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Near net shape SiC–mullite composites from a powder precursor prepared through an intermediate Al-hydroxyhydrogel

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Abstract

SiC–mullite composites with low dimensional changes on sintering were fabricated by partial oxidation of SiC followed by reaction bonding using hydroxyhydrogel derived alumina keeping SiC as dispersed phase in the intermediate gel-like mass as starting material. The sintering-induced shrinkage is compensated by volume expansion caused by the silicon carbide oxidation-induced-volume expansion. This work describes a new processing route to fabricate SiC–mullite composites where in situ formation of mullite takes place that proceeds at much lower temperatures ($\leqslant 1600°C$) than in normal ceramics processing routes. Specimens containing $Al_2O_3 \leqslant 40\%$ are not suitable due to the formation of large amount of low eutectic aluminosilicates at processing temperatures. Specimens containing $\geqslant 40\%$ Al_2O_3 yield different aluminosilicates, mainly mullite, which acted as a retarder for oxidation of SiC and at the same time it helped to consolidate SiC compacts. Final phases in fired compact were identified by XRD and different phases present were calculated on the basis of X-ray diffraction results. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: B. Composites; D. Mullite; D. SiC; Near net shape; Hydroxyhydrogel

1. Introduction

Both mullite and silicon carbide are prospective materials in the field of engineering ceramics due to their superior high temperature mechanical properties [1–5] and resistance toward chemical attack. But, both the materials suffer from poor fracture resistance [6] which renders them unsuitable for applications in a diverse field. Since, thermal expansion coefficient of mullite and silicon carbide are very close ($\alpha_{\mathrm{Mullite}} = 5.4 \times 10^{-6}/°C$, $\alpha_{\mathrm{SiC}} = 4.7 \times 10^{-6}/°C$) to each other, it is possible to fabricate sintered compacts of SiC and mullite, fracture toughness of which is considerably higher than both the components [7–10]. Fabrication of the composite consisting of SiC and mullite, however, is to some extent difficult and an inert atmosphere during consolidation is always maintained to have a check on the oxidation of SiC [11]. Conventional processes encompass pressureless sintering and hot pressing [12]. A newer fabrication route involves reaction sintering where metallic aluminium was used along with SiC and the compact was sintered in air where oxidation product of SiC, i.e. SiO_2 and oxidation product of aluminium i.e. Al_2O_3 combined together to form mullite at higher temperature [13,14]. In this process it was difficult to control oxidation of SiC and in some instances almost all of the SiC were ultimately converted to SiO_2 and in turn mullite [7].

It is now established [15] that oxidation of SiC can be prevented if mullitisation takes place at such temperature where oxidation of SiC is not much. In the present investigation reactive alumina is generated in the intermediate hydroxyhydrogel in which SiC particles are kept dispersed so that a uniform mullite phase is formed around SiC particles which will ultimately help in preventing further oxidation of SiC and form the compositing mullite phase.

2. Experimental[1]

A suspension of α-SiC, of characteristics given elsewhere [16], was mixed with aluminium salt in required

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[1] The preparation part is protected in India by Patent application No. 376/DEL/98.

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amount. The entire mixture was brought to a gel-like mass consisting of hydroxyhydrogel of aluminium in which silicon carbide particles were dispersed by following known methods [16,17]. The gel- like mass was washed after ageing for 24 h, dried at 110°C and heat treated at 800°C for 1 h.

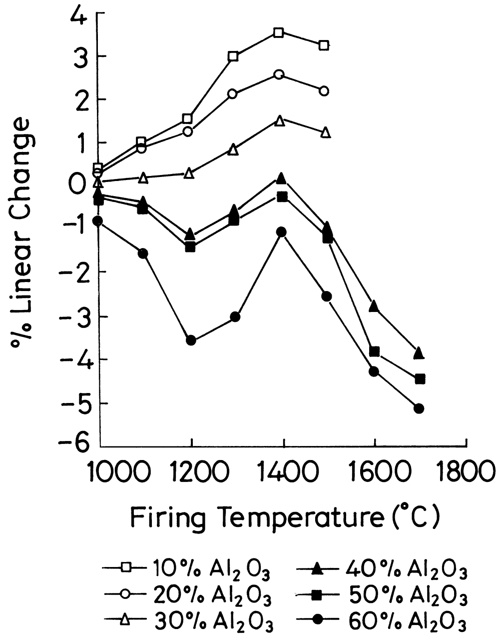

Fig. 1. Linear changes of specimens at different temperatures.

Heat treated mass was ball milled and sieved to pass through 100 mesh B.S. Pellets and bars were prepared uniaxially at a pressure of 42 MPa followed by isostatic pressing at 180 MPa. The specimens were fired in the temperature range of 1000–1700°C in ambient atmosphere with 2 h soaking.

3. Results and discussion

Dimensional changes of the specimens heat treated at different temperatures in ambient atmosphere are shown in Fig. 1, where linear changes were represented against the temperature of heat treatment. With increasing temperature of heat treatment, expansion of specimens were noted. The extent of dimensional changes was found to decrease with increasing amount of oxide material present in the specimens. The entire phenomenon is supposed to be linked to three distinct processes occurring simultaneously.

(i). During heat treatment, hydroxyhydrogel components present in the specimens gradually released H_2O

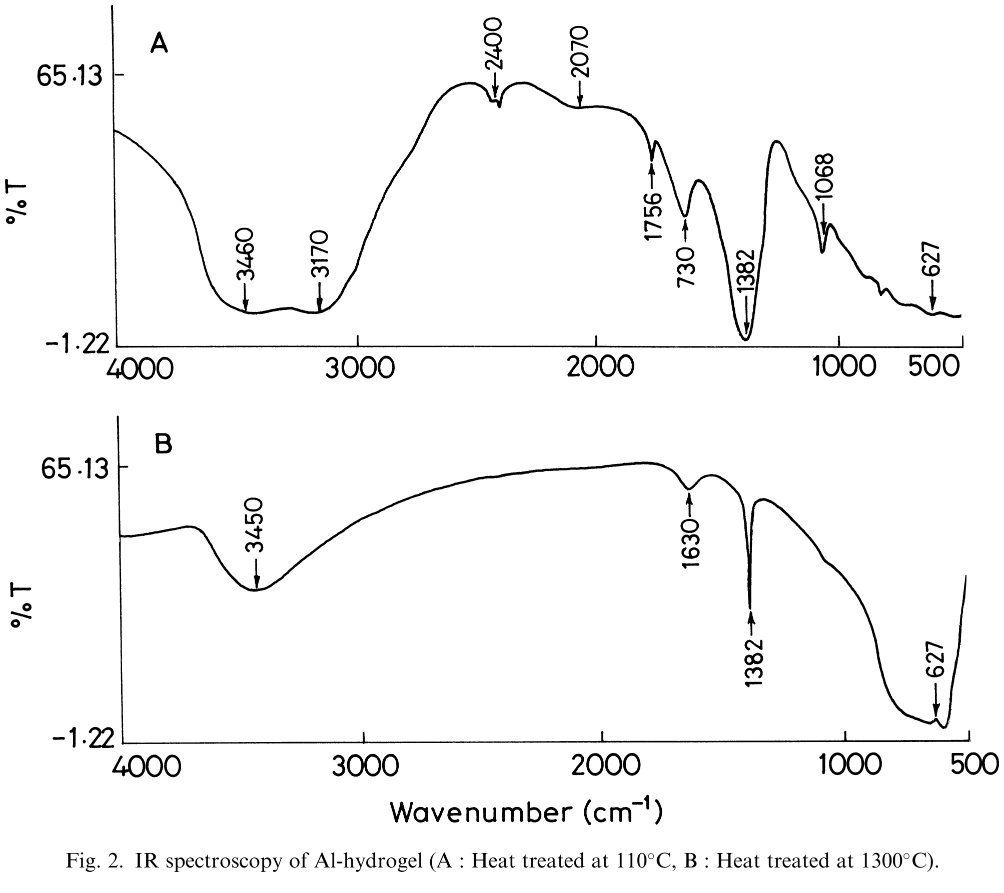

Fig. 2. IR spectroscopy of Al-hydrogel (A : Heat treated at 110°C, B : Heat treated at 1300°C).

resulting in a skeleton structure with pores and cavities inside it [15]. It was found that OH linkages remained in Al–O–Al skeleton even at 1400°C, which was established by IR measurements (Fig. 2). At the temperature range studied, this network structure collapsed leading to linear shrinkage. The amount of linear shrinkages of such type of hydrogels are indicated in Fig. 3 where fast shrinkage was noted up to 1200°C with a small increment beyond.

(ii). During heat treatment of SiC in the presence of oxygen, SiC converts to SiO_2 with a theoretical volume increase of 108% [7]. The volume increase noted for SiC pellets under similar conditions without oxide additives are indicated in Fig. 4.

(iii). The formed SiO_2 and the original SiO_2 present as a surface layer over SiC particles combined with Al^{+3} incorporated as reactive hydroxylated form to form aluminosilicates, mostly mullite, which was identified by XRD analysis. This $SiO_2 \rightarrow$ mullite conversion leads to a volume increase of around 4.8% [7].

The above three processes lead to a net change in the dimensions which was always positive in the present range of composition i.e. it leads to a net volume increase. It was reported earlier [15] that in such systems the oxidation of SiC was retarded due to the formation of aluminosilicates which protected SiC particles by forming an impervious layer over it. Now, the system may be visualised as a matrix of aluminosilicates in which SiC particles are embedded as a dispersed phase. The type of aluminosilicate formed is dependent on the Al_2O_3:SiO_2 mol ratio and in the present system samples

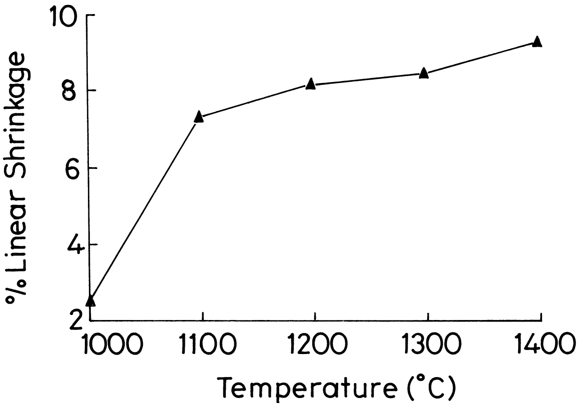

Fig. 3. Linear shrinkage of Al- hydrogel in relation to heat treatment at different temperatures.

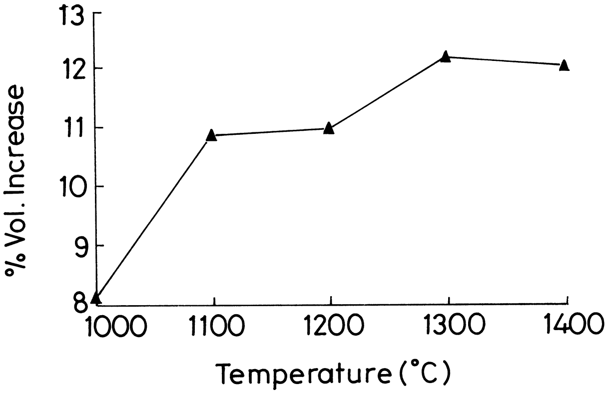

Fig. 4. Volume expansion of SiC powder in pelletised form fired at different temperatures in ambient gas atmosphere.

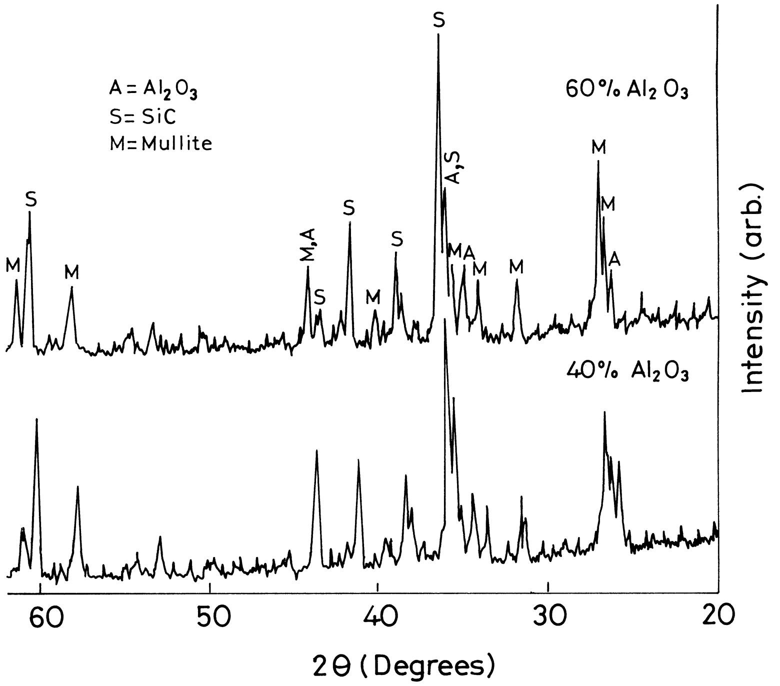

Fig. 5. XRD patterns of SiC–Al_2O_3 compact fired in ambient gas atmosphere.

containing <40% Al_2O_3 were found to be unsuitable for heat treatment above 1500°C due to the formation of a large amount of liquid. Therefore, specimens with 40% and more Al_2O_3 were heat treated up to 1700°C in ambient atmosphere. XRD analysis of the heat treated specimens indicated the presence of SiC, mullite and small amount of Al_2O_3 without any measurable SiO_2 (Fig. 5). From this analysis and the weight gain of the specimens different phases present in the sintered compacts were calculated. Different phases formed at the final heat treatment temperature with respect to Al_2O_3 content is represented in Fig. 6. It appeared from Fig. 6 that up to 40% Al_2O_3, amount of SiO_2 went on decreasing with increasing amount of mullite. SiC remained almost as unchanged amount implying protection of SiC from further oxidation even with 10% Al_2O_3 in the present system. Ten percent Al_2O_3 containing specimens were fired up to 1500°C due to the reason stated above.

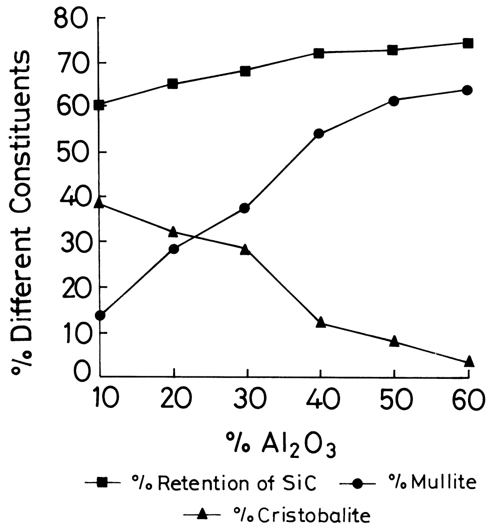

Fig. 6. Variation of different constituents in relation to Al_2O_3 content fired at 1600°C.

Specimens fired above 1400°C developed a white outer layer for all the samples which were consisting mainly of mullite (Fig. 7). Unlike normal sintering process, here both expansion and contraction processes proceeded simultaneously with the possibility of obtaining a sintered material with low to no volume change. Volume expansion was calculated on the basis of the formation of SiO_2 from SiC and conversion of SiO_2 to mullite, both leading to volume expansion. It was found that by increasing Al_2O_3 content of the specimens volume changes decreased and with 40% Al_2O_3 the increase in net volume was ~3% at 1400°C. The similar specimens, i.e. samples containing 40–60% Al_2O_3 were fired at 1700°C in ambient atmosphere. Those specimens were found to shrink and it ranged from 9.85 to 14.23 vol% when the porosity was <2%. Thus, in such systems formation of near-net-shape sintered materials are difficult as lower amount of Al_2O_3 will make the sample unsuitable above 1500°C due to high liquid formation and higher Al_2O_3 brought in through hydrogel intermediates will lead to excessive shrinkage which are likely to overweighs the expansion due to chemical conversions. Moreover, a normal sintering shrinkage would add on to this. Though the process is not likely to lead to a near-net-shape sintered body at the present range of compositions but due to high retention of SiC with mullite as a major phase in the sintered compacts with comparatively lower shrinkages accompanying the process may find use of the material as engineering ceramics. Moreover, the ambient processing would lead to lowering of cost of production to a large extent. This processing route, thus, is likely to be a good alternative for making SiC–mullite–Al_2O_3 composite materials or a base material for a host of other composites compatible with the system.

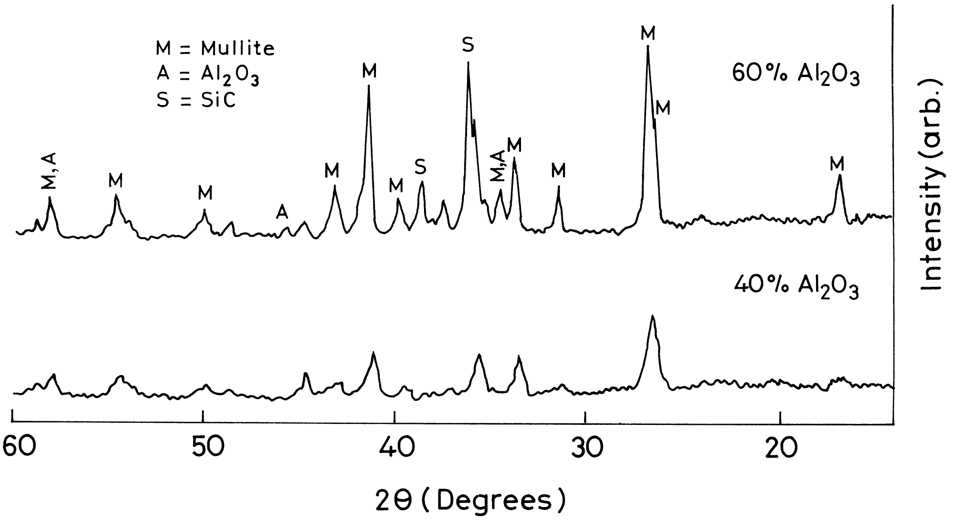

Fig. 7. XRD patterns of white surface formed during consolidation of specimens.

4. Conclusions

1. A very low shrinkage material could be synthesised in the SiC–Mullite–Al_2O_3 composite system by using powder precursors prepared through intermediate hydroxyhydrogel formation.
2. Sintering and processing of the materials possible without Ar or N_2 atmosphere as the presence of oxygen in the firing atmosphere was favourably used up to a limit and oxidation of remaining SiC could be totally prevented afterward.
3. Al_2O_3 above 40% was found to be the minimum amount to be used for obtaining products of utility.

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