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# Sintering behavior of $Cr_2O_3$–$Al_2O_3$ ceramics

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## Abstract

We investigated the sintering behavior of $Cr_2O_3$–$Al_2O_3$ ceramic materials. In our observation of the isothermal shrinkage behavior of $Cr_2O_3$–$Al_2O_3$ ceramic, the activation energy of sintering reaction was measured to be 102 kJ/mol, that is, the near value of the activation energy of diffusion of Al ions in $Al_2O_3$ single crystal. Therefore the diffusion of cations is believed to control the sintering behavior of this material. With the addition of $TiO_2$, (the compound chosen to accelerate the diffusion of cations) to $Cr_2O_3$–$Al_2O_3$, the sintering behavior was accelerated.

*Keywords:* $Al_2O_3$–$Cr_2O_3$; Microstructure-final; Sintering

## 1. Introduction

Due to their low solubility in molten salts formed in energy plants[1] such as $V_2O_5$ and $Na_2SO_4$, $Cr_2O_3$–$Al_2O_3$ are expected to possess superior corrosion resistance against these molten salts.[2] The corrosion resistance of ceramics is believed to depend not only on their solubility, but also on the relative density of the sintered body.[3] Therefore it is necessary to obtain $Cr_2O_3$–$Al_2O_3$ ceramics with dense sintered bodies. $Cr_2O_3$ and $Al_2O_3$ forms solid solutions over the entire range of composition, indicated in Fig. 1.[4] So, we can obtain specimens with any composition.

$Cr_2O_3$ is not stable and changes to $CrO_3$ in an atmosphere whose oxygen partial pressure is relatively high such as air.[5] $CrO_3$ exhibits a high vapor pressure, so it is difficult to obtain a dense sintered body of $Cr_2O_3$ in an air atmosphere.[5] In order to obtain a dense sintered body of $Cr_2O_3$, the sintering should be performed in an atmosphere with a low oxygen partial pressure in which $Cr_2O_3$ remains stable.[6] In an investigation with $Cr_2O_3$–$Al_2O_3$ ceramics, Uematsu et al.[7] have shown that the sintering of these ceramics in an atmosphere with a controlled pressure is effective in increasing relative density, especially for those with a high $Cr_2O_3$ content of 10 mol% or more. They sintered $Cr_2O_3$–$Al_2O_3$ ceramics in a $H_2$ atmosphere and obtained a relative density of 90% for alloys with a $Cr_2O_3$ content of 10 mol% or more. They mentioned that with a $Cr_2O_3$ content of 10 mol% or less, relative density did not increase up to 85%.

Yamaguchi et al.[8] have shown that the relative densities of $Cr_2O_3$–$Al_2O_3$ ceramics with a $Cr_2O_3$ content of 90 mol% or more increase up to 95% when they are sintered in the carbon powder. They also mentioned that with a $Cr_2O_3$ content of 85 mol% or less, relative density did not increase up to 90%.

In the present work, we investigated the sintering behavior of $Cr_2O_3$–$Al_2O_3$ ceramics in various atmospheres. Next, we looked at the effect of the addition of $TiO_2$ as a sintering aid in order to obtain a dense sintered body with a relative density of 95% or more for all $Cr_2O_3$ contents.

## 2. Experimental procedures

The raw powders used were $Cr_2O_3$ (Nihon Kagaku Kogyo Ltd.; $\alpha$-$Cr_2O_3$; purity, 99%; average particle size, 0.2 μm), $Al_2O_3$ (Showa Denko Ltd.; $\alpha$-$Al_2O_3$; purity, 99.9%; average particle size, 0.2 μm), and $TiO_2$ (synthesized from Ti alchoxide; average particle size, 0.02 μm). These powders were mixed by ball-milling in ethanol for 100 h with small amounts of additives for homogeneous mixing. Then, the powder–ethanol mixture was dried in an oven at 80°C. The derived powder

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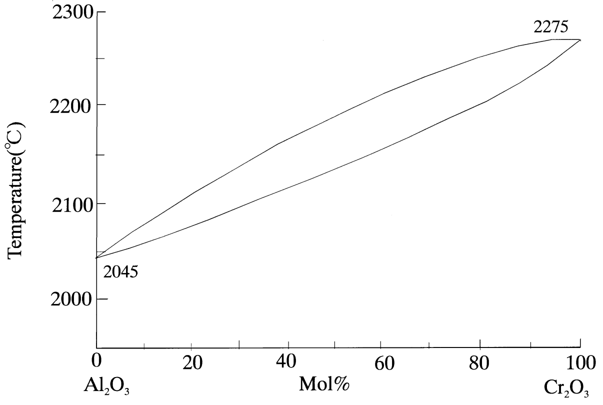

Fig. 1. Phase relationship between $Cr_2O_3$ and $Al_2O_3$.

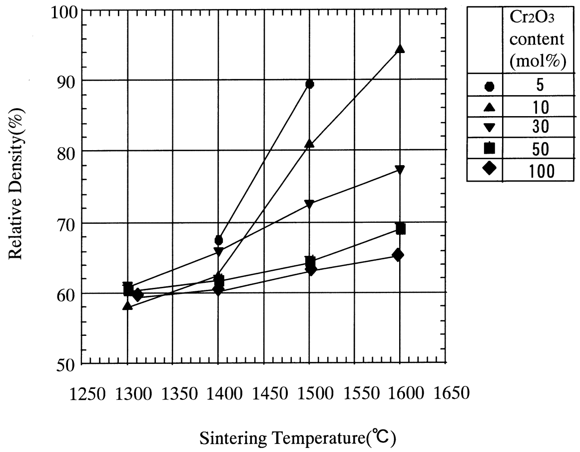

Fig. 2. Relationship between the relative densities of $Cr_2O_3$–$Al_2O_3$ ceramics and the sintering temperature (in air).

was pressed into disks of about 20 mm in diameter and 5 mm in thickness. These compacts were sintered for 3 h at various temperatures in both air and a vacuum. The densities of the sintered bodies were derived from their weights and volumes. The relative densities were calculated using the calculated values derived from the composition of the sintered bodies and the theoretical density of $Cr_2O_3$, $Al_2O_3$, and $TiO_2$ (5.22, 3.98, and 4.70 g/cc, respectively).

The isothermal shrinkage behavior was measured by a thermal mechanical analyzer (TMA, Shinagawa Shiro Renga Ltd., Model: SL-1600B) at various temperatures in both air and a vacuum. The phases included in the sintered bodies were examined by XRD (Rigaku Ltd., Model: Rotaflex RU-300, operating conditions: 40 kV, 100 mA). The microstructures of the specimens were observed by an optical microscope (OM, Olympus Ltd., Model: VANOX-T) and a scanning electron microscope (SEM, JEOL Ltd., Model: JSM-T330A).

## 3. Results and discussion

Fig. 2 shows the relationship between the sintering temperature and the relative density of $Cr_2O_3$–$Al_2O_3$ ceramics sintered in air. The relative density of a $Cr_2O_3$–$Al_2O_3$ ceramic with a low $Cr_2O_3$ content increases when the sintering temperature increases. At a temperature of 1600°C it exhibits a relative density of 95%. Whereas, as the $Cr_2O_3$ content increases, the relative density of the $Cr_2O_3$–$Al_2O_3$ ceramic decreases. When the $Cr_2O_3$ content becomes 50 mol% or more, the sintered bodies do not become dense in air. Therefore the presence of $Cr_2O_3$ is believed to prevent the densification of $Cr_2O_3$–$Al_2O_3$ compact. It was shown that pure $Cr_2O_3$ does not become dense because its sintering mechanism is the vaporization and condensation of $Cr_2O_3$.[5]

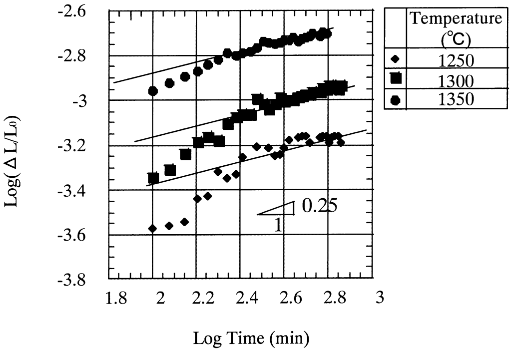

Fig. 3. Isothermal shrinkage behavior of 50 mol% $Cr_2O_3$–$Al_2O_3$ in an air.

Fig. 3 shows the isothermal shrinkage behavior of 50 mol%$Cr_2O_3$–$Al_2O_3$ in air. The shrinkages have the initial curved portion, indicated by Moriyoshi et al.[9] Then, the shrinkages are proportional to the time raised to the power of 0.25, which indicates that the grain boundary diffusion of the ions controls the sintering behavior.[10] Photo 1 shows scanning electron micrographs of the $Cr_2O_3$–$Al_2O_3$ powder before and after the heat treatment at a temperature of 1400°C in air. After heat treatment, a remarkable dimension change was observed without any shrinkage. We consider that this coarsening of $Cr_2O_3$–$Al_2O_3$ powder prevents densification of $Cr_2O_3$–$Al_2O_3$ compact bodies. It was shown that $Cr_2O_3$ changes to $CrO_3$ at high temperatures in air and that the $CrO_3$ would then vaporize because of the high partial pressure of the $CrO_3$.[5] As for $Cr_2O_3$–$Al_2O_3$, the vapor pressure becomes higher than that of $Al_2O_3$ because of the high $CrO_3$ vapor pressure.[11] Therefore, we consider that the vaporization and condensation of $Cr_2O_3$–$Al_2O_3$ will coarsen $Cr_2O_3$–$Al_2O_3$ powder, when it is heated in air. Therefore, under a condition in which

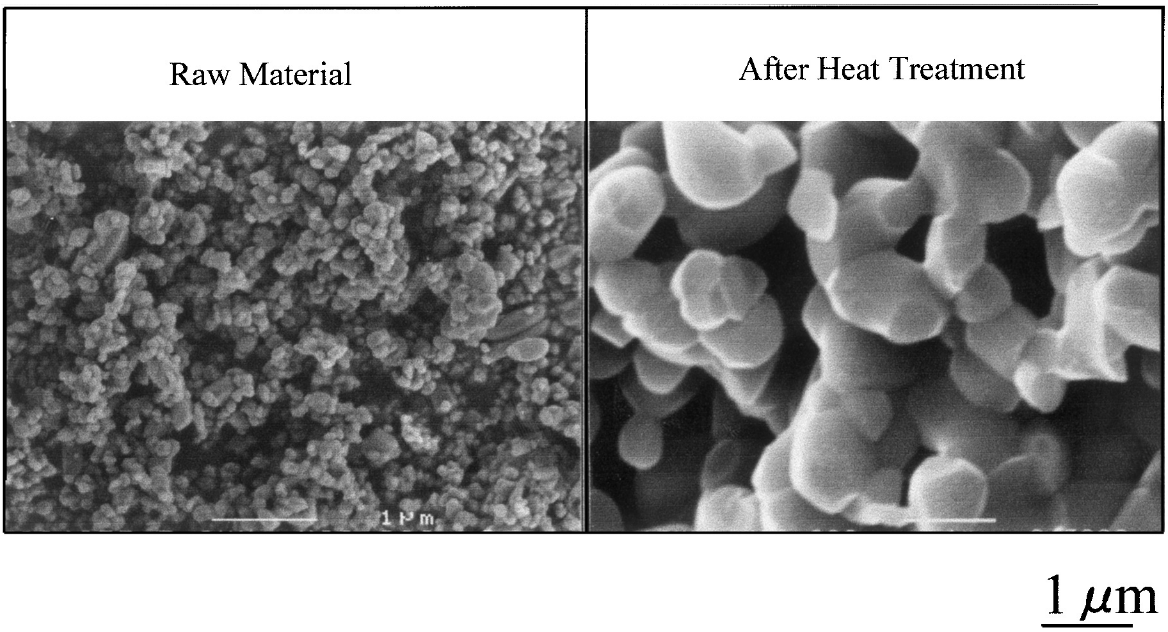

Photo 1. Dimension change of 50 mol% $Cr_2O_3$–$Al_2O_3$ powder during heat treatment (temperature, 1450°C; holding time, 3 h; atmosphere, air).

the $Cr_2O_3$ is stable, we can obtain dense $Cr_2O_3$–$Al_2O_3$ sintered bodies.

Fig. 4 shows the relationship between sintering temperature and relative density of $Cr_2O_3$–$Al_2O_3$ ceramic sintered in a vacuum. At all $Cr_2O_3$ contents, the relative density increases up to 95%. Photo 2 shows the microstructures of $Cr_2O_3$–$Al_2O_3$ ceramics sintered at 1550°C. We can observe hardly any pores in the sintered bodies. $Cr_2O_3$–$Al_2O_3$ compact bodies were sintered in a furnace with carbon heating elements in the vacuum. Since the total pressure of gases is about $10^{-2}$ Torr and oxygen is removed by the carbon of the heating elements of the furnace, the oxygen partial pressure seems very low. So, in this vacuum the $Cr_2O_3$ is considered to be stable and coarsening of the $Cr_2O_3$ powder is prevented.

Fig. 5 shows the isothermal shrinkage behavior of the 50 mol% $Cr_2O_3$–$Al_2O_3$ compact in a vacuum at various temperatures. The dependence of shrinkage on heating time has a slope of 0.25, i.e. the same as that of the isothermal shrinkage behavior in the air atmosphere. Therefore the same process can be assumed to control the sintering behavior in both the air and vacuum and this process is prevented by the coarsening of $Cr_2O_3$–$Al_2O_3$ in air. Fig. 6 shows the dependence of the rate constant of the sintering behavior on the reciprocal of the temperature. The activation energy of the sintering process derived from this figure is 102 kJ/mol. This value is almost the same as that of the diffusion of Al ions in $Al_2O_3$ lattice.[12]

Therefore we assume that the diffusion of cations controls the sintering process of $Cr_2O_3$–$Al_2O_3$ ceramics. That is, by accelerating the diffusion of cations, we can obtain a denser sintered body of $Cr_2O_3$–$Al_2O_3$ ceramic. In order to accelerate the diffusion of cations, we need to increase cation vacancies. As a means to do so, the addition of impurities with cations of larger valences is well known to be effective.[13] As an additive, we chose $TiO_2$ which has cations of four plus valence.

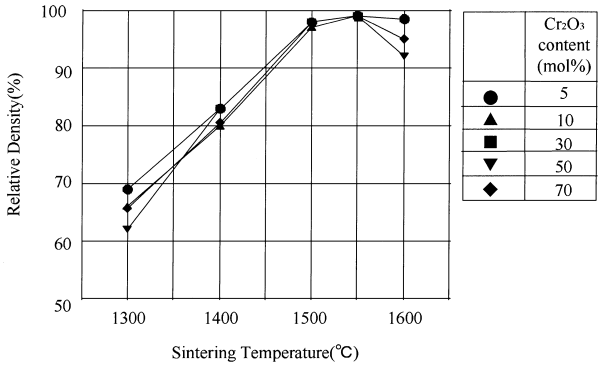

Fig. 4. Relationship between the relative densities of $Cr_2O_3$–$Al_2O_3$ ceramics and the sintering temperature (in a vacuum).

Fig. 7 shows the relationship between the relative density of $Cr_2O_3$–$Al_2O_3$ with $TiO_2$ and the sintering temperature. The addition of $TiO_2$ to $Cr_2O_3$–$Al_2O_3$ decreases the temperature for densification about 100°C compared to that of $Cr_2O_3$–$Al_2O_3$. W. D. Callister et al. showed that the densification of $Cr_2O_3$ promoted by adding $TiO_2$.[14] They assumed the creation of cation vacancies enhanced the densification of $Cr_2O_3$. In this

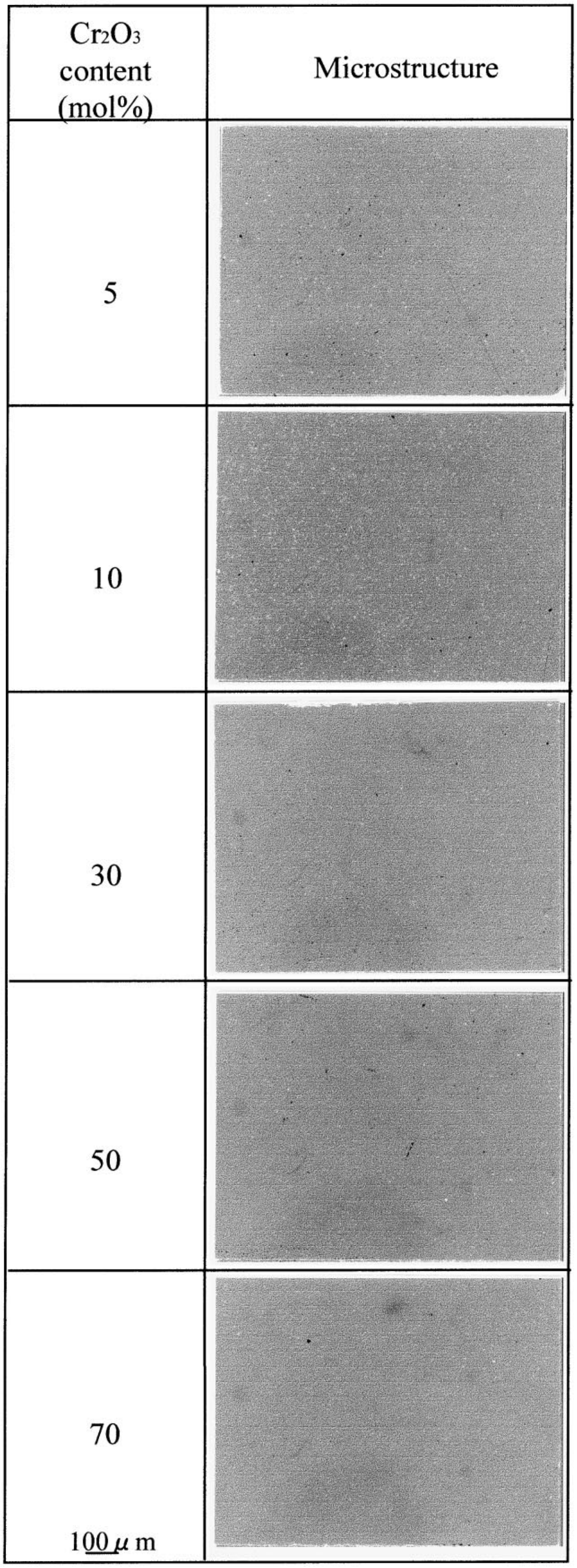

Photo 2. Microstructures of $Cr_2O_3$–$Al_2O_3$ ceramics sintered in a vacuum at 1550°C.

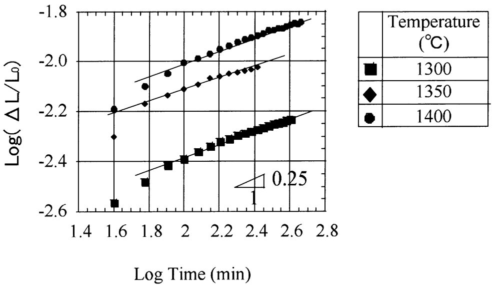

Fig. 5. Isothermal shrinkage behavior of 50 mol% $Cr_2O_3$–$Al_2O_3$ in a vacuum.

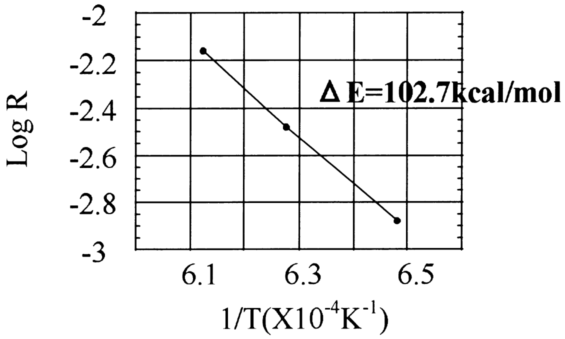

Fig. 6. Dependence of the rate constant on temperature (50 mol% $Cr_2O_3$–$Al_2O_3$; atmosphere: vacuum; $\Delta E$ denotes the activation energy of sintering).

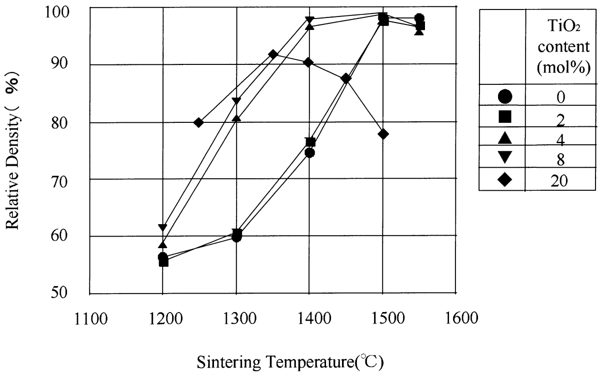

Fig. 7. Relationship between sintering temperatures and the relative density of 50 mol% $Cr_2O_3$–$Al_2O_3$ ceramics with constituent $TiO_2$ as a sintering aid (in a vacuum).

work, it is also considered that cation vacancies were made by adding $TiO_2$ to $Cr_2O_3$–$Al_2O_3$ and the $Cr_2O_3$–$Al_2O_3$ ceramics were then thought to become the dense sintered bodies at the lower temperature. Relative density increases up to 8 mol% $TiO_2$. When 20 mol% $TiO_2$ is added, the relative density decreases. Fig. 8 shows XRD (X-ray diffraction) pattern of sintered bodies with 0, 4, 8 and 20 mol% $TiO_2$. From 0 to 8 mol%$TiO_2$, the XRD pattern exhibits peaks only from $Cr_2O_3$–$Al_2O_3$. However, in the sintered body with 20 mol% $TiO_2$, peaks are observed from $(Al,Cr)_2Ti_7O_{15}$. Therefore the formation of $(Al,Cr)_2O_3$–$TiO_2$ compound is believed to prevent the densification of $Cr_2O_3$–$Al_2O_3$ compacts.

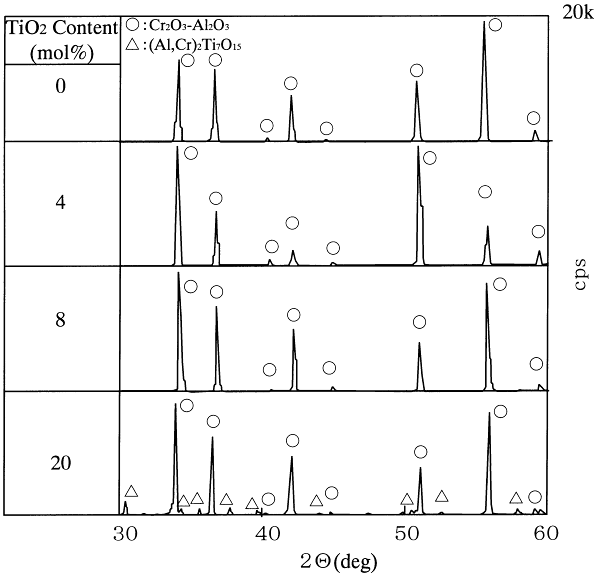

Fig. 8. Dependence of the X-ray diffraction pattern of 50 mol% $Cr_2O_3$–$Al_2O_3$ ceramics on $TiO_2$ content.

## 4. Conclusions

In this work, we investigated the sintering behavior of $Cr_2O_3$–$Al_2O_3$ ceramics in various atmospheres. We obtained the following results:

1. In the air atmosphere, $Cr_2O_3$–$Al_2O_3$ ceramic exhibits remarkable coarsening of its particles at sintering temperatures due to vaporization and condensation of $Cr_2O_3$. Therefore we cannot obtain a dense $Cr_2O_3$–$Al_2O_3$ sintered body under this condition.
2. In our observation of the isothermal shrinkage behavior of $Cr_2O_3$–$Al_2O_3$ ceramic in a vacuum, the activation energy of the sintering reaction was 102 kJ/mol. Since this value is almost equal to the activation energy of diffusion of Al ions in $Al_2O_3$ single crystal, the diffusion of cations is believed to control the sintering behavior of this material.
3. With the addition of $TiO_2$, the compound chosen to accelerate the diffusion of cation, to $Cr_2O_3$–$Al_2O_3$, the sintering behavior was accelerated.
4. Adding $TiO_2$ up to 8 mol% accelerated the shrinkage at lower temperatures. When the $TiO_2$ content became higher than 20 mol%, the relative density of the sintered body decreased due to formation of $(Al, Cr)_2O_3$–$TiO_2$ compound.

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