Ceramics International 26 (2000) 757–762

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: I. Phase relations between LaAlO$_3$, SiO$_2$ and SiC in 1300–1600°C

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 25 October 1999; received in revised form 29 October 1999; accepted 17 January 2000

Abstract

La_2O_3 and Al_2O_3 are considered as promising additions to improve SiC fracture toughness by forming $LaAlO_3$ and promoting SiC liquid phase sintering. Thus, phase relations between $LaAlO_3$, SiO_2 and SiC in the temperature range 1300–1600°C were studied. It was shown that although $LaAlO_3$ reacts with SiO_2, forming a La–Al–Si–O glass at 1500°C, addition of SiC to the glass causes devitrification and crystallization of $LaAlO_3$ above 1550°C. SiC is considered to generate the oxygen-deficient glass. Crystallized $LaAlO_3$ phase is found to be stable on reheating at temperatures lower than 1400°C and higher than 1500°C. Thus, SiC–$LaAlO_3$ ceramic materials obtained by liquid phase sintering are expected to show the deterioration of high temperature mechanical properties in the temperature range 1400–1500°C. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: C. Thermal properties; D. Glass; D. SiO_2; D. SiC; $LaAlO_3$

1. Introduction

SiC is known as a material with high temperature strength and oxidation resistance but, due to Si–C covalent bonding, it shows a transgranular fracture behavior that results in lower fracture toughness when compared to silicon nitride. One way to improve SiC fracture toughness is by incorporating compounds able to generate the residual compressive stresses at SiC matrix-compound grain interfaces. Among these compounds, yttria-alumina combination is often used [1–4]. It is favorable, since on heating, Y_2O_3 and Al_2O_3 form yttrium alumina garnet (YAG) having a high melting point and thermal expansion coefficient (8×10^{-6}/°C) [5] higher than that of SiC, which causes compressive stresses at SiC–YAG interface [4]. Y_2O_3 and Al_2O_3 react with SiC [6] forming a silica-containing liquid phase [3], and are thus good sintering additives for SiC materials. Combinations of Al_2O_3 with such rare earth oxides as holmium, samarium and gadolinium also showed their effectiveness as sintering aids for SiC [7–9]. These experimental data are consistent with Negita's thermodynamic considerations which state that feasible sintering aids of SiC must include alumina, yttria and a rare earth oxide [6]. The present research considers the feasibility of application of alumina with another rare earth oxide, La_2O_3. This combination is worthy of research since, on heating, La_2O_3 and Al_2O_3 form a lanthanum aluminate, which is characterized by its high melting point (2130°C) [10] and high thermal expansion coefficient (10.8×10^{-6}/°C) [11] along with moderate hardness (about 13 GPa) [12] and is expected to play a positive role in the improvement of SiC fracture toughness. On the other hand, it is known that melting point of eutectic phase in La_2O_3–SiO_2–Al_2O_3 system is as low as 1280°C [13]; this could enhance the sintering of SiC at low temperature. However, since formation of La–Al–Si–O liquid phase is likely to affect the high temperature properties of ceramic material, it also requires more knowledge on the behavior of the liquid phase in

---

* 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 © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.
PII: S0272-8842(00)00021-3

the presence of SiC. Thus, the present research discloses the phase relations between silica, La–Al–Si–O liquid phase, lanthanum aluminate and SiC at high temperatures.

2. Experimental procedure

2.1. Materials

$La_2(CO_3)_3$ of reagent grade (Kishida reagent chemicals Co., LTD) and Al_2O_3 (0.2 μm, Taimicron by Taimei Chemicals Co., Ltd) of 99.99% purity were used to synthesize $LaAlO_3$ via calcination of component mixture at 1500°C for 7 h in air.

The synthesized $LaAlO_3$ had particle size of 1–2 μm as determined by SEM observation. SiO_2, quartz, with 0.8 μm grain size and 99.9% purity was used. Ultrafine β-SiC (Betarundum by Ibiden Co., Ltd) with a mean particle size of 0.28 μm and containing about 0.8 wt% free carbon and about 0.43 wt.% free silica was used.

2.2. Sample preparation and analysis

To investigate the interaction between $LaAlO_3$ and SiO_2, four kinds of batches with 90:10, 85:15, 80:20 and 70:30 weight ratios of $LaAlO_3$ and SiO_2 were prepared. Powders of each batch were compacted into pellets by cold pressing at 50 MPa. The pellets were buried in

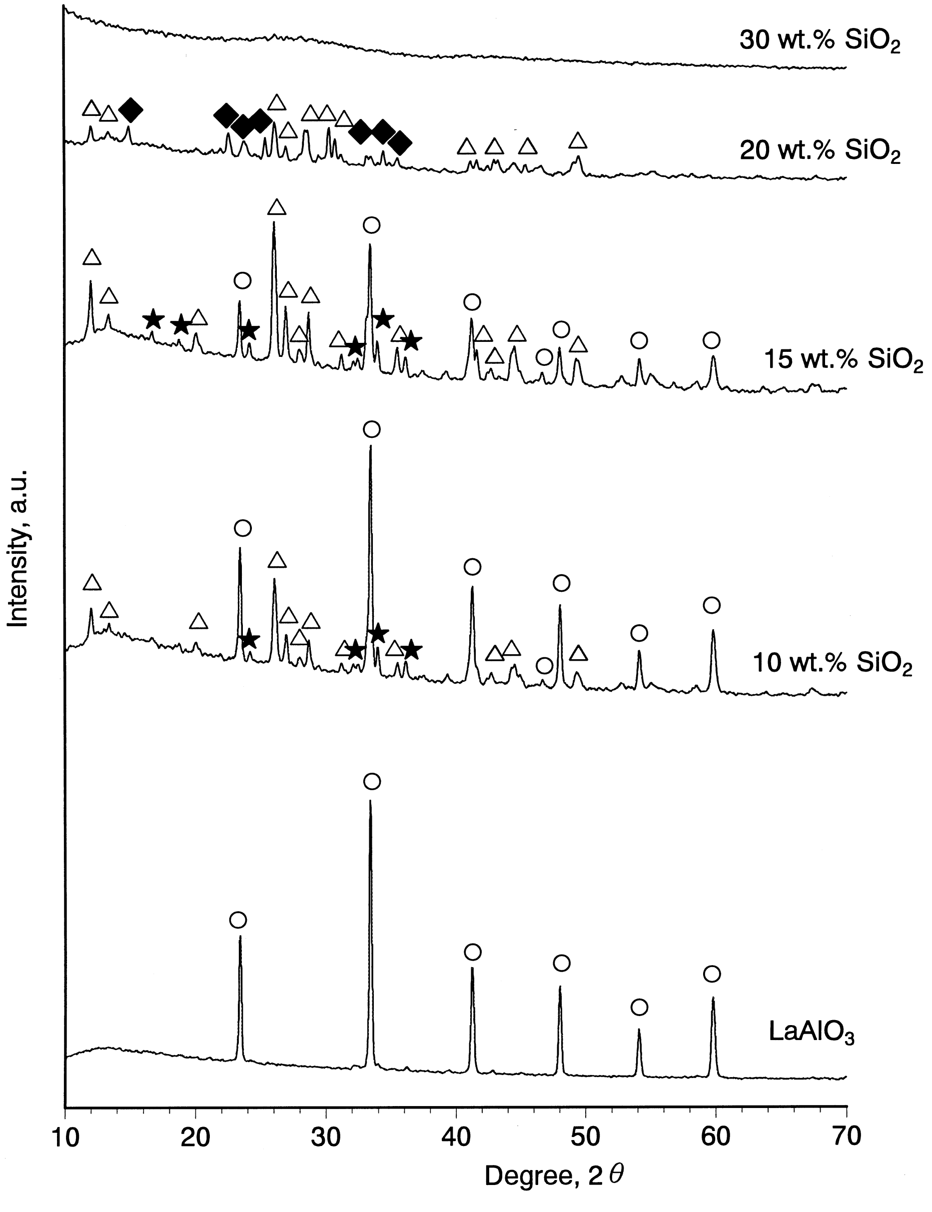

Fig. 1. XRD patterns of $LaAlO_3/SiO_2$ mix samples after heating at 1500°C for 5 h in graphite: (○) $LaAlO_3$; (★) $La_{0.9}Al_{11.76}O_{19}$; (△) $La_2Si_2O_7$; (◆) unidentified phase.

graphite powder in an alumina crucible fitted with a tight lid and heated at 1500°C for 5 h to achieve the most complete interaction. As-obtained La–Al–Si–O glass samples were cut into two parts. The first part was again cut into small samples, which were used for analysis of the glass devitrification behavior by reheating the glass samples in graphite at 1300–1600°C for 5–20 h. The second part was milled and mixed with 1, 15 and 30 wt% SiC. These powder mixtures were compacted and heated in graphite at 1600°C for 2 h. Graphite powder was to used to prevent SiC from much oxidation at high temperature. Heating of the pure glass sample in graphite was performed to exclude the effect of different environment on changing the phase composition between SiC-containing and SiC-free glass samples.

Additionally, the sample of glass mixed with 30 wt% SiC were heated at 1500, 1550°C for 5 h and at 1600°C for 2 and 5 h in graphite. The samples were cooled to room temperature at a rate of 35 K/min to preserve the high temperature phase composition.

To investigate the stability of phase composition formed after heating at 1600°C in the sample containing 30 wt% SiC, it was cut into parts which were reheated in graphite at 1300–1550°C for 5 and 20 h.

All phase changes were observed with X-ray diffraction (XRD) analysis using powders prepared from the heat-treated samples from which the outer surface was mechanically removed to exclude the effects of possible reactions between the glass and graphite at high temperatures.

3. Results and discussion

Fig. 1 illustrates interaction between $LaAlO_3$ and SiO_2 at 1500°C. As seen the interaction begins at 10 wt% SiO_2 and lanthanum disilicate forms as a main product. $LaAlO_3$ also decomposes with formation of β-alumina group compound, $La_{0.9}Al_{11.76}O_{19}$. On increase in SiO_2 content higher than 20 wt%, a liquid phase forms as it can be deduced by a halo observed on XRD pattern at 30 wt% SiO_2. These results are similar to that of Shiokawa et al. [14], who observed the formation of the melt from $LaAlO_3$ and SiO_2 at 22 wt%.

Devitrification behavior of an as-received glass phase is presented in Fig. 2. The main devitrification phase in the temperature range 1300–1400°C is found to be $La_2Si_2O_7$. This phase is stable only up to 1400°C and at higher temperatures, halos on XRD patterns at 1500 and 1600°C show that melt, preserved as glass, formed. The $La_2Si_2O_7$ phase as reported by Karlsson, crystallizes in the La–Al–Si–O glasses of a wide composition range and is stable up to 1420°C [13]; this is consistent with the results of the present research. Nevertheless, addition of SiC to the glass caused the formation of devitrification phases at 1600°C as is evident from Fig.

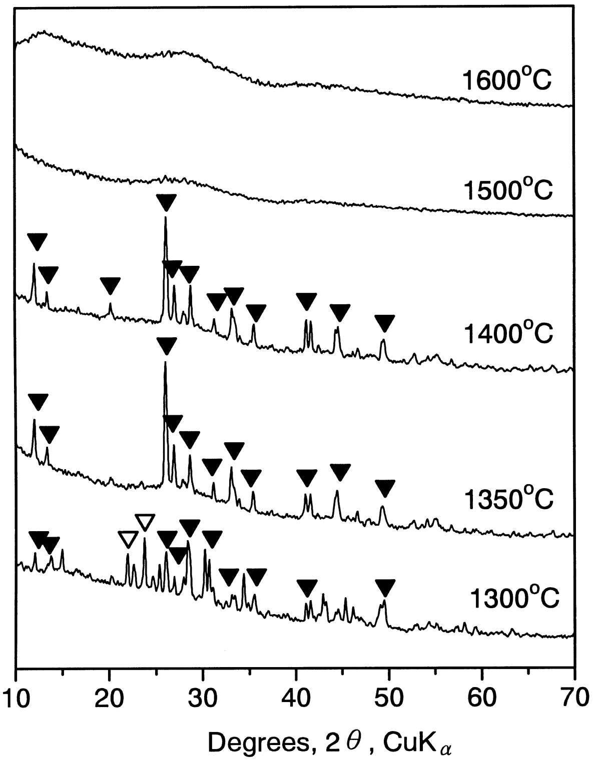

Fig. 2. XRD patterns of the glass heated at 1300, 1350, 1400, 1500 and 1600°C in graphite: (▼) $La_2Si_2O_7$; (▽) SiO_2 quartz.

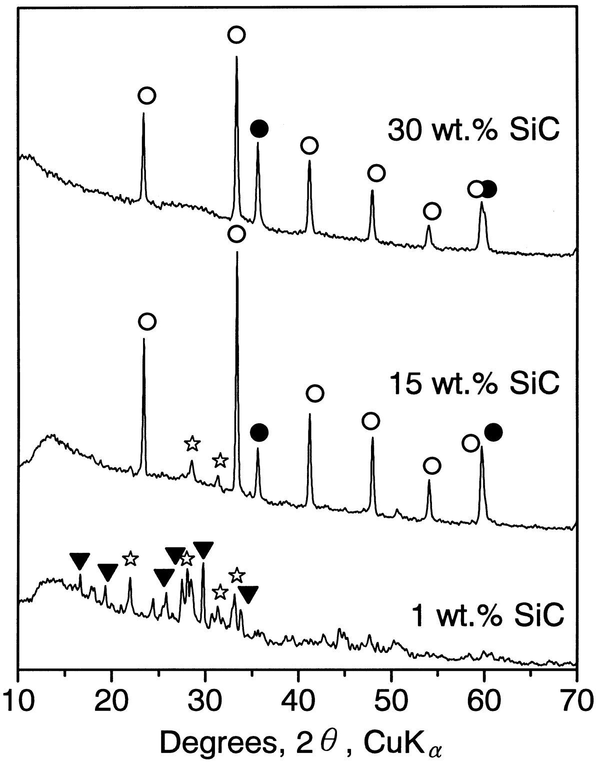

Fig. 3. XRD patterns of the glass containing 1, 15 and 30 wt% SiC and heated at 1600°C in graphite for 2 h: (●) SiC; (○) $LaAlO_3$; (☆) $La_3(Al,Si)_6(N,O)_{14}$; (▼) $La_2Si_2O_7$ or $Ln_2Si_2O_7$ type mineral.

3. Even at 1 wt% SiC, weak reflections of lanthanum disilicate occur. On increasing in the SiC content, $LaAlO_3$ is mainly observed. Since the pure glass at 1600°C showed no crystallization phases, the appearance of $LaAlO_3$ is related to an effect of SiC addition.

More details of phase transformations in the glass with 30 wt% SiC during heating from 1500 to 1600°C are presented in Fig. 4. In the presence of SiC, glass persists up to 1500°C and starts to devitrify at 1550°C, giving intermediate phases, among which $La_3(Al,Si)_6(N,O)_{14}$ is observed both at 1550 and 1600°C. This compound was also present on XRD patterns of the glass samples with lower content of SiC at 1600°C. As reported by Grins et al. [15], $La_3(Al,Si)_6(N,O)_{14}$ is characterized by accurate formula, $La_3Si_{3-x}Al_{3+x}O_{12+x}N_{2-x}$ where x varies between 0 and 0.5. It forms by devitrification of rare earth sialon glasses heat-treated in the temperature range 1000–1400°C. Thus, the appearance of similar phase in the La–Al–Si–O glass containing SiC after heat-treatment at 1600 or 1550°C, is considered to be caused by formation of oxygen-deficient glass. Oxygen vacancies are believed to be filled by nitrogen from the environment, which included N_2 and CO gases due to a reaction of residual air with graphite above 1000°C [16]. Oxygen vacancies in the La–Al–Si–O glass are considered to form as a consequence of partial dissolution of SiC into the glass. An effect of SiC dissolution in glass was observed by Coon [17], who reported a change of crystallization behavior of a magnesia–lithia–alumina–silica glass containing small amounts of SiC. In that research the glass showed crystallization at temperature higher than the glass melting point. This change of the crystallization behavior was explained by formation of oxycarbide glass in presence of SiC [17,18].

Probable formation of $La_3(Al,Si)_6(N,O)_{14}$ and $LaAlO_3$, due to a decrease in SiO_2 content via evaporation of SiO through a reaction between SiC and SiO_2 at 1550°C [19], is thought to be unlikely. Although, the reaction of SiO_2 with SiC starts at 1600°C [19], nevertheless, the presence of gases such as CO and N_2, which are able to be chemically adsorbed by SiC, retards the above reaction [20]. Thus, crystallization of phases as shown in Fig. 4 instead arises from partial dissolution of SiC into the La–Al–Si–O glass.

The stability of phases crystallized in the La–Al–Si–O glass with 30 wt% SiC during reheating in the temperature range 1300–1550°C is shown in Fig. 5; $LaAlO_3$ is found to be stable up to 1400°C regardless of heating duration. In the temperature range 1400–1500°C, lanthanum aluminate is transformed into a liquid or a glass phase during prolonged heating. Nevertheless, lanthanum aluminate is also stable also at temperatures higher

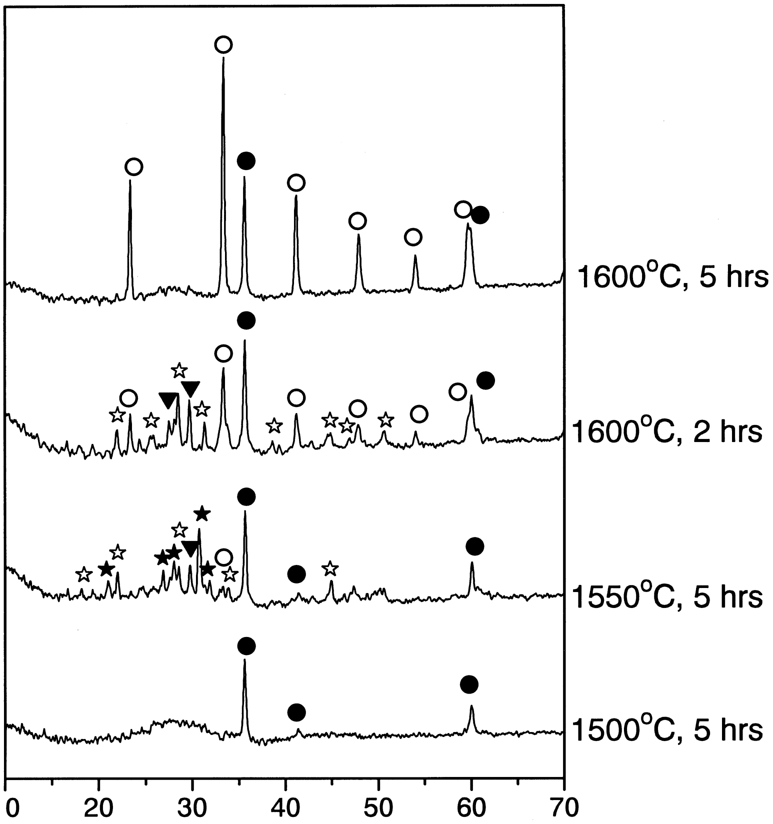

Fig. 4. XRD patterns of glass + 30 wt% SiC samples heated in graphite at 1500, 1550 and 1600°C, and then fast-cooled till room temperature at a rate of 35°C/min: (●) SiC; (○) $LaAlO_3$; (☆) $La_3(Al,Si)_6(N,O)_{14}$; (★) $La_5Si_3NO_{12}$; (▼) $Ln_2Si_2O_7$.

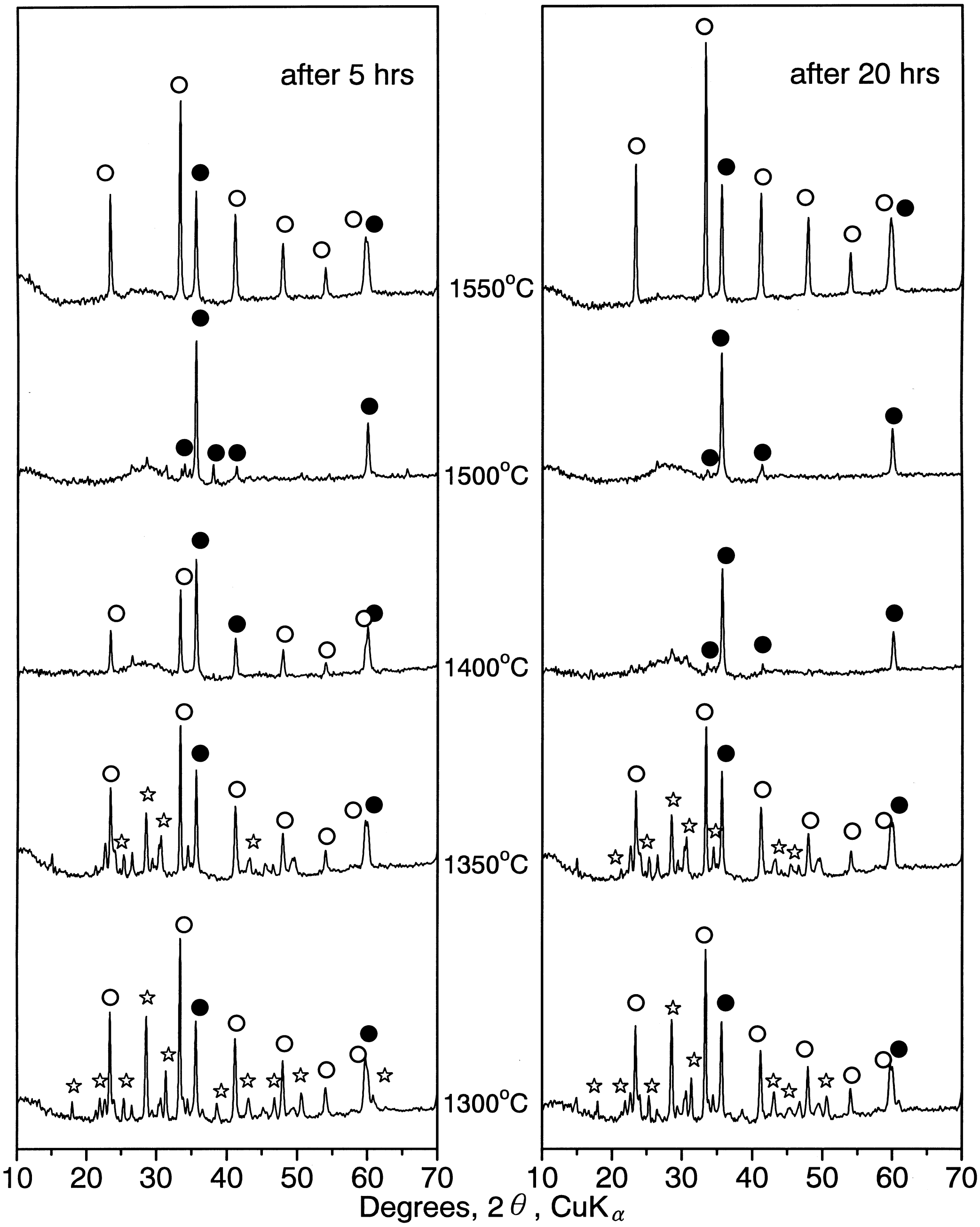

Fig. 5. XRD patterns of glass + 30 wt% SiC samples after reheating at 1300, 1350, 1400, 1500, 1550°C for 5 and 20 h in graphite: (●) SiC; (○) $LaAlO_3$; (☆) $La_3(Al,Si)_6(N,O)_{14}$.

than 1500°C. At 1300–1350°C, during reheating, $La_3(Al,Si)_6(N,O)_{14}$ crystallizes; this is believed to confirm the formation of oxygen-deficient glass on heat-treatment of the La–Al–Si–O glass containing SiC at 1600°C.

4. Conclusions

The devitrification behaviors of the pure La–Al–Si–O glass and the La–Al–Si–O glass containing SiC additions were investigated in the temperature range 1300–1600°C in CO and N_2 mixed gas. With addition of SiC the La–Al–Si–O glass devitrifies commencing from 1550°C; $LaAlO_3$ and $La_3(Al,Si)_6(N,O)_{14}$ are formed. The pure glass, free of SiC, gave mainly lanthanum disilicate in 1300–1400°C and no devitrification phases at higher than 1400°C. Crystallization of $LaAlO_3$ from the La–Al–Si–O glass in presence of SiC is considered to be caused by formation of a oxygen-deficient glass due to partial dissolution of SiC. In the presence of SiC, the crystallized $LaAlO_3$ was found to be stable at temperatures lower than 1400°C and again, higher than 1500°C.

Thus, SiC–$LaAlO_3$ ceramic materials obtained by liquid phase sintering probably show the deterioration of the high temperature mechanical properties in the temperature range 1400–1500°C. Nevertheless, the SiC–$LaAlO_3$ ceramic materials would be stable and dependable at temperatures lower than 1400°C and higher than 1500°C.

References

[1] 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., 1991, pp. 1327–1335.

[2] P.N. Padture, In situ-toughened silicon carbide, J. Am. Ceram. Soc. 77 (1994) 519–523.

[3] J.-K. Lee, H. Tanaka, H. Kim, Movement of liquid phase and the formation of surface reaction layer on the sintering of β-SiC with an additive of yttrium aluminum garnet, J. Mater. Sci. Lett. 15 (1996) 409–411.

[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] D. Taylor, Thermal expansion data XI. Complex oxides, A_2BO_5 and the garnets, Br. Ceram. Trans. J. 86 (1) (1987) 1–6.

[6] K. Negita, Effective sintering aids for silicon carbide ceramics: reactivities of silicon carbide with various additives, J. Am. Ceram. Soc. 69 (1986) C308–C310.

[7] C. Zhao, Pressureless sintering of silicon carbide with additives of samarium oxide and alumina, Mater. Lett. 17 (1993) 27–30.

[8] C. Zhao, L. Zeng, Pressureless sintering of silicon carbide with additives of holmium oxide and alumina, Mater. Res. Bull. 30 (1995) 265–270.

[9] C. Zhao, Effects of gadolinia and alumina addition on the densification and toughening of silicon carbide, J. Am. Ceram. Soc. 79 (1996) 530–532.

[10] E.T. Fritsche, L.G. Tensmeyer, Liquidus in the alumina-rich system La_2O_3–Al_2O_3, J. Am. Ceram. Soc. 50 (1967) 167–168.

[11] D. Taylor, Thermal expansion data VIII. Complex oxides, ABO_3 the perovskites, Br. Ceram. Trans. 84 (6) (1985) 181–188.

[12] P.N. Kotru, K.K. Raina, S.K. Kachroo, B.M. Wanklyn, Microhardness measurements on single crystal of flux-grown rare earth perovskites (orthoferrites, orthochromites and aluminates), J. Mater. Sci. 19 (1984) 2582–2592.

[13] K. Karlsson, The system La_2O_3–Al_2O_3–SiO_2. Part II. The lanthanum aluminium silicate $La_4Al_4Si_5O_{22}$, and lanthanum trisilicate, $La_2Si_3O_9$, Suom. Kem. B43 (1970) 302–305.

[14] J. Shiokawa, G. Adachi, M. Tanaka, Phase relations in the system La_2O_3–Al_2O_3–SiO_2 at 1550°C, Asahi Garasu Kougyou Gijutsu Shyoureikai Kenkyuhoukoku 14 (1968) 227–233.

[15] J. Grins, P.-O. Kall, Sialon U-phase: a new crystalline grain-boundary phase for β′-sialon ceramics, Inst. Phys. Conf. Ser. (1990) 427–434.

[16] A. Yamaguchi, Affects of oxygen and nitrogen partial pressure on stability of metal, carbide, nitride and oxide in carbon-containing refractories, Taikabutsu Overseas 7 (1986) 4–13.

[17] D.N. Coon, Effect of silicon carbide additions on the crystallization behavior of a magnesia–lithia–alumina–silica glass, J. Am. Ceram. Soc. 72 (1989) 1270–1273.

[18] J. Homeny, S.H. Risbud, Novel multianoin Mg–Si–Al–O–N oxycarbide glasses, Mater. Lett. 3 (1985) 432–434.

[19] V.G. Borisov, Reaction of silicon dioxide with silicon carbide at 1870–2670 K, Tr. Vses. Inst. Nauch.-Issled. Proekt. Rab. Ogneupor. Prom. 39 (1967) 128–145.

[20] W. Hertl, W.W. Pultz, SiO_2 + SiC reaction at elevated temperature II. Effect of added gases, Trans. Faraday Soc. 62 (1966) 3440–3445.