

## Sintering of $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ Powder Prepared by Sol-Gel Process <sup>†</sup>

by

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The sol-gel method was applied to create  $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$  ceramics using aluminum ethylacetate diisopropylate and chromium (III) chloride hexahydrate as starting materials. In the calcination at 600-1200°C it was found that the grains of  $\text{Cr}_2\text{O}_3$ -rich solid solution grew when they were exposed to the surrounding  $\text{Al}_2\text{O}_3$ -rich amorphous particles. The composition of the powders obtained by the sol-gel process changed with calcining temperature.  $\text{Cr}_2\text{O}_3$ -rich solid solutions firstly crystallize at low temperature and the composition of the crystallites changes as the crystals grow and react with the surrounding  $\text{Al}_2\text{O}_3$ -rich phases. The final sintered bodies fired under an Ar atmosphere showed higher relative densities as compared with those fired in air. A dense sintered body was not obtained when abnormal grains grew when calcining occurred.

**Key words :**  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , Solid solution, Sol-gel process, Sintering

### 1 Introduction

The amount of municipal wastes in Japan is about 50 million tons/year. About 80% of waste disposal relies on incineration. In this case, however, endocrine disrupters such as dioxin are present in the gas and fly ash exhausted from the incineration facilities. This problem has become serious social issues. Melting type incinerators such as gasification melting furnaces have been developed as a solution to this problem. In high temperature melting type incinerators the wastes are burnt and melted above 1300°C. Generally  $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$  refractories are used in such conditions.<sup>1), 2)</sup>

The alkali and alkali-earth elements such as Na, K and Ca are present in the municipal wastes and corrode furnace lining refractories. Porous microstructure refractories are attacked so a dense body is used to avoid damage. Hirata et al. investigated densification and corrosion of  $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$  by addition of  $\text{TiO}_2$ .<sup>3), 4)</sup>

Aluminium organometallic compound<sup>5)-7)</sup> starting materials were used to obtain dense ceramics. The powders obtained from the starting material contained uniformly dispersed fine particles. The sintered  $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$  body seemed to have corrosion resistance when the material was used in the same way.

$\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$  ceramic is a solid solution of  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  has high chemical stability even at high temperatures and hence it is used as a refractory brick in gasification melting furnaces. Both  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  are chemically stable at high temperature and take a corundum crystal

structure forming a solid solution  $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3$  in the entire composition region at high temperature (Fig. 1). At relatively low temperatures a miscibility gap is present in which two crystalline phases of  $\text{Al}_2\text{O}_3$ -rich and  $\text{Cr}_2\text{O}_3$ -rich solid solutions are present. As shown in Fig. 1, the critical temperature  $T_c$  depends on the surrounding pressure.<sup>8)-10)</sup> A thermodynamically stable solid solution is necessary to obtain, and some conditions of the metastability are being researched now. Murakami et al.<sup>11)</sup> confirmed a metastable two-phase region at around 1300°C. Bondioli<sup>12)</sup> investi-

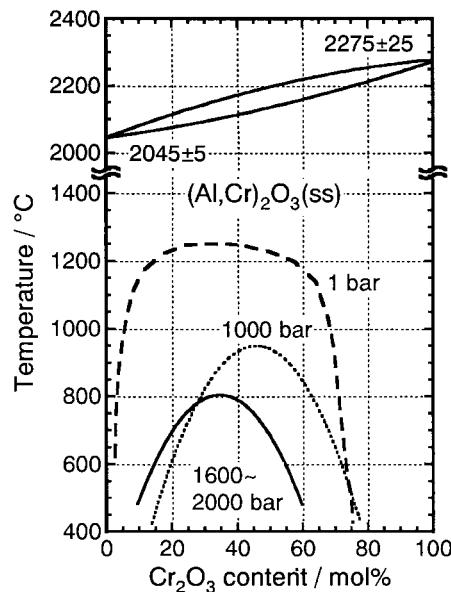


Fig. 1 Phase diagram of alumina-chromia ( $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ ) system.<sup>8)-10)</sup>

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gated two metastable phase by solid phases reaction and coprecipitation. When the different phases were observed in the heat-treated powder, reactivity was thought to influence sintering behavior.

Moreover, the vapor pressure of  $\text{CrO}_3$  and  $\text{CrO}_2$  is high so that the sintered body of  $\text{Cr}_2\text{O}_3$  becomes porous due to the evaporation of Cr-compounds when fired in air.

We prepared uniform precursor powder mixed at a molecular level, and then got  $\text{Al}_2\text{O}_3$ - $\text{Cr}_2\text{O}_3$  dense ceramics. In this paper we investigated the mechanism for the formation of solid solution. The effects of powder size and sintering atmosphere on sintering were investigated.

## 2 Experimental Procedures

The raw materials used were aluminum ethylacetate diisopropylate (ALCH, Kawaken Fine Chemicals Co., Ltd.) and  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (Wako Pure Chemical Industries Ltd.). ALCH and  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  were dissolved in a 10 times the amount of raw material mole ratio of ethanol and were stirred and mixed with a homogenizer for 30 minutes and a supersonic homogenizer for 5 minutes. 30 times mole ratio of ion exchange water was slowly dropped with stirring and was mixed for 30 minutes with a magnetic stirrer to obtain gels at room temperature. The gels were dried in a rotary evaporator and calcined at 600–1200°C for 1 h in air. After the calcinations the powders were mixed with a ball mill for 10 h using an ethanol solvent and pressed into pellets of about 25 mm in diameter. The green bodies were sintered at 1600°C for 1 h in an atmosphere of air or Ar. Fig. 2 shows the sample preparation procedures.

For comparison  $\text{Al}_2\text{O}_3$ - $\text{Cr}_2\text{O}_3$  ceramics were also prepared by a conventional solid phase reaction. The starting powders of  $\text{Cr}_2\text{O}_3$  (Kanto Chemical Co., Inc.) and  $\alpha$ - $\text{Al}_2\text{O}_3$  (AES-12 Sumitomo Chemical Co., Ltd.) were mixed with a ball mill for 10 h using an ethanol solvent.

The bulk densities of the sintered bodies were measured and the relative densities were also estimated

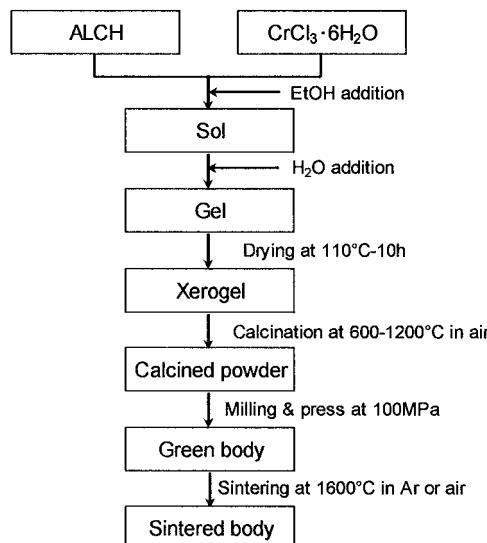


Fig. 2 Sample preparation procedures.

from the experimental values and the theoretical densities calculated from the compositions. The crystalline phases were identified by X-ray diffraction (XRD ; Rigaku RINT2200VHF + /PC) with  $\text{CuK}\alpha$  radiation. The microstructures of the specimens were observed by optical microscope and scanning electron microscope (SEM ; JEOL JSM-6340F).

## 3 Results and Discussion

### 3.1 Formation of solid solution

Fig. 3 shows the XRD patterns of the sol-gel derived powders of 10, 30 and 50 mol%  $\text{Cr}_2\text{O}_3$  calcined at 600–1200°C. A/C = 50/50 implies an equimolar ratio of  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ . Two phases in the A/C = 50/50 sample calcined at 600°C with a  $\text{Cr}_2\text{O}_3$  content richer than the nominal composition, were observed. The double peak turned into a single peak above 700°C. In the A/C = 70/30 sample, no peak appeared when calcined at 600°C, and a phase was found when calcined above 800°C. In A/C = 90/10 sample no peak appeared when calcined at 800°C, and a crystalline phase was found as calcined above 900°C. In all the compositions as the calcination temperature increased the peak shifted to the higher diffraction angle side ( $\text{Al}_2\text{O}_3$ -rich side). These results indicate that  $\text{Cr}_2\text{O}_3$ -rich solid solutions firstly crystallize at low temperature and the composition of the crystallites changes

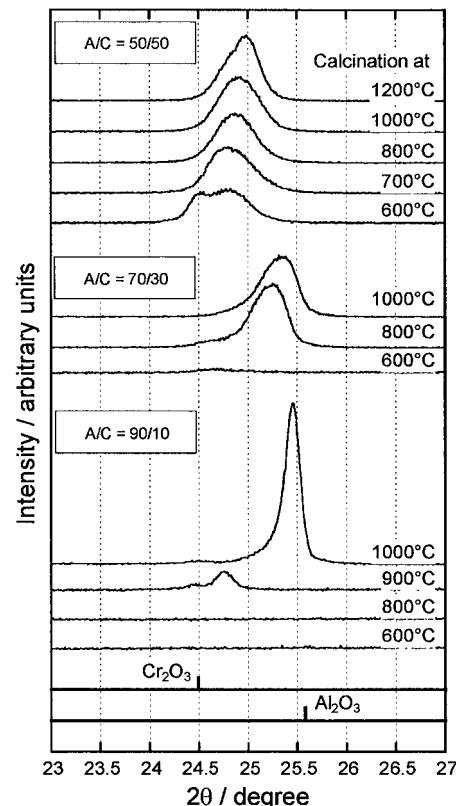


Fig. 3 XRD patterns of the sol-gel derived powders of A/C = 90/10, A/C = 70/30 and A/C = 50/50 calcined at 600–1200°C. Solid lines indicate the position of respective (012) plane in pure  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ .

as they grow and react with the surrounding  $\text{Al}_2\text{O}_3$ -rich phases. When  $\text{Cr}_2\text{O}_3$ -rich phase was formed, the remained composition must be more excessive about  $\text{Al}_2\text{O}_3$  content than the mixed composition. However, no  $\text{Al}_2\text{O}_3$  excessive XRD peaks were seen. Hence  $\text{Al}_2\text{O}_3$ -rich phases are considered to be amorphous.

Fig. 4 shows the SEM micrographs of the  $\text{A/C} = 50/50$  sol-gel derived powders calcined at  $1000^\circ\text{C}$  and  $1200^\circ\text{C}$ . There was one peak in the sample of  $\text{A/C} = 50/50$  whose critical temperature is reported to be  $1250^\circ\text{C}$ <sup>10)</sup> even when calcined at  $700^\circ\text{C}$  and  $800^\circ\text{C}$ . These powders, which were calcined at  $1000^\circ\text{C}$  and  $1200^\circ\text{C}$ , are thought to be metastable. At  $1000^\circ\text{C}$  fine particles adhere to the larger particles however at  $1200^\circ\text{C}$  the fine particles disappear and hexagonal plates with smooth surfaces are observed. This suggests that the fine particles which vanish at  $1200^\circ\text{C}$  are the  $\text{Al}_2\text{O}_3$ -rich amorphous phases.

Fig. 5 shows the lattice constants of the sol-gel derived  $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$  powders calcined at  $1000^\circ\text{C}$  for 1h. The straight line of Fig. 5 is the theoretical line of the solid solution, which is a line drawn between the lattice constants<sup>14), 15)</sup> of corundum ( $a = 0.476\text{nm}$ ,  $c = 1.295\text{nm}$ ) and eskolite ( $a = 0.496\text{nm}$ ,  $c = 1.360\text{nm}$ ). As the results in Fig. 3 show, the XRD peak of  $\text{A/C} = 70/30$  and  $\text{A/C} = 50/50$  were broader than  $\text{A/C} = 90/10$ . It is thought that, with a high  $\text{Cr}_2\text{O}_3$  content, the particles are divided into  $\text{Cr}_2\text{O}_3$ -rich crystalline and  $\text{Al}_2\text{O}_3$ -rich amorphous phases which resist unification into theoretical composition.

### 3.2 Sintering behavior of $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ system

Fig. 6 shows the relative density of  $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$  ceramics sintered at  $1600^\circ\text{C}$  in Ar and air atmospheres. As for the sample in Ar with  $\text{A/C} = 70/30$  and with  $\text{A/C} = 50/50$  prepared by the sol-gel method, the relative density increases up to 95% at all calcining temperatures. When the calcining temperature was high, relative density was low at  $\text{A/C} = 90/10$ . In the sintered bodies that were made from the powder prepared by a solid state reaction, the relative density was about 92% at all the content levels. As for the sintering atmospheres the samples sintered in air show lower density and the samples with higher  $\text{Cr}_2\text{O}_3$

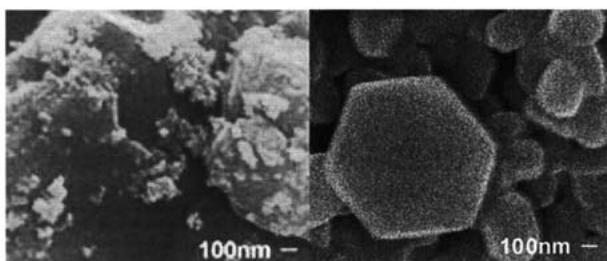


Fig. 4 SEM micrographs of the sol-gel derived powders of  $\text{A/C} = 50/50$  calcined at  $1000^\circ\text{C}$  (left) and  $1200^\circ\text{C}$  (right).

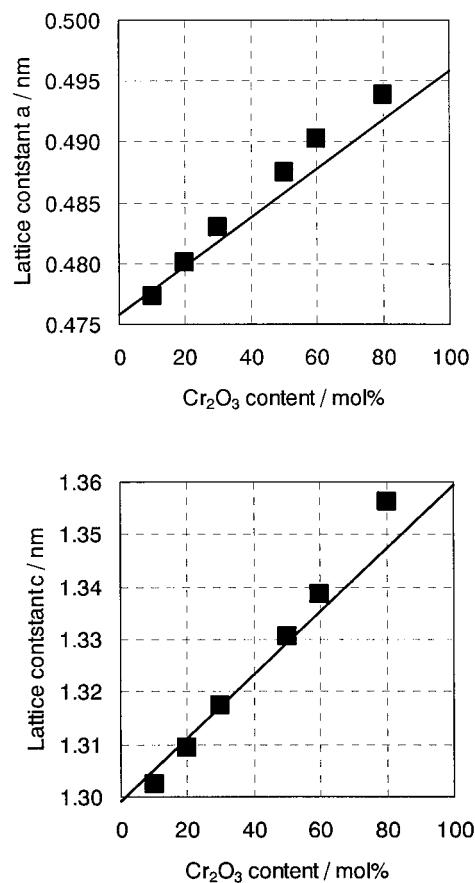


Fig. 5 Lattice parameters of the sol-gel derived powders of  $(\text{Al}, \text{Cr})_2\text{O}_3$  calcined at  $1000^\circ\text{C}$  for 1h.

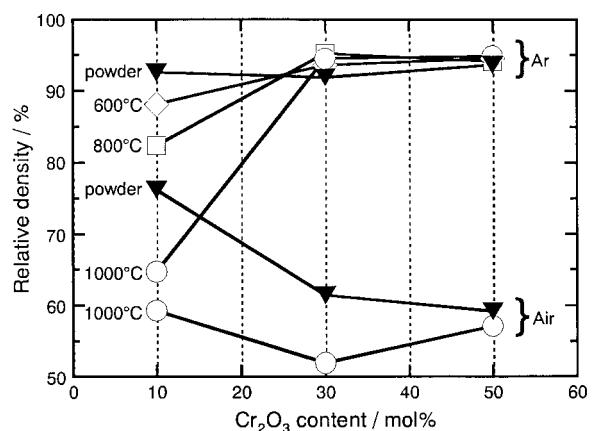


Fig. 6 Relative densities of  $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$  ceramics sintered at  $1600^\circ\text{C}$  in Ar and air atmospheres. Temperatures in the figure indicate the calcination temperature of the sol-gel derived samples. The samples prepared by the solid phase reaction are shown as "powder".

content have loosely packed structures. When the powder prepared by sol-gel method was used and calcined at  $1000^\circ\text{C}$ , the relative density of the sintered bodies was about 60% at all the  $\text{Cr}_2\text{O}_3$  content levels.

Fig. 7 shows the vapor pressure diagrams of the compounds of  $\text{Al}-\text{O}$  and  $\text{Cr}-\text{O}$  at  $1900\text{K}$ . Pressure is shown

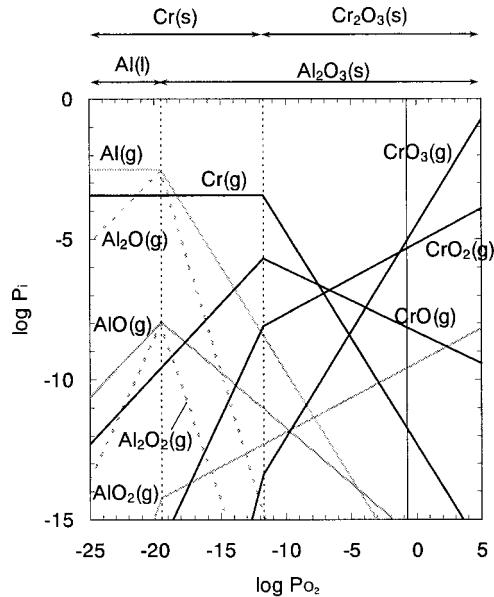


Fig. 7 Vapor pressure diagrams of Al-O and Cr-O compounds at 1900K.<sup>13)</sup>

without the dimension standardized under the standard-state pressure ( $10^5\text{Pa}$ ). None of the sample heated in air were dense. This results can be explained as follows, based on the Fig. 7.  $\text{CrO}_3(g)$  and  $\text{CrO}_2(g)$ , which partial pressure is the highest in Cr-O system, undergo high pressure increase under  $\text{O}_2$  partial pressure. In air atmosphere,  $\text{CrO}_3(g)$  partial pressure has  $\log P_{\text{CrO}_3} = -5$ . Therefore, the powder was sintered without shrinkage because of the vaporization and condensation mechanism.

Although  $\text{Cr}_2\text{O}_3$  may discharge  $\text{Cr}(g)$  under low  $P_{\text{O}_2}$  conditions, the sintered bodies did not loses weight in an Ar atmosphere nor did the metal  $\text{Cr}(s)$  separate. This suggests that the evaporation speed was very slow. Therefore dense sintered bodies were obtained in an Ar atmosphere.

Fig. 8 shows the SEM micrographs of the A/C = 90/10 samples after calcination at 1000°C and 600°C in air and after sintering at 1600°C for 1h in Ar. The particle diameter of powder calcined at 600°C was  $0.1\mu\text{m}$ , and grain growth to  $5\mu\text{m}$  was confirmed when sintered at 1600°C. The powder calcined at 1000°C had a  $5\mu\text{m}$  particle diameter which grew to  $10\mu\text{m}$  when sintered. When calcining temperature was changed to 1000°C from 600°C, grain diameter also changed from  $5\mu\text{m}$  from  $0.1\mu\text{m}$ . This is the result of unusual grain growth during calcination. In the A/C = 90/10 samples the relative density of the final products decreased with an increase in calcination temperature.

Fig. 9 shows the microstructure of the sol-gel derived  $\text{Al}_2\text{O}_3$ - $\text{Cr}_2\text{O}_3$  ceramics sintered at 1600°C in Ar after the calcination at 600°C. The particle size increases with increasing  $\text{Cr}_2\text{O}_3$  content. This tendency was also seen in

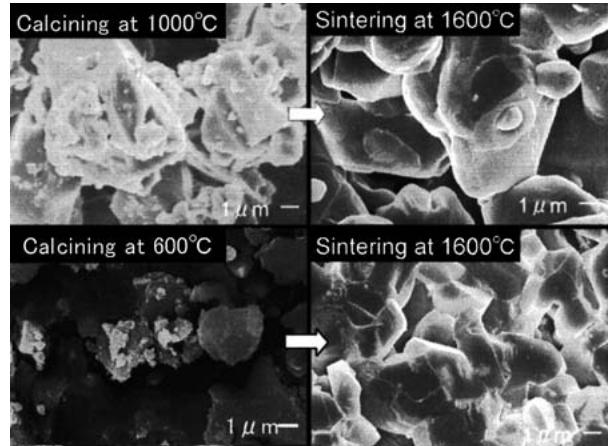


Fig. 8 SEM micrographs of the A/C = 90/10 samples after the calcination at 1000°C and 600°C in air and after sintering at 1600°C for 1h in Ar.

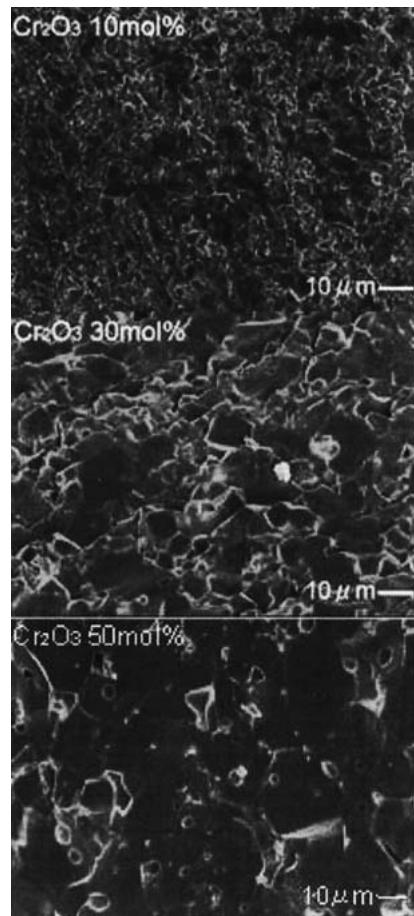


Fig. 9 SEM micrographs of the sol-gel derived  $\text{Al}_2\text{O}_3$ - $\text{Cr}_2\text{O}_3$  ceramics sintered at 1600°C in Ar after the calcination at 600°C.

the sintered bodies made from the powder prepared by the solid state reaction.

Fig. 10 shows a relation between the grain size of the calcined powder and the relative density of the sintered body at 1600°C in Ar by the sol-gel method. For the A/C = 50/50 samples, the relative density was 95% and the

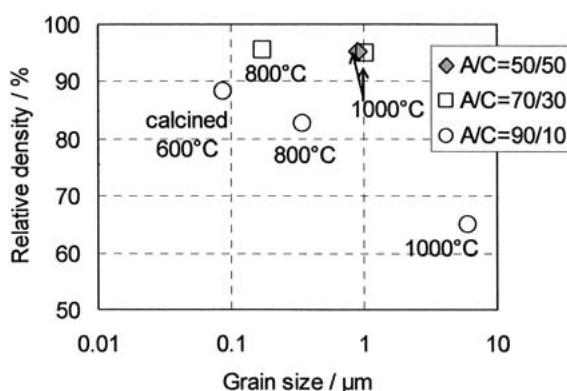


Fig. 10 Relation between grain size of calcined powder and relative density of body sintered at 1600°C in Ar by sol-gel method.

grain size of the powder calcined at 1000°C was 1 μm. For the A/C = 70/30 samples, the relative density was 95% and the grain size of the powder calcined at 1000°C was 1 μm and at 800°C was 0.2 μm. In the A/C = 90/10 sample, the relative density increased in inverse proportion to the logarithmic grain size. This tendency was very different from that for A/C = 30/70 and 50/50. The separated phase state of the calcined powder was divided into Cr<sub>2</sub>O<sub>3</sub>-rich crystalline and Al<sub>2</sub>O<sub>3</sub>-rich amorphous phases. This is considered to be the cause for dense sintering to proceed.

#### 4 Conclusions

Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> ceramics were prepared by the sol-gel method and the formation mechanism of solid solution and the sintering process were examined.

- (1) The composition of the crystallized phases changes with the calcined temperature.
- (2) Cr<sub>2</sub>O<sub>3</sub>-rich solid solution firstly crystallize at low temperature and the composition of the crystallites changes as they grow and react with the surrounding Al<sub>2</sub>O<sub>3</sub>-rich phase.
- (3) Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> precursor becomes much denser when sintered at 1600°C in Ar.
- (4) A dense sintered body was obtained when abnormal grains did not grow when calcining occurred.

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