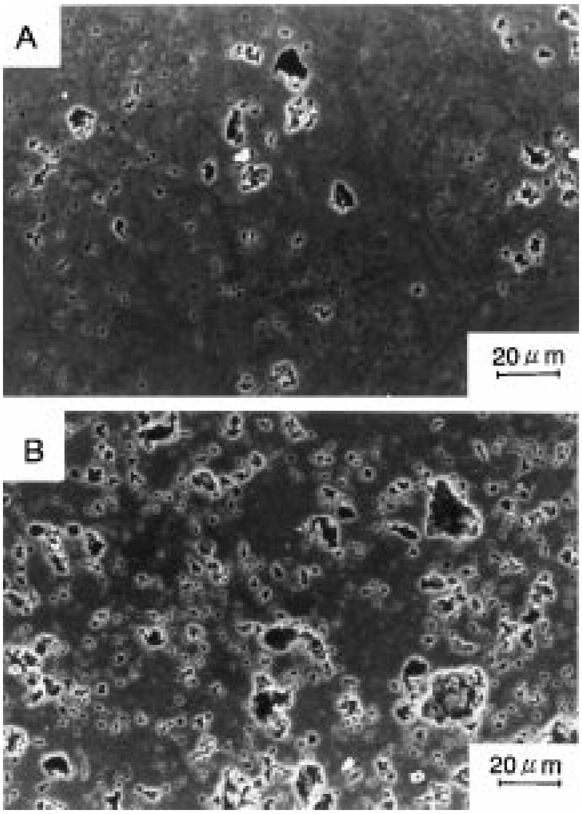

Fig. 7. SEM micrographs of microstructures of (A) 60SiC–30LaCrO$_3$–10Al$_2$O$_3$ compact and (B) compact prepared with use of LaAlO$_3$, Al$_2$O$_3$ and Cr$_2$O$_3$ as sintered in graphite for 2 h.

4. Conclusion

Dense ceramic material with matrix of SiC and $LaAlO_3$ was obtained by heating the compacts of SiC, $LaCrO_3$ and Al_2O_3 starting materials under reducing atmosphere generated by carbon powder and oxygen of residual air. The use of $LaCrO_3$ and Al_2O_3 additions resulted in facilitating of sintering and material with improved fracture toughness compared to SiC. The best densification at 1700°C was achieved for $60SiC–30LaCrO_3–10Al_2O_3$ composition with about 90% of theoretical density. The sintered material has a mix-composition matrix of tiny $LaAlO_3$ crystals dispersed over SiC grains and containing the inclusions of 2–4 μm chromium carbide. The sintering is promoted by formation of the liquid phase through reaction between $LaCrO_3$, Al_2O_3 and SiC. Such effect was not observed for the compositions contained only $LaAlO_3$ and SiC, except for the compositions, which additionally contained Cr_2O_3 and Al_2O_3 along with $LaAlO_3$. However, use of free Cr_2O_3 was responsible for generation of big pores in the material.

Mechanism of sintering of $SiC–LaCrO_3–Al_2O_3$ material is considered to involve a liquid phase and reaction sintering.

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