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Preparation and characterization of ceramic porous sheet composed of platelet (Cr, Al)$_2$O$_3$ crystals

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A compact powder mixture consisting of $3Al_2O_3 \cdot 2SiO_2$ (mullite) and Cr_2O_3, which was heated in a carbon powder bed, was cut into a 1 mm thickness sheet. The ceramic porous sheet composed of platelet (Cr, Al)$_2$O$_3$ crystals was prepared by leaching SiO_2 contained in the sheet by hydrofluoric acid. The porous sheet produced from the 50 mass % mullite/50 mass % Cr_2O_3 compact, heated at 1500 °C for 2 h, was composed of platelet crystals with 30 μm average length and 4.6 μm average thickness. Its relative density and specific surface area were 73% and 4.4 $m^2 g^{-1}$ respectively.

1. Introduction

Porous ceramics are used as filters, ion-exchangers, gas sensors, insulators, catalysts, and so on. Some studies on porous ceramics composed of needle-like crystals, in which the crystals interlink with each other, have been reported [1–4]. However, porous ceramics composed of the platelet crystals have not been reported.

Previously, Yamaguchi [5] reported the sintering behaviour of a compact composed of the compositions in the Al_2O_3–Cr_2O_3–SiO_2 system. The microstructure of the sintered compact after leaching by hydrofluoric acid was a skeleton-like structure composed of rectangular Cr_2O_3–Al_2O_3 solid solution, namely (Cr, Al)$_2$O$_3$, crystals. According to further detailed observation, most of the (Cr, Al)$_2$O$_3$ crystals were plate-like. Porous (Cr, Al)$_2$O$_3$ ceramics have been used as a ceramic foam filter for molten materials such as aluminium [6, 7]. In this study, new ceramic porous sheet, composed of platelet (Cr, Al)$_2$O$_3$ crystals, was prepared and characterized. This ceramic porous sheet is expected to be used as a thin ceramic filter for molten aluminium.

2. Experimental procedure

A powder mixture consisting of $3Al_2O_3 \cdot 2SiO_2$ (mullite, purity 98.5%; 0.36% Fe_2O_3, 0.29% TiO_2, 0.23% Na_2O, and 0.09% K_2O) and Cr_2O_3 (purity 99.9%) was pressed uniaxially with 80 MPa into a $20 \times 20 \times 5$ mm^3 to form a compact. Five powder compacts, whose composition ratios mullite mass %/Cr_2O_3 mass % were 75/25, 60/40, 50/50, 35/65, and 25/75, were used. Each of the compacts was embedded in graphite powder (purity 99.0%) in an alumina crucible covered with an alumina lid and heated at 1400–1600 °C for various times. Reaction products were analysed by X-ray diffractometry (XRD). The microstructure of the sintered compacts was examined by electron probe microanalysis (EPMA). The compacts were cut into rectangular sheets in $5 \times 5 \times 1$ mm^3. Those sheets were immersed in 15.7% hydrofluoric acid under reflux. The fractured surface and the polished surface of the porous sheet were observed by scanning electron microscopy (SEM). The average diameter and thickness of the platelet (Cr, Al)$_2$O$_3$ crystals were obtained from about 30 crystals. To observe the characteristics of the compact at high temperature, the 50/50 compact was rapidly cooled from 1500 °C into water and then analysed by XRD. The relative density of the sintered compacts and the prepared porous sheets was determined by the apparent and the true density. The specific surface areas of the porous sheets were measured by the BET method.

3. Results and discussion

3.1. Characterization of the mullite/Cr_2O_3 compacts heated in a carbon powder bed

Fig. 1 shows relative density of the compacts consisting of mullite and Cr_2O_3 after heating at 1500 °C

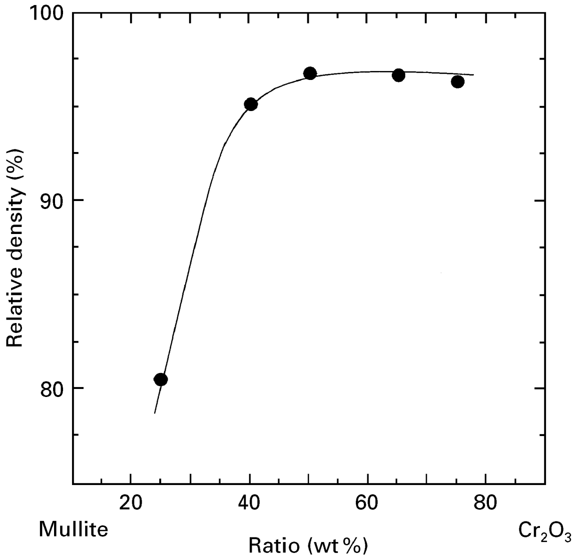

Figure 1 Relative density of the compacts consisting of mullite and Cr_2O_3 after heating at 1500 °C for 2 h in a carbon powder bed.

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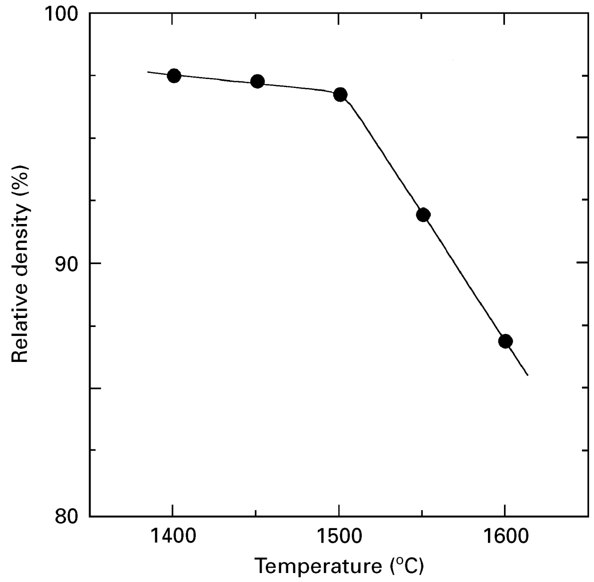

Figure 2 Relative density of the 50 mass % mullite/50 mass % Cr_2O_3 compacts heated in a carbon powder bed at various temperatures for 2 h.

for 2 h. The relative density was above 95% in the compacts containing above 40 mass % Cr_2O_3. Fig. 2 shows change of relative density of the 50/50 compact heated with temperature for 2 h. On heating at 1400–1500 °C, the density was the same, about 97%, while on heating at above 1500 °C, it decreased with temperature. The decrease in the density at higher temperature was considered to be caused by the increase in the vaporization of gaseous species such as a SiO(g) [5]. In all heated compacts, a $(Cr, Al)_2O_3$ crystal and SiO_2 (cristobalite) were identified, while mullite was not detected. Fig. 3 shows SEM and EPMA photographs of the polished surface of the 50/50 compact heated at 1500 °C for 2 h. It was confirmed that the rectangular matter was a $(Cr, Al)_2O_3$ crystal and the gap between the crystals was filled by SiO_2.

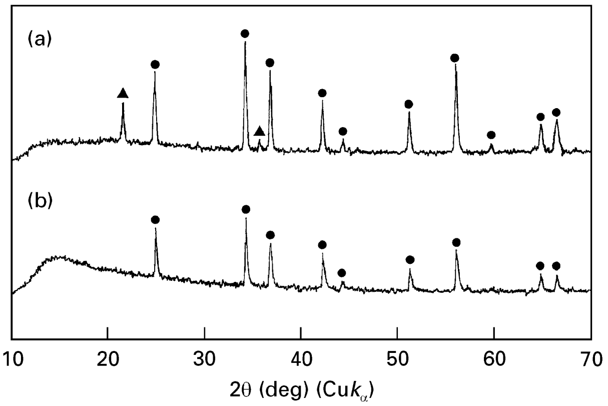

Figure 4 XRD patterns of (a) the 50 mass % mullite/50 % Cr_2O_3 compact cooled at the rate of 600 °C h^{-1} after heating at 1500 °C for 2 h, and (b) that cooled rapidly into water after heating at 1500 °C for 2 h. (▲) SiO_2 (cristobalite), (●) $(Cr, Al)_2O_3$s.s.

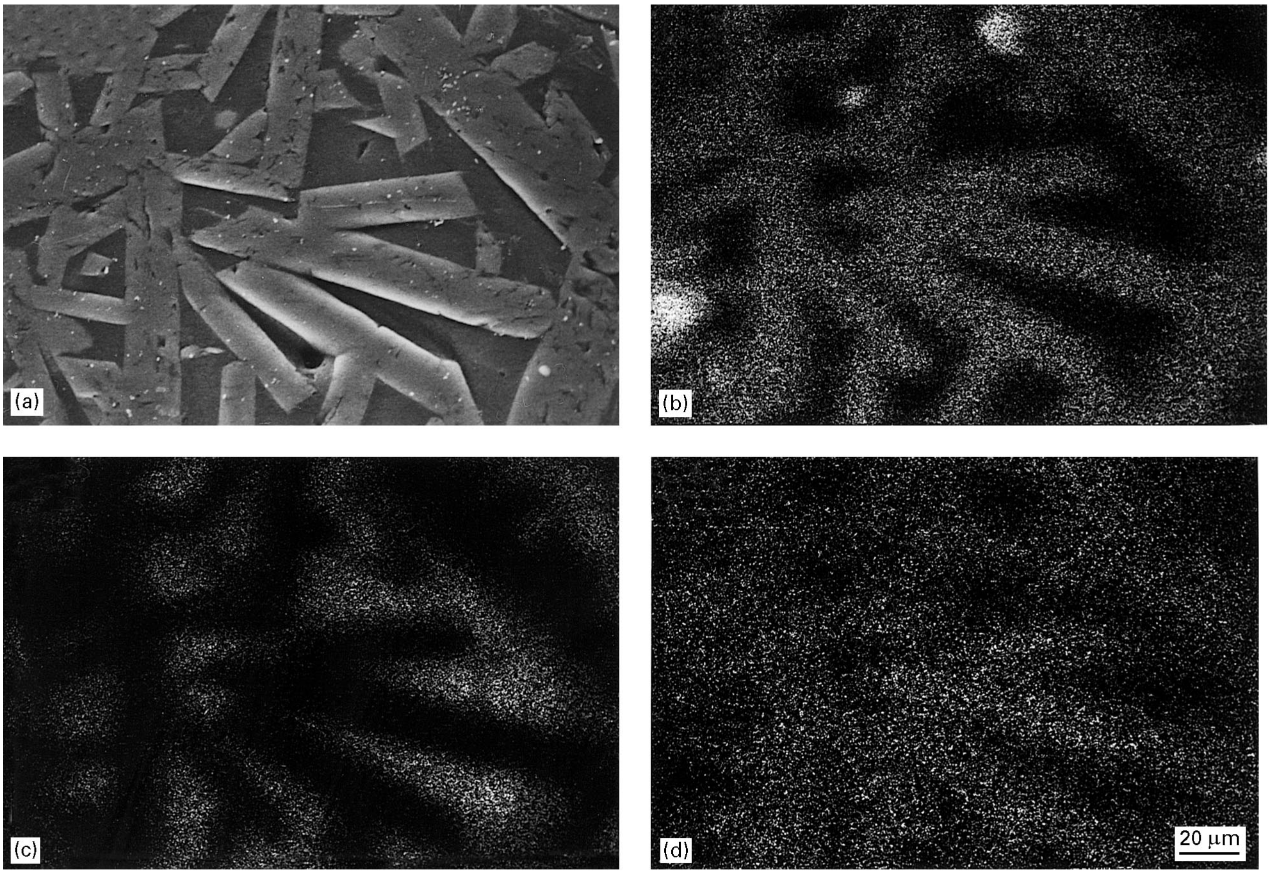

Figure 3 (a) Scanning electron micrograph and (b–d) EPMA photographs of the polished surface in the 50 mass % mullite/50 mass % Cr_2O_3 compact heated in a carbon powder bed at 1500 °C for 2 h (b) Cr, (c) Si, (d) Al.

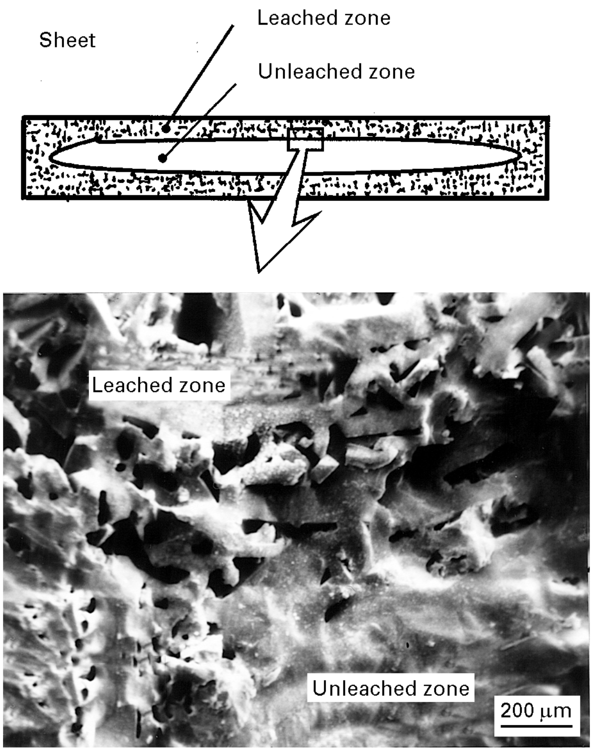

Figure 5 Drawing and scanning electron micrograph of the cross-section of the sheet which was cut from the 50 mass % mullite/50 Cr_2O_3 mass % compact heated in a carbon powder bed at 1500 °C for 2 h and then immersed in 15.7% hydrofluoric acid for 48 h.

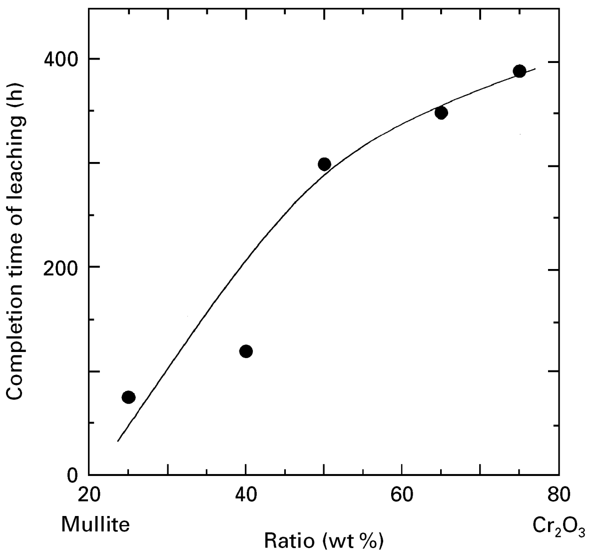

Figure 6 Completion time for leaching SiO_2 contained in the 1 mm thick sheets which were cut from the mullite/Cr_2O_3 compacts heated in a carbon powder bed at 1500 °C for 2 h.

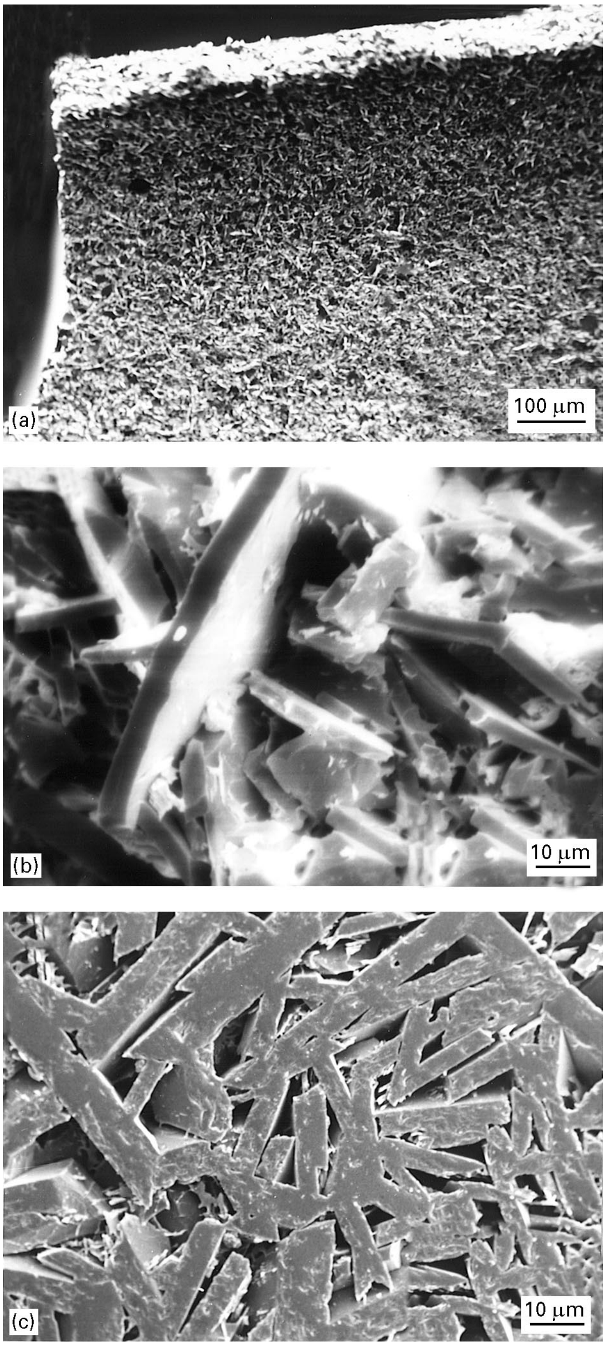

Figure 7 Scanning electron micrographs of the fractured surface (a, b) and the polished surface (c) of the sheet which was cut from the 50 mass % mullite/50 mass % Cr_2O_3 compact heated in a carbon powder bed at 1500 °C for 2 h and then immersed in 15.7% hydrofluoric acid.

3.2. Growth mechanism of the (Cr, Al)$_2$O$_3$ crystal

When a compact powder mixture consisting of mullite and Cr_2O_3 was heated in a carbon powder bed in an alumina crucible, they reacted to form (Cr, Al)$_2$O$_3$ and SiO_2. The atmosphere inside the alumina crucible with carbon is considered to be about 0.1 MPa of CO above 1000 °C [8, 9]. No liquid phase is formed below 1575 °C in the Al_2O_3–Cr_2O_3–SiO_2 system [10]. However, the growth of the rectangular (Cr, Al)$_2$O$_3$ crystals suggested that the liquid phase formed in the compact during heating. SiO_2, which is present at high temperature under 0.1 MPa of CO, is thermodynamically unstable. Under a strong reductive atmosphere, the presence of SiO_{2-x} $(0 < x \leqslant 2)$ as unstable phase has been proposed [5]. The melting point of the Al_2O_3–Cr_2O_3–SiO_2 system is considered to be below 1405 °C, because the melting points of Si–SiO and Cr–CrO are 1405 and 1645 °C, respectively [11], and Al_2O_3 coexists in this system. In fact, it was recorded that a eutectic temperature in the Al_2O_3–Cr_2O_3–SiO_2

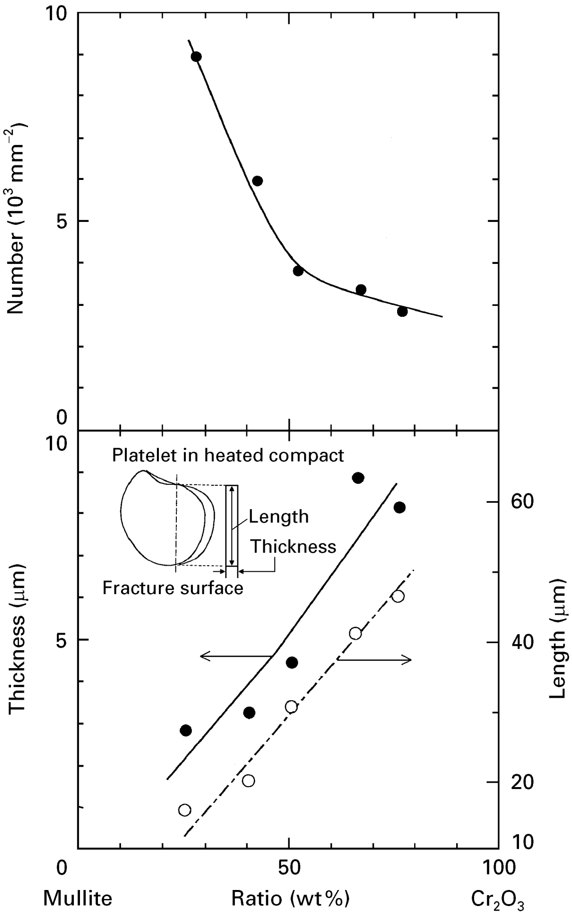

Figure 8 Changes in number, average thickness and average length of the platelet (Cr, Al)$_2$O$_3$ crystals in the mullite/Cr$_2$O$_3$ compacts heated in a carbon powder bed at 1500 °C for 2 h.

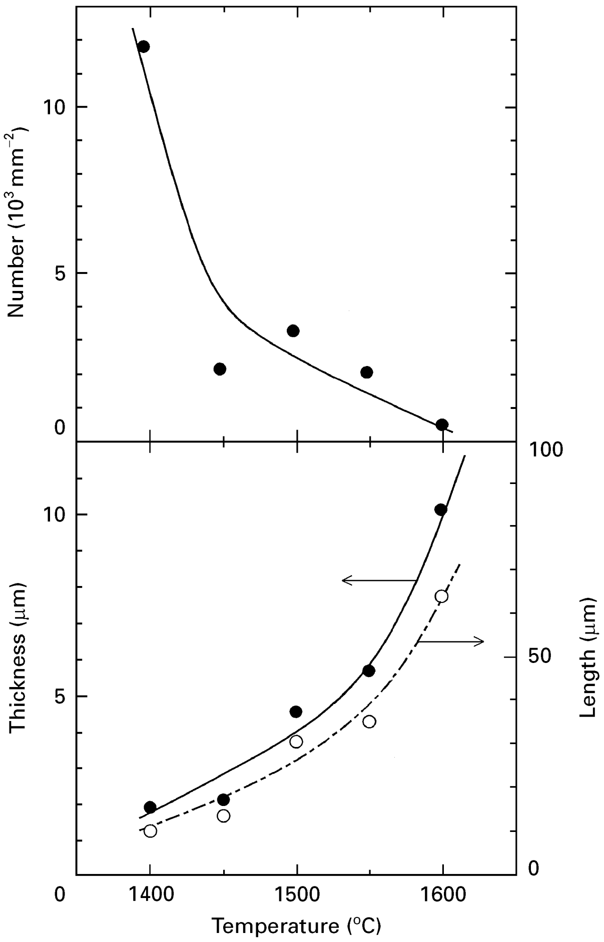

Figure 9 Changes in number, average thickness and average length of the platelet (Cr, Al)$_2$O$_3$ crystals in the 50 mass % mullite/50 mass % Cr$_2$O$_3$ compact in a carbon powder bed, with temperature for 2 h.

system coexisting with carbon, is about 1290 °C [12]. Fig. 4 shows XRD patterns of (a) the 50/50 compact cooled slowly at the rate of 600 °C h^{-1} after heating at 1500 °C for 2 h, and (b) that cooled rapidly from 1500 °C into water. Cristobalite was not detected in the rapidly cooled sample. Therefore, the glass phase (liquid phase) formed is considered to crystallize during cooling.

3.3. Preparation of porous (Cr, Al)$_2$O$_3$ sheet

When the 1 mm thick sheet cut from the mullite/Cr$_2$O$_3$ compact heated in a carbon powder bed was immersed in hydrofluoric acid, many pores were formed, as shown in Fig. 5. The completion time of leaching SiO$_2$ was determined by observing pores formation up to the middle of the sheet. Fig. 6 shows completion time of the leaching for the sheets which were cut from the mullite/Cr$_2$O$_3$ compacts heated at 1500 °C for 2 h. It lengthened with increasing amount of Cr$_2$O$_3$ in the compact.

3.4. Characterization of the porous (Cr, Al)$_2$O$_3$ sheet

Fig. 7 shows scanning electron micrographs of the fractured surface (a, b) and the polished surface (c) of the sheet immersed in hydrofluoric acid, which was cut from the 50/50 compact heated at 1500 °C for 2 h. Most of the crystals in the porous sheet were platelet-shaped, as shown in Fig. 7b. Fig. 8 shows changes in number, average length and average thickness of the platelet cystals with the mullite/Cr$_2$O$_3$ ratio in the starting compact heated at 1500 °C for 2 h. The thickness and the length of a platelet crystal are defined as shown in the Fig. 8. Both the average thickness and length of the platelet crystals increased with increasing amount of Cr$_2$O$_3$. For example, the average thickness and length of the platelet crystals prepared from the 50/50 compact were 4.6 and 30 μm, respectively. The number of platelet crystals decreased with increasing amount of Cr$_2$O$_3$. Fig. 9 shows number, average thickness and average length of the platelet (Cr, Al)$_2$O$_3$ crystals in the 50/50 compact heated for 2 h. Both the average thickness and length increased with temperature, and the number of the platelet crystals decreased with temperature. Fig. 10 shows changes in number, average thickness and average length of the platelet (Cr, Al)$_2$O$_3$ crystals in the 50/50 compact with duration time at 1500 °C. After both the average thickness and length increased rapidly up to 1 h, they continued to increase gradually with time. The number of platelet crystals increased up to 0.5 h after reaching 1500 °C, because nucleation and nuclear growth of

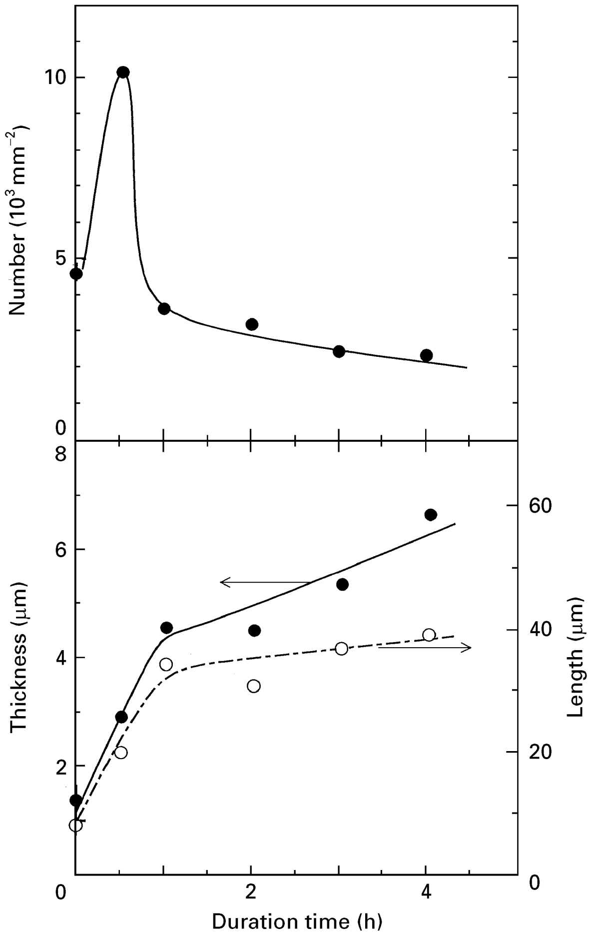

Figure 10 Changes in number, average thickness and average length of the platelet (Cr, Al)$_2$O$_3$ crystals in the 50 mass % mullite/50 mass % Cr$_2$O$_3$ compact heated at 1500 °C, with duration time in a carbon powder bed.

the crystals steeply occurred in the liquid phase. On the other hand, the number of the platelet crystals rapidly decreased at duration times from 0.5–1 h. It is considered that the small crystals dissolved into the liquid phase and then precipitated at the surface of the larger crystals. That is, the small crystals disappeared and large crystals grew more in appearance. After 1 h, the number of the crystals continued to decrease.

Fig. 11 shows changes in relative density and specific surface area of the prepared porous sheet with the mullite/Cr$_2$O$_3$ ratio in the starting compact. The relative density increased with increasing amount of Cr$_2$O$_3$, while the specific surface area was maximum in the 50/50 compact and its value was 4.4 m^2 g^{-1}. The relative density of the porous sheet with maximum specific surface area was 73%. In the samples with above 50 mass % Cr$_2$O$_3$, the relative density decreased with increasing Cr$_2$O$_3$ content. It is considered to be caused by the increase in the average size of the formed platelet crystals and the decrease of the number of platelet crystals per unit area, as shown in Fig. 8. In the sample below 50 mass % Cr$_2$O$_3$, the decrease of the specific surface area with increasing amount of mullite is considered to be caused by the increase in the amount of SiO$_2$.

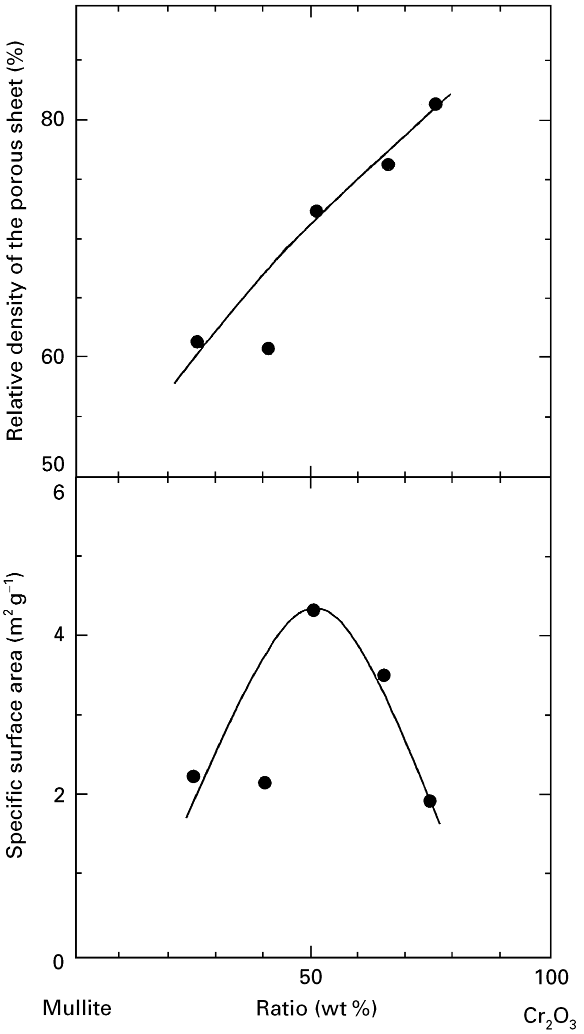

Figure 11 Changes in relative density area and specific surface of the prepared porous sheets with the mullite/Cr$_2$O$_3$ ratio in the starting compact.

4. Conclusion

When the powder compact consisting of mullite and Cr$_2$O$_3$ was heated in a carbon powder bed, the compact densified, in which the platelet (Cr, Al)$_2$O$_3$ crystals grew and the gap between the crystals was filled by SiO$_2$. With increasing amount of Cr$_2$O$_3$ in the compact, and increasing temperature, the average size of the grown platelet (Cr, Al)$_2$O$_3$ crystals increased. The ceramic porous sheet composed of platelet (Cr, Al)$_2$O$_3$ crystals was prepared by leaching SiO$_2$ by hydrofluoric acid. The porous sheet which was prepared from the 50 mass % mullite/50 mass % Cr$_2$O$_3$ compact heated at 1500 °C for 2 h was composed of platelet crystals with 4.6 μm average thickness and 30 μm average length. The relative density and the specific surface area of the porous sheet were 73% and 4.4 m^2 g^{-1}, respectively.

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