Effect of Liquid Phase on Sintering of Magnesium Oxide with Zirconium Diphosphate Addition

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The sintering of MgO with ZrP_2O_7 additions in the concentrations of 0.1, 0.5, 1.0 and 3.0 mol% was studied in the presence of the liquid phase at increasing temperatures (room temperature to 1450°C) and at a constant temperature (1450°C , 5 h). The densification of the MgO compact was inhibited above 1300°C by the addition of 1.0 mol% or less of ZrP_2O_7 , whereas it was promoted by 3.0 mol% ZrP_2O_7 addition. The difference in the densification behavior was considered to be due to variations in the amount of the liquid phase present in the MgO- $\text{Mg}_3(\text{PO}_4)_2$ system above 1300°C : an amount of the liquid phase sufficient to spread over the grains promoted the densification of the MgO compact through accelerating the rearrangement of the grains and through eliminating the open pores.

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ニリン酸ジルコニウムを添加した酸化マグネシウムの 焼結に及ぼす液相の影響

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ZrP_2O_7 を 0.1 mol%, 0.5 mol%, 1.0 mol% 及び 3.0 mol% の濃度で添加した MgO 試験片について、液相が存在するときの焼結挙動を昇温法 (室温 $\sim 1450^\circ\text{C}$) 及び定温法 (1450°C , 5 h) によって検討した。

MgO の密化は ZrP_2O_7 が 1.0 mol% 以下の添加量において 1300°C 以上で抑制されたが、3.0 mol% 添加試料においてそれは促進された。MgO の密化挙動が ZrP_2O_7 の添加量によって異なるのは 1300°C 以上で生成する MgO- $\text{Mg}_3(\text{PO}_4)_2$ 系液相量の違いによるものと考えられた。すなわち、粒子全体を被覆した液相が粒子の再配列をうながし開放気孔を減少させるために、MgO の密化が促進されることが分った。

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1. Introduction

Magnesium oxide (MgO) is often used practically as a representative basic refractory. MgO refractories are generally produced with a small amount of additive introduced for the purpose of promoting the densification¹⁾.

Phosphoric acid (H_3PO_4) is well-known as a typical phosphate additive; however, it can not be used for the MgO refractory because of a violent reaction of MgO with H_3PO_4 ²⁾. Instead

of H_3PO_4 , therefore, metal phosphates and metal acid phosphates are employed for additives³⁾⁻⁵⁾.

The authors have already been investigated the effects of some metal diphosphates, such as $\text{Mg}_2\text{P}_2\text{O}_7$, $\text{Ca}_2\text{P}_2\text{O}_7$, SiP_2O_7 and ZrP_2O_7 , on the sintering of MgO⁶⁾⁻⁸⁾. The densification of MgO was promoted with the above diphosphates addition via (1) mass transfer accelerated by the reaction between MgO and an additive and

(2) the liquid phase formed by the fusion of the reaction products.

In our previous papers, the sintering of MgO with ZrP_2O_7 addition was investigated up to 1300°C ⁶⁾. In the MgO- ZrP_2O_7 system, however, an appreciable amount of liquid is expected to form above 1300°C .

The purpose of this study is to clarify the role of the liquid phase on the sintering of MgO with ZrP_2O_7 addition in the temperature region of 1300°C to 1450°C .

2. Experimental

2.1 Materials and sample preparations

MgO was obtained by heating $\text{Mg}(\text{OH})_2$ (Kanto Chemicals Co., Inc.) at 900°C for 1 h. ZrP_2O_7 was prepared as follows⁶⁾: $\text{ZrO}(\text{NO}_3)_2$ solution was mixed with a little excess of H_3PO_4 (85%) to form a zirconium bis (hydrogen phosphate) hydrate ($\text{Zr}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$). The product was then heated at 1050°C for 5 h to obtain ZrP_2O_7 .

ZrP_2O_7 was mixed with MgO in the concentrations of 0, 0.1, 0.5, 1.0 and 3.0 mol%: part of the obtained mixture was pressed into disks (5 mm diam. and 3 mm high) at $3000 \text{ kg} \cdot \text{cm}^{-2}$, and part into rectangular solids (7 mm by 10 mm by 70 mm) at $500 \text{ kg} \cdot \text{cm}^{-2}$. The former were used for the measurements of shrinkages and the latter for the measurements of other properties.

2.2 Shrinkages

Shrinkages of MgO compacts with ZrP_2O_7 addition were measured by using a dilatometer from room temperature up to 1450°C at increasing temperatures of $10^\circ\text{C} \cdot \text{min}^{-1}$ in air. Differential thermal analysis (DTA) was also carried out under the same heating conditions.

2.3 Relative density and porosities

MgO compacts with various amounts of ZrP_2O_7 addition were placed on platinum foils and inserted into an electric furnace (SiC). They were heated at 1450°C for 5 h and then were quenched to room temperature.

The relative density, the total porosity, the open porosity and the closed porosity of sintered samples were determined by the conventional methods reported previously^{9), 10)}.

2.4 Phase identification

The crystalline phases formed during sintering were identified by using powder X-ray diffractometry with Ni-filtered Cu $K\alpha$ radiation,

operating at 40 kV and 30 mA.

2.5 SEM observation and EPMA

The observation of scanning electron microscopy (SEM) and electron probe X-ray microanalysis (EPMA) for sintered samples were performed under the conditions reported previously⁷⁾. Samples for SEM observations were etched by concentrated HNO_3 at 0°C for 90 minutes.

3. Results and discussion

3.1 Densification process of MgO with ZrP_2O_7 addition

It is important to make clear the relationship between the phase changes and the densification during sintering.

We have reported that MgO reacted with ZrP_2O_7 to form monoclinic ZrO_2 , tetragonal ZrO_2 and $\text{Mg}_3(\text{PO}_4)_2$ from 900°C to 1300°C . Figure 1 shows the X-ray diffraction pattern of MgO with 3.0 mol% ZrP_2O_7 addition sintered at 1450°C for 5 h. Two kinds of products were observed: cubic ZrO_2 and $\text{Mg}_3(\text{PO}_4)_2$. The lattice constant of the cubic ZrO_2 was about $5.076 \text{ \AA}$, which is in good accord with that of the ZrO_2 stabilized by MgO ¹¹⁾. The presence of the cubic ZrO_2 is therefore considered to be due to the solid-solution of MgO into ZrO_2 .

The DTA curve of MgO with 3.0 mol% ZrP_2O_7 addition showed weak endothermic effects at $1172^\circ\text{--}1295^\circ\text{C}$ and $1394^\circ\text{--}1418^\circ\text{C}$. From the phase diagram of MgO- P_2O_5 system¹²⁾ the first endothermic effect is attributable to the formation of the liquid phase in the $\text{Mg}(\text{PO}_3)_2\text{--Mg}_2\text{P}_2\text{O}_7$ system and the second effect to the formation of the liquid phase in the $\text{MgO--Mg}_3(\text{PO}_4)_2$ system. In these systems, the crystalline compounds of both $\text{Mg}(\text{PO}_3)_2$ and $\text{Mg}_2\text{P}_2\text{O}_7$ could not be detected by X-ray

Fig. 1. Powder X-ray diffraction pattern of MgO with 3.0 mol% ZrP_2O_7 addition heated at 1450°C for 5 h.

● : MgO, ▲ : ZrO_2 (cubic), □ : $\text{Mg}_3(\text{PO}_4)_2$

Fig. 2. Isothermal shrinkage curves of MgO compacts with various amounts of ZrP_2O_7 added (heating rate: $10^\circ\text{C} \cdot \text{min}^{-1}$).

diffractometry. It seems that the amounts of those compounds are too small to be detected by the X-ray diffractometry and/or that an amorphous phase whose composition ratio of $\text{MgO}/\text{P}_2\text{O}_5$ is 1 to 2 may be present.

Figure 2 shows the isothermal shrinkage curves of MgO compacts with various amounts of ZrP_2O_7 addition. Up to 1300°C , little effect of ZrP_2O_7 addition on the shrinkage behavior of the MgO compact was detected. However, further heating promoted the densification of the MgO compact with 3.0 mol% ZrP_2O_7 addition.

From the SEM observation an appreciable amount of the liquid phase was observed to be formed above 1300°C . The liquid phase formed in this temperature region may consist of MgO and $\text{Mg}_3(\text{PO}_4)_2$ ¹²⁾. Thus the densification of the MgO compact is found to be promoted by the liquid phase in the MgO- $\text{Mg}_3(\text{PO}_4)_2$ system.

3.2 Changes in the relative density and porosities

Figure 3 shows the relative density, the total porosity, the open porosity and the closed porosity of MgO compacts, with various amounts of ZrP_2O_7 added, sintered at 1450°C for 5 h.

The relative density of MgO decreased with an increase in the amount of additive from 0 to 0.5 mol%, whereas it increased with a further increase in the amount of additive up to 3.0 mol%. The change of the total porosity is contrary to that of the relative density: the total porosity of MgO showed a maximum value at 0.5 mol% ZrP_2O_7 addition. A similar result was also obtained in the measurement of the open

Fig. 3. Changes of relative density and porosities of MgO compacts, with various amounts of ZrP_2O_7 added, sintered at 1450°C for 5 h.

○: Total porosity, ◐: Open porosity, ●: Closed porosity

porosity. The closed porosity appeared to show a slight reduction with increasing the amount of additive.

A behavior similar to this swelling may be observed when small amounts of the liquid which formed during sintering have a high wetting angle¹³⁾. An increase in the liquid contents promotes the rearrangement of grains which leads to a closer packing¹³⁾. Therefore, a marked effect of the rearrangement of the grains may be expected for the sintering of MgO with 3.0 mol% ZrP_2O_7 addition. In addition, the change of the total porosity is found to be affected more by changes of the open porosity than by changes of the closed porosity. The EPMA showed that Zr and P concentrated in the region of the grain boundaries in the case of 3.0 mol% ZrP_2O_7 addition. It can be said from these results that the liquid phase does not contribute to the elimination of the open pores until it surrounds the grains by adding 3.0 mol% ZrP_2O_7 .

Figure 4 shows the etched surfaces of pure MgO compact and of the MgO compact with 3.0 mol% ZrP_2O_7 addition sintered at 1450°C for 5 h. The photograph (a) of the pure MgO revealed that the grains had irregular shapes and were about $10\text{--}20\ \mu\text{m}$ in size. Pores whose mean diameter was about $5\ \mu\text{m}$ were located at the grain boundaries and in the bulk of the grains. The photograph (b) of MgO with 3.0 mol%

Fig. 4. Etched surfaces of (a) MgO compact and (b) MgO compact with 3.0 mol% ZrP_2O_7 addition sintered at 1450°C for 5 h.

ZrP_2O_7 addition showed that smaller grains were present in the intergranular regions between larger grains, to give a closer packing. Few pores were located in the bulk of the grains.

As shown in Fig. 4, the liquid phase promotes the rearrangement of the grains, which also contributes to the elimination of pores. In addition, the solution and precipitation of grains is considered to take place simultaneously in the presence of the liquid phase¹⁴⁾. This process will continue until the smaller grains disappear and will produce uniform grains¹⁴⁾.

4. Conclusion

The sintering of MgO with ZrP_2O_7 addition was studied in the presence of the liquid phase at and below 1450°C .

The densification of MgO was affected by the ZrP_2O_7 addition above 1300°C : the densification was inhibited by the addition of 1.0 mol% or less ZrP_2O_7 , whereas it was promoted by the further increase in the amount of additive up to 3.0 mol%.

The liquid phase in the $\text{MgO-Mg}_3(\text{PO}_4)_2$ system was formed above 1300°C : it did not contribute to the densification of the MgO compact until the liquid surrounded the grains. A large amount of the liquid had an appreciable effect on the rearrangement of MgO grains and on the elimination of open pores.

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