ELSEVIER

Ceramics International 26 (2000) 763–768

CERAMICS INTERNATIONAL

The effect of post-sintering heat treatment on the properties of SiC–$LaAlO_3$-chromium carbide ceramic material fabricated by a liquid phase sintering: II. Effect of heat-treatment at 1500°C on properties of SiC–$LaAlO_3$-chromium carbide ceramic materials

Andrei Kirianov [a,b,*], Akira Yamaguchi [a]

[a] *Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, 466-8555, Japan*
[b] *Department of Chemical Technology of Ceramics, Mendeleyev University of Chemical Technology of Russia, Miusskaya sq.9, Moscow, 125190, Russia*

Received 18 January 2000; received in revised form 18 January 2000; accepted 21 February 2000

Abstract

SiC–$LaAlO_3$-chromium carbide ceramic materials were prepared from 55–70 wt% β-SiC, 20–35 wt% $LaCrO_3$ and 10 wt% Al_2O_3 by liquid phase sintering at 1700°C. The mechanical properties and microstructure of the SiC–$LaAlO_3$-chromium carbide ceramics before and after heat-treatment at 1500°C were studied. During heat-treatment, a La–Al–Si–O glass phase was formed by reaction of $LaAlO_3$ with residual silica. After heat treatment the sample prepared from 70 wt% SiC, 20 wt% $LaCrO_3$ and 10 wt% Al_2O_3, showed a significant improvement in bending strength from 80 to 307 MPa and in fracture toughness from 3.4 to 4.9 MPa·$m^{1/2}$. SEM observation showed that in the sample after heat-treatment, a La–Al–Si–O glass was present over large areas and formed the ramified structure. However, in the samples with a higher content of lanthanum oxide, a similar structure was not observed and the glass was found to be concentrated in local areas. The ramified structure of the glass phase is considered to enhance a bonding effect of the glass phase in the material and could cause improvement in strength.

Keywords: C. Mechanical properties; C. Strength; D. Glass; D. SiC; $LaAlO_3$

1. Introduction

Sintering and properties of SiC materials with incorporated oxides have been widely studied [1–7]. These oxides are added to improve the fracture toughness of SiC materials. A number of researches have been carried out on materials with additions of yttria/alumina mix [2–4]. The oxide phase greatly improved the fracture toughness of the materials because an in situ yttrium aluminum garnet phase formed [3,4]. Rare earth oxides (samarium, gadolinium and holmium) with alumina also showed their effectiveness as aids for sintering SiC and forming an aluminate phase, which contributes to improvement in fracture toughness of SiC materials [5–7]. $LaAlO_3$, another rare earth oxide aluminate, is also a promising candidate for improving the fracture toughness of SiC materials. Similar to the effect of yttrium aluminum garnet on fracture toughness of SiC–Y_2O_3–Al_2O_3 materials, a thermal expansion mismatch between silicon carbide (4.5×10^{-6}/°C) and lanthanum aluminate (10.8×10^{-6}/°C) [8] is believed to develop compressive stresses at the interphase. However, SiC-oxide materials obtained by a liquid phase sintering or subjected to oxidation can include some silica. Thus, on heating, the silica and the oxides can form crystalline or glassy silicates. The formation of silica-containing phases can affect the mechanical properties of SiC-oxide materials. Kondoh et al. [9] reported that on heating spinel-SiC composites, improvement in strength occurred because of the growth of silicate crystals via a reaction between the oxidized SiC and spinel. The study done by Yoshimura et al. [10] showed that in SiC–Y_2O_3 composites, oxidation in air at 900°C resulted in toughening and strengthening of the composites due to the generation of residual surface stresses developed by oxidation of SiC particles. In Part I of the present work,

* Corresponding author. Tel.: +81-052-735-5293; fax: +81-052-735-5294.
E-mail address: ankir@mse.nitech.ac.jp (A. Kirianov).

0272-8842/00/$ - see front matter
PII: S0272-8842(00)00017-1

it was shown that in a SiC–La_2O_3–Al_2O_3–SiO_2 system, $LaAlO_3$ is stable at temperatures lower than 1400°C or higher than 1550°C. In the 1400–1500°C temperature range, $LaAlO_3$ transforms into a La–Al–Si–O melt via a reaction between $LaAlO_3$ and SiO_2. On cooling, the melt is preserved as a La–Al–Si–O glass phase, which has a lower thermal expansion coefficient (7.7×10^{-6} 1/°C) [11] and lower hardness than $LaAlO_3$. Thus, glass formation, as a result of reduction of the compressive stresses at the interphase, can affect the fracture toughness and strength of the material. The aim of this study is to investigate the discrepancy in strength and microstructure between the SiC–$LaAlO_3$ material and SiC–La–Al–Si–O glass material. The SiC–$LaAlO_3$ materials were produced by liquid phase sintering with $LaCrO_3$, Al_2O_3 and SiC as starting components. $LaCrO_3$ was used as a component for in situ synthesis of $LaAlO_3$ and for formation of a La–Al–Si–O liquid phase by reaction between Cr_2O_3 of $LaCrO_3$ and SiC yielding silica [12]. This provided densification of the materials at 1700°C. This temperature is lower than for other oxide-containing SiC materials [1–3]. The SiC–La–Al–Si–O glass material was obtained by heating the liquid-phase sintered SiC–$LaAlO_3$ material at 1500°C. The reaction of $LaCrO_3$ with SiC also produced chromium carbides, which are known to contribute to improving SiC fracture toughness [13].

2. Experimental procedure

2.1. Materials

Ultrafine β-SiC (0.28 μm, Betarundum by IBIDEN Co., Ltd) with about 0.8 wt% free carbon and about 0.43 wt% free silica, Al_2O_3 (0.2 μm, Taimicron by TAIMEI CHEMICALS CO., Ltd) of 99.99% purity and reagent grade Cr_2O_3 and La_2O_3 powders (Kishida Reagent Chemicals Co., Ltd) were used as the starting materials.

$LaCrO_3$ was synthesized by calcining an equimolar mixture of chromium and lanthanum oxides in air at 1400°C for 4 h. As-synthesized $LaCrO_3$ powder consisted of spherical particles with mean sizes of about 2–3 μm, as determined by scanning electron microscope (SEM).

2.2. Fabrication of ceramics

The ceramic compositions were prepared by thorough ethanol wet mixing of $LaCrO_3$, Al_2O_3 and SiC taken in ratios as shown in Table 1. The wet mixed compositions were dried and again mixed with a water solution of 2 to 3 wt% polyethylene glycol. The resultant mixtures were dried, passed through a 250 μm sieve, prepressed at 10 MPa and cold isostatically pressed at 100 MPa to form the compacts of $20\times20\times14$–16 mm and bars of $4\times5\times45$ mm. The bars were used for bending strength tests. The compacts were buried in graphite powder enclosed in an alumina crucible fitted with a tight alumina lid and heated at 1700°C for 2 h to obtain the sintered ceramic bodies. After this first heat treatment, half of those samples were again buried in graphite powder and heat-treated at 1500°C for 5 h. Surface layers of all samples after every heat treatment were removed by polishing with 10 μm diamond powder. The polishing was performed to minimize surface stresses which might be induced by reactions at the material–graphite interface during heat-treatment.

2.3. Characterization

The densities of samples before and after heat-treatment were determined by Archimedes' method with non-aqueous fluid. The phases in the samples were determined by X-ray diffraction (XRD) with CuK_α radiation using an X-ray diffractometer (Shimadzu, XD-D1) operating at acceleration voltage of 30 kV and anode current of 30 mA.

The strength of samples was determined by three point bending tests at room temperature in a testing machine (Shimadzu, Autograph AGS-500D) with a span of 30 mm. Load was applied with a crosshead speed of 0.5 mm/min. The fracture toughness was evaluated by an indentation fracture method using a Vicker's hardness tester (Akashi, AVK-A). Indention was performed at a load of 200 N and a loading duration of 15 s. The fracture toughness values were calculated using the equation proposed by Niihara et al. [14].

Microstructures of the samples were examined by an optical microscope (Nikon, Optiphot) and by a scanning electron microscope (JEOL, JSM-5200). Microstructural examinations were performed on polished

Table 1
The compositions and densities of the ceramics before and after heat-treatment at 1500°C in graphite for 5 h

Starting composition, wt%			True density, g/cm^3		Apparent density, g/cm^3		Relative density, %	
$LaCrO_3$	Al_2O_3	SiC	Before	After	Before	After	Before	After
20	10	70	3.5	3.4	2.97	3.06	84.9	90
25	10	65	3.62	3.55	3.09	3.13	85.4	88.2
30	10	60	3.77	3.65	3.27	3.31	86.7	90.7
35	10	55	3.93	3.78	3.44	3.5	87.5	92.6

surfaces, either chemically etched in 1 molar HF aqueous solution for 30–45 min at room temperature to leach SiO_2, or thermally etched at 1300°C for 30 min under flowing argon. Elements of microstructures of the samples were examined by an electron microscope equipped with an energy-dispersive X-ray analyzer (Philips, EDAX PV 9801).

3. Results and discussion

The compositions and densities for the samples before and after heat-treatment are summarized in Table 1. After heat-treatment, the total porosity of all samples was decreased by 3–5%: the apparent density is increased by 1–3% and true density is decreased by 1–5%. The porosity decrease is attributed to a phase transformation of $LaAlO_3$, of high true density (5.84 g/cm^3), into La–Al–Si–O glasses of low true density (2.81–3.46 g/cm^3) [11].

Figs. 1 and 2 show the results of X-ray analysis for the samples before and after heat-treatment. Table 2 summarizes the phase compositions of the samples. All as-sintered samples contain SiC and $LaAlO_3$ as dominant phases. Chromium carbides are observed in the samples with $LaCrO_3$. After sintering, the compound $Cr_{6.2}C_{3.5}N_{0.3}$ is observed for the sample containing 20 wt% $LaCrO_3$. The $Cr_{5-x}Si_{3-z}C_{x+z}$ compound is found in samples having higher contents of $LaCrO_3$ (>20 wt%). After heat-treatment at 1500°C, β-SiC is identified by XRD as a dominant phase. This indicates that

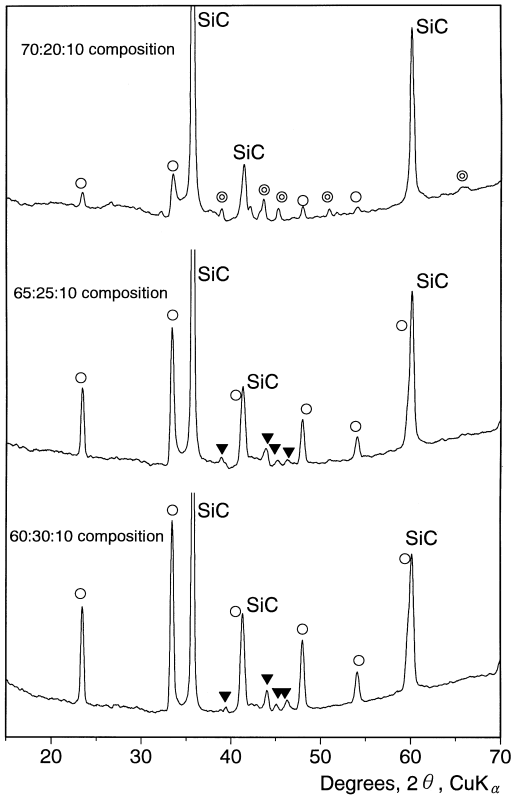

Fig. 1. XRD patterns of the ceramic compositions sintered at 1700°C for 2 h. [(○)-$LaAlO_3$; (▼)-$Cr_{5-x}Si_{3-z}C_{x+z}$; (◎)-$Cr_{6.2}C_{3.5}N_{0.3}$].

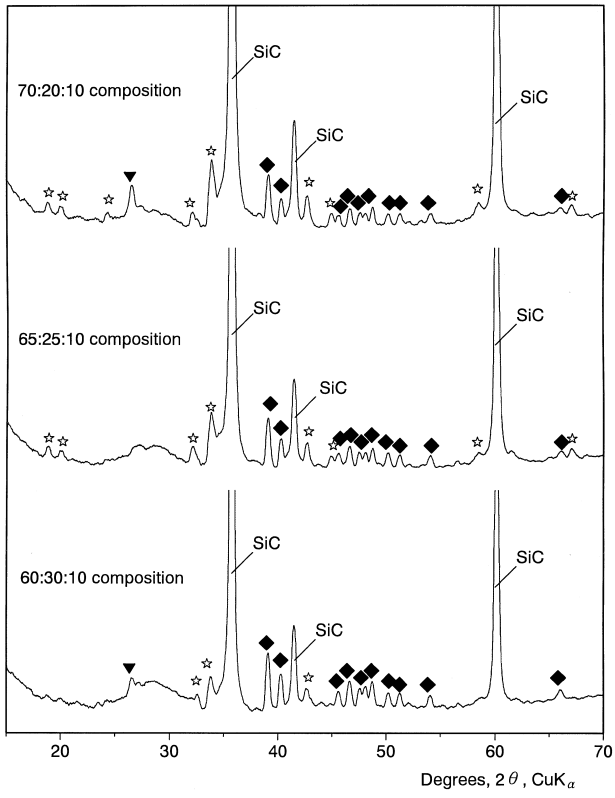

Fig. 2. XRD patterns of the ceramic compositions after heat-treatment at 1500°C for 5 h in graphite. [(◆)-Cr_3C_2; (☆)-$LaAl_{11}O_{18}$; (▼)-carbon].

Table 2
Phase compositions of the samples before and after heat-treatment

Starting composition wt%			Phase composition			
			Before (as sintered at 1700°C)		After heat-treatment at 1500°C	
SiC	$LaCrO_3$	Al_2O_3	Dominant phases	Secondary phases	Dominant phases	Secondary phases
70	20	10	SiC, $LaAlO_3$	$Cr_{6.2}C_{3.5}N_{0.3}$	SiC, La–Al–Si–O glass	Cr_3C_2, $LaAl_{11}O_{18}$
65	25	10	SiC, $LaAlO_3$	$Cr_{5-x}Si_{3-z}C_{x+z}$	SiC, La–Al–Si–O glass	Cr_3C_2, $LaAl_{11}O_{18}$
60	30	10	SiC, $LaAlO_3$	$Cr_{5-x}Si_{3-z}C_{x+z}$	SiC, La–Al–Si–O glass	Cr_3C_2, $LaAl_{11}O_{18}$

$LaAlO_3$ decomposed forming a La–Al–Si–O glass phase and a β-alumina group compound: $LaAl_{11}O_{18}$. As has been shown in Part I, La–Al–Si–O melt, which is preserved on cooling as glass, is stable between 1400–1500°C: thus $LaAlO_3$ is subject to decomposition on reheating to 1500°C. Previously observed chromium carbides were found to transform to Cr_3C_2, which is known to be stable in an inert atmosphere up to 1550°C: chromium carbides with less structural carbon are stable at temperatures higher than 1600°C [12]. The distribution pattern of chromium carbide grains in samples is shown in Fig. 3. The chromium carbide grains have size of 2–3 μm and are uniformly distributed in the samples. Optical microscopic examination showed that size, shape of chromium carbide grains were unchanged comparing the samples before and after heat-treatment.

The mechanical properties of samples before and after heat-treatment are shown in Fig. 4. After heat-treatment, a remarkable improvement in fracture toughness and bending strength up to 4.9 and 307 MPa·$m^{1/2}$, respectively, were observed for a sample prepared from 70 wt% SiC and 20 wt% $LaCrO_3$. In the case of other compositions their bending strength showed only a

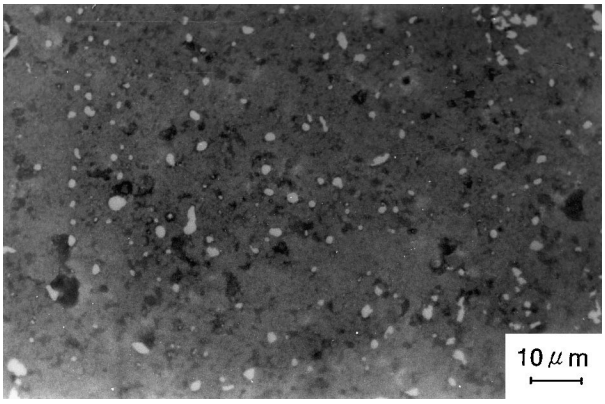

Fig. 3. Optical microscope photograph showing the distribution of chromium carbide (white particles) inside the material prepared from SiC, $LaCrO_3$ and Al_2O_3.

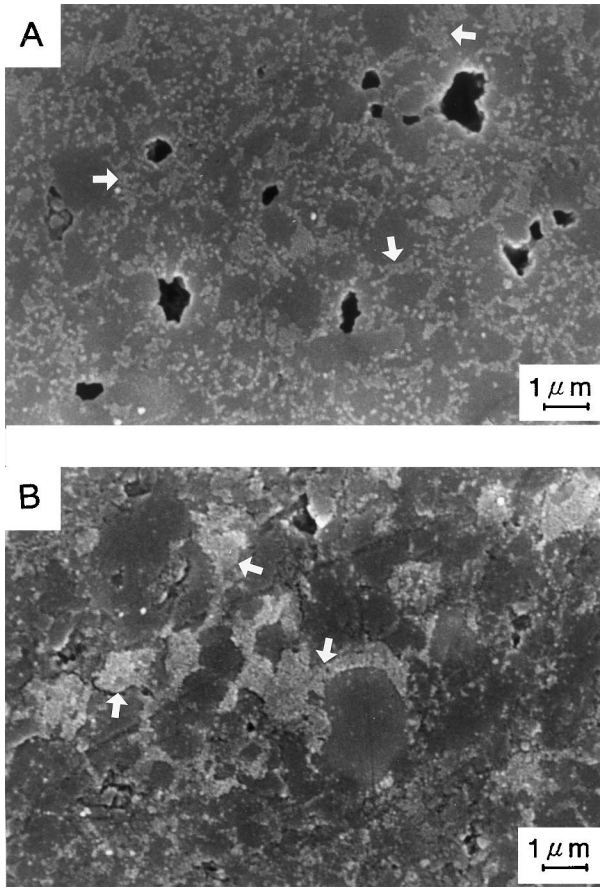

Fig. 5. SEM micrographs of the HF-treated surfaces of the 70:20:10 sample (A) and 60:30:10 sample (B) after heat-treatment. Arrows point out the areas of a former glass phase.

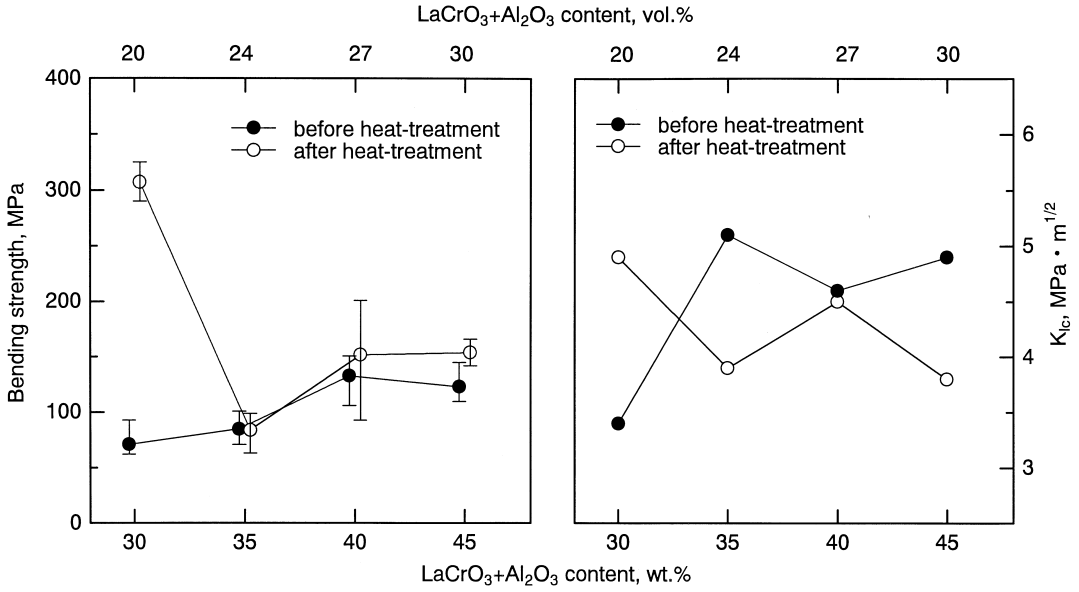

Fig. 4. Mechanical properties of the samples with different content of $LaCrO_3 + Al_2O_3$/10 wt% Al_2O_3 before and after heat-treatment at 1500°C.

small improvement and fracture toughness remained unchanged or decreased.

To clarify the reason for this significant improvement in strength of the 70:20:10 sample after heat-treatment, microstructural examination was performed. Treatment of the samples with HF revealed that the heat-treated samples with different contents of $LaCrO_3$ have different microstructures as shown in Fig. 5. Two phases can be distinguished in SEM micrographs. One phase is optically bright and is comprised of numerous fine particles. As stated above, the dominant phases in the samples after heat-treatment are SiC and the La–Al–Si–O glass. Treatment of the samples with HF mostly resulted in dissolution of silica from the glass, whereas poorly soluble lanthanum and aluminum oxides of the La–Al–Si–O glass were not much affected by HF and were preserved as a grainy-looking phase. Moreover, both lanthanum and aluminum oxides are poorly electron conductive phases. Thus, they appear bright in SEM images, compared to a dark appearance of conductive phases such as SiC. Therefore, a bright and grainy-looking phase observed is likely to represent the sites of a former La–Al–Si–O glass phase. The other phase observed in SEM micrograph as dark grains of 1–2 μm is likely to be SiC. In the 70:20:10 sample, sites of a former glass phase are found to be present over large areas as shown in Fig. 5A. In contrast, in a sample with a high content of lanthanum oxide (Fig. 5B), the glass phase is observed to be concentrated locally. Such a difference in distribution of the glass phase is believed to control the different effects of the glass phase formation on the strength of samples. It is known that the glass phase exhibits a bonding effect in ceramic materials. Therefore, formation of the glass phase over extensive areas in the 70:20:10 sample after heat-treatment is believed to enhance a bonding effect of the glass phase, as contact surface between the glass and SiC was increased. This is supposed to bring about a significant improvement in the strength of the sample. More details on a structure of the glass phase in the 70:20:10 sample was obtained by observation of sample surfaces after thermal etching at 1300°C. The thermal etching caused devitrification of the La–Al–Si–O glass at 1300°C: it was found in Part I of the present study that the La–Al–Si–O glass easily devitrifies in the 1300–1400°C temperature interval. The devitrification allowed us to distinguish the boundaries and the structure of the glass phase areas in the samples. As shown in Fig. 6, elongated regions grouped in clusters and forming a ramified structure over a large area are observed in the 70:20:10 sample. A similar microstructure was not found in the 70:20:10 sample without the glass phase, or for other compositions. As presented in Table 3, elemental analysis showed that in the sites of the elongated regions, the concentrations of La and O elements are higher than those in areas free from the elongated regions. It implies that the elongated regions

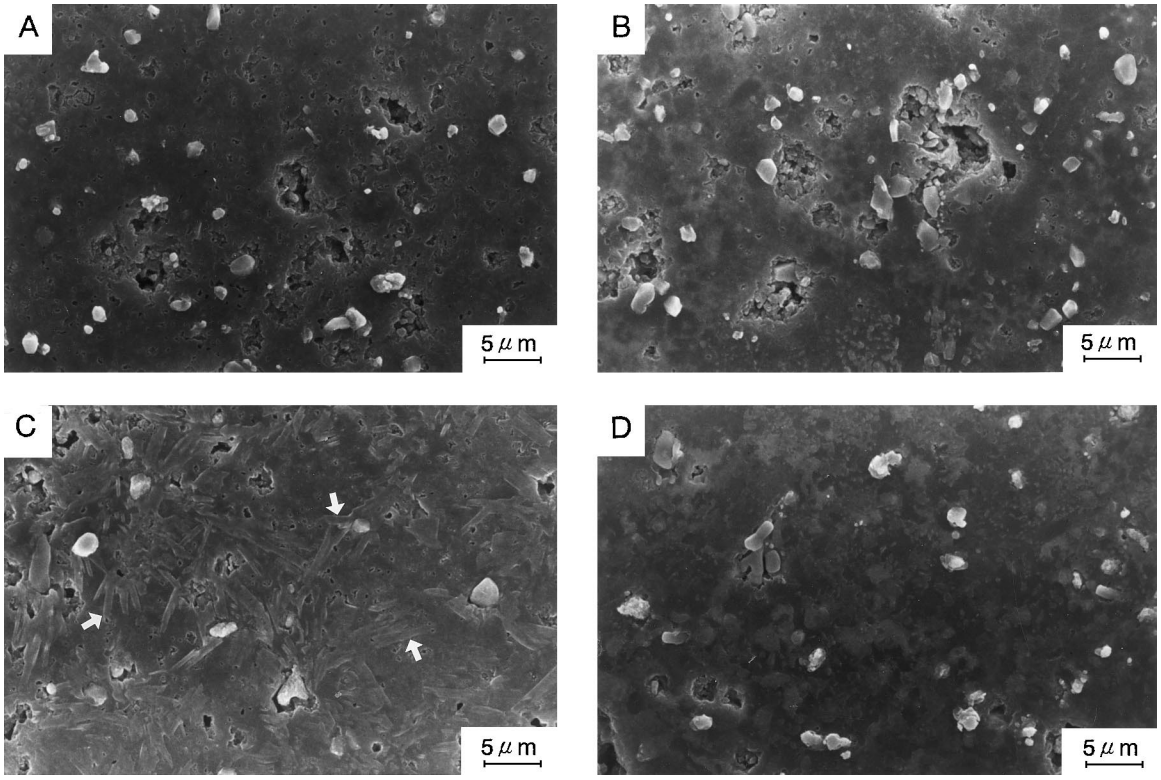

Fig. 6. The SEM micrographs of surfaces of the samples after thermal etching at 1300°C under argon. 70:20:10: composition: A — before, C — after heat-treatment; 60:30:10 composition: B — before, D — after heat-treatment. Arrows point out the elongated regions of the devitrified La–Al–Si–O glass.

Table 3
The results of elemental analysis for the 70:20:10 sample Containing glass and thermally etched at 1300°C

Element, at%					Remarks
O	Al	Si	La	Cr	
30.1	4.05	32.1	30.1	3.6	Elongated region
5	1.8	84.8	8.4	0	Area between elongated regions
29.4	6	30	34	0.6	Elongated region

are likely to be rich in lanthanum oxide. Since a dominant component of the La–Al–Si–O glass phase is lanthanum oxide and amounts of lanthanum oxide incorporated in a secondary phase $LaAl_{11}O_{18}$ are negligible, the elongated regions are likely to be derived from regions of the devitrified glass area. Thus, it is clear that in the 70:20:10 sample, the glass formed the extensive ramified structure. Therefore, the main role in significant strength improvement of the 70:20:10 sample is likely to be attributed to the ramified structure of the glass phase, which enhanced the bonding effect of the glass phase as contact surface between SiC phase and the glass was increased.

4. Conclusions

The mechanical properties and microstructure of the SiC–$LaAlO_3$-chromium carbide ceramic materials prepared from SiC, $LaCrO_3$ and Al_2O_3 via heating at 1700°C were studied.

Heat-treatment at 1500°C resulted in the significant improvement in bending strength from 80 to 307 MPa and fracture toughness from 3.4 to 4.9 MPa·$m^{1/2}$ for the sample prepared from 70 wt% SiC, 20 wt% $LaCrO_3$ and 10 wt% Al_2O_3. In the SEM study, the sample showed the presence of the glass phase over a vast area and the ramified structure of the La–Al–Si–O glass phase was observed. This ramified structure enhanced the bonding effect of the glass phase that is proposed as the most plausible reason for the strength improvement. The formation of the ramified structure of La–Al–Si–O glass in SiC–$LaAlO_3$ materials could be useful in strengthening the SiC-oxide ceramics.

References

[1] M.A. Mulla, V.D. Krstic, Pressureless sintering of β-SiC with Al_2O_3 additions, J. Mater. Sci. 29 (1994) 934–938.
[2] M. Omori, A.S. Akuma, T. Hirai SiC sintered composite with Y_2O_3 and Al_2O_3 In: Ceramics Today — Tomorrow's Ceramics, Elsevier Science Publishers B.V., Amsterdam, 1991, pp. 1327–1335.
[3] P. Nitin, Padture, In situ-toughened silicon carbide, J. Am. Ceram. Soc. 77 (1994) 519–523.
[4] D.-H. Kim, C.H. Kim, Toughening behavior of silicon carbide with additions of yttria and alumina, J. Am. Ceram. Soc. 73 (1990) 1431–1434.
[5] C. Zhao, Pressureless sintering of silicon carbide with additives of samarium oxide and alumina, Mater. Lett. 17 (1993) 27–30.
[6] C. Zhao, L. Zeng, Pressureless sintering of silicon carbide with additives of holmium oxide and alumina, Mater. Res. Bull. 30 (1995) 265–270.
[7] C. Zhao, Effects of gadolinia and alumina addition on the densification and toughening of silicon carbide, J. Am. Ceram. Soc. 79 (1996) 530–532.
[8] D. Taylor, Thermal expansion data VIII. Complex oxides, ABO_3 the perovskites, Br. Ceram. Trans. 84 (6) (1985) 181–188.
[9] I. Kondoh, T. Tanaka, N. Tamari, Oxidation behavior of spinel/silicon carbide whisker composite ceramics, J. Ceram. Soc. Japan 102 (1994) 799–801.
[10] M. Yoshimura, T. Ohji, K. Niihara, Oxidation-induced toughening and strengthening of Y_2O_3/SiC nanocomposites, J. Am. Ceram. Soc. 80 (1997) 797–799.
[11] K. Karlsson, The system La_2O_3–Al_2O_3–SiO_2. Part III. Physical properties of some glasses, Suom. Kem. B43 (1970) 479–482.
[12] C.T. Ho, An internal synthesis method for producing a mullite-chromium carbide composite, J. Mater. Res. 8 (1993) 2035–2039.
[13] B.W. Lin, D.M. Liu, Improved mechanical properties of Cr_3C_2 using particulate SiC reinforcement, in: Proceedings of Ceramic Matrix Composite, 95th Annual Meeting of the American Ceramic Society, Cincinnati, Ohio, April, 1993.
[14] K. Niihara, R. Morena, D.P.H. Hasselman, Evaluation of K_{IC} of brittle solids by the indention method with low-crack-to-indent ratios, J. Mater. Sci. Lett. 1 (1982) 13.