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Formation mechanism of $ZrSiO_4$ powders

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The formation mechanism of $ZrSiO_4$ powders from ZrO_2 and colloidal SiO_2 sols has been studied. The change in the $ZrSiO_4$ yield rate with seeding and non-seeding has also been investigated. The induction period of the $ZrSiO_4$ yield-rate curve corresponded to the $n = 1$ region, a simple nucleation region, on the Avrami plot. The $n = 1$ region was a rather wide range at 1200–1300 °C and the nucleation reaction was promoted in this temperature range. It was found that the $ZrSiO_4$ yield rate became high, even if seeding was not used, when the heating rate was controlled at less than 1 °C min^{-1}.

1. Introduction

Zircon ($ZrSiO_4$) is an oxide ceramic material known for its low thermal expansion coefficient [1]. $ZrSiO_4$ sintered bodies are used as refractories [2–4], developed for use under severe conditions, such as elevated temperatures. However, it is well known that the preparation of high-purity $ZrSiO_4$ powder is very difficult, because $ZrSiO_4$ is composed of only Si/Zr molar ratio = 1.0.

A few researchers have discussed the preparation of high-purity $ZrSiO_4$ powder. Komarneni and Roy [5] reviewed the synthesis process of $ZrSiO_4$, including the sol–gel and hydrothermal methods. Suzuki and Kanno [6–10] discussed the formation process by way of the sol–gel method. We have investigated the preparation method of high-purity $ZrSiO_4$ powders [11], and found that the $ZrSiO_4$ precursor with a Zr–O–Si bond was produced, and that single-phase $ZrSiO_4$ powder could be prepared using $ZrOCl_2 \cdot 8H_2O$ and SiO_2 sol.

In the present work, the preparation method of high-purity $ZrSiO_4$ powder without $ZrSiO_4$ precursor was examined and the formation mechanism of the powder is discussed here.

2. Experimental procedure

ZrO_2 sol (containing 20 wt % ZrO_2, Nissan Kagaku, Chiba, Japan) and colloidal SiO_2 sol (Snowtex-O, containing 20 wt % SiO_2, Nissan Kagaku, Chiba, Japan) were used as starting materials. The solution of each starting material was adjusted to pH = 5 with ammonia water as this was the optimum pH required to mix ZrO_2 and SiO_2 sols uniformly; the difference between ζ-potential of the ZrO_2 and SiO_2 solutions was greatest above that pH, the former being positive while the latter was negative.

These solutions were mixed in a separable flask for 24 h to produce an equimolar mixture solution. The mixture was dried and 1 wt % commercial $ZrSiO_4$ (purified zircon sand, purity 98%, Kojundo Kagaku Kenkyusho, Saitama, Japan) was added as a seed and then ball-milled for 24 h with ethanol. The resultant slurry was subsequently dried in the evaporator to form the starting powder. It was heated to 700 °C at 20 °C min^{-1} and then up to a given temperature (1200–1400 °C) at 0.15–10 °C min^{-1}, at which it was held for 20 min. The yield for the calcined $ZrSiO_4$ powders was determined using X-ray diffractometry. The four peaks appearing at a diffraction angle 2θ in the range 26°–32° in the X-ray diffraction patterns related to $ZrSiO_4(2 0 0)$, m-$ZrO_2(1 1 1, 1 1 -1)$, t-$ZrO_2(1 0 1)$ planes, were used as standards to determine the relative intensity from each peak, and then the yield, α_{ZrSiO_4}, was calculated using the equation

$$\alpha_{ZrSiO_4} = I_{ZR}(2 0 0)/[I_{ZR}(2 0 0) + I_M(1 1 1) + I_M(1 1 -1) + I_T(1 0 1)] \quad (1)$$

where subscripts ZR, M and T stand for $ZrSiO_4$, m-ZrO_2 and t-ZrO_2, respectively. The numbers in parentheses indicate the plane index.

3. Results and discussion

Fig. 1 shows relation between holding time and $ZrSiO_4$ yield rate, α_{ZrSiO_4}, at 1300 °C, at the heating rate of 1.25 °C min^{-1}, with and without seeding. The $ZrSiO_4$ yield increased with increasing holding time in each case. Vilmin *et al.* [12] reported that $ZrSiO_4$ preparation was affected by seeding. Therefore, in order to research the formation mechanism of $ZrSiO_4$, the nucleation behaviour was investigated with and without seeding. Fig. 2 shows the relation between holding time and $ZrSiO_4$ yield rate at 1200–1400 °C without seeding, at a heating rate of 1.25 °C min^{-1}. The $ZrSiO_4$ yield rate increased with increasing hold-

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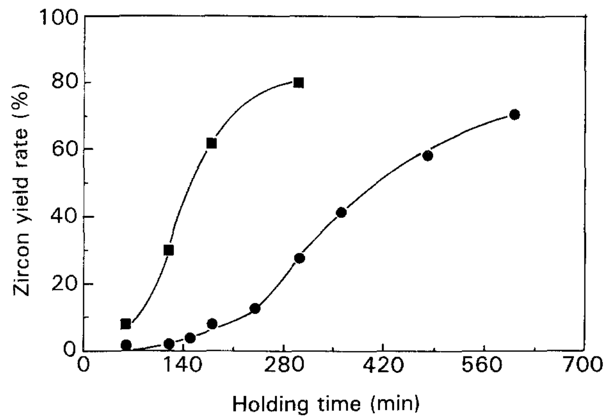

Figure 1 Zircon yield rate as a function of holding time. Calcination temperature 1300 °C, heating rate 1.25 °C min^{-1}. (■) 1.5 wt % seeding, (●) unseeded.

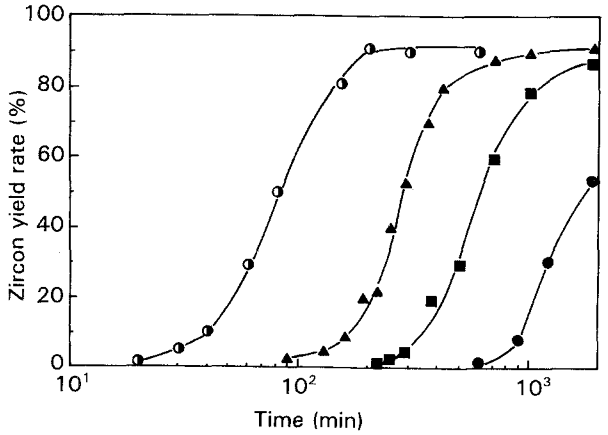

Figure 2 Zircon yield rate as a function of time, without seeding. Heating rate 1.25 °C min^{-1}. (●) 1200 °C, (■) 1250 °C, (▲) 1300 °C, (○) 1400 °C.

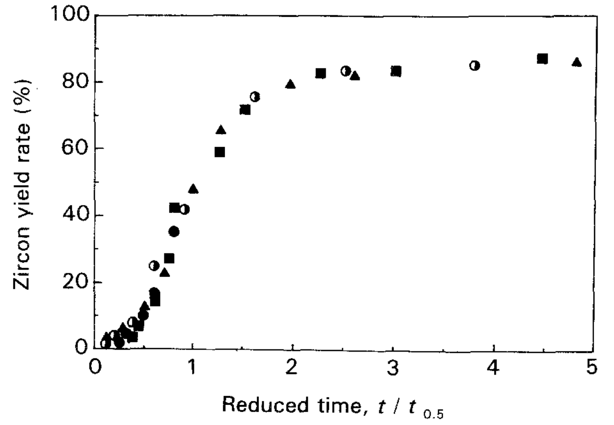

Figure 3 Zircon yield rate as a function of reduced time, without seeding. (●) 1200 °C, (■) 1250 °C, (▲) 1300 °C, (◑) 1400 °C.

ing time, and the $ZrSiO_4$ yield-rate curve was observed to be "S"-shaped.

Fig. 3 shows the relation between the $ZrSiO_4$ yield rate and the reduced time, $t/t_{0.5}$, based on the results of Fig. 2, where the $t_{0.5}$ is the half the time at which the $ZrSiO_4$ yield rate was saturated and t is the holding time. If the $ZrSiO_4$ yield as a function of reduced time, $t/t_{0.5}$, fitted a curve in some temperature region, the reaction mechanism was the same in that temperature range. In Fig. 3, the results fitted a single curve at these temperatures, and consequently the reaction mechanism was the same.

Fig. 4 shows the result of an Avrami plot obtained from the data of Fig. 2. The line of the Avrami plot comprised two slopes; one with $n = 1$ and the other with $n \geqslant 2$. On the basis of the results of Fig. 4, the $n = 1$ region was determined. Table I shows the $n = 1$ region using the Avrami plot on Fig. 4 and the induction period of the $ZrSiO_4$ yield-rate curve at each calcination temperature, the initial region of "S"-shaped curve. The $n = 1$ region is a region of a simple nucleation reaction without nucleus growth corresponding to the induction time of the $ZrSiO_4$ yield-rate curve on Fig. 2. The $n = 2$–3 region means the mixed region of nucleation and nucleus growth. Therefore, the simple nucleation region has a wide range from 1200–1300 °C.

Thus, in order to compare the results with the unseeded case, the effect of seeding was investigated. Fig. 5 shows the relation between holding time and $ZrSiO_4$ yield rate with 1.5 wt % seeding in the same manner as Fig. 2. The $ZrSiO_4$ yield-rate curve was again "S"-shaped. The tendency of these results was similar to that in Fig. 3. Fig. 6 shows the results of an Avrami plot using data of Fig. 5. On the basis of the results of Fig. 6, the $n = 1$ region was determined. Table II shows the induction time in Fig. 5 and the time to reach the $n = 1$ region in Fig. 6 at 1200, 1250 and 1300 °C. The tendency was similar to Table I and these data corresponded to each other.

The $n = 1$ region decreased rapidly with increasing temperature. Thus, in order to enhance the effect of nucleation, the heating rate was varied from 0.15–10 °C min^{-1} and then the $ZrSiO_4$ yield rate was

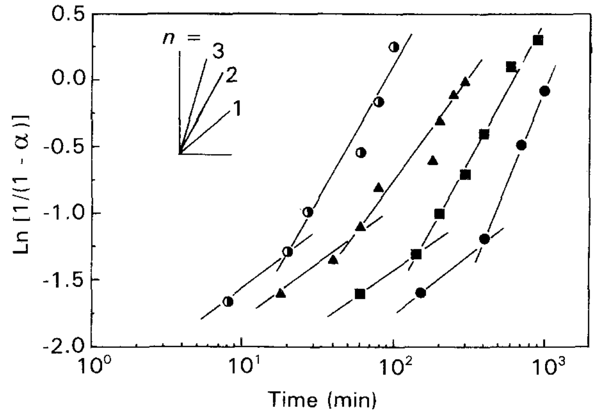

Figure 4 Ln[1/(1 − α)] as a function of time, without seeding. Heating rate 1.25 °C min^{-1}. (●) 1200 °C, (■) 1250 °C, (▲) 1300 °C, (○) 1400 °C.

TABLE I Time at the $n = 1$ region and the induction time without seeding at various temperatures

Calcination temperature (°C)	Time at $n = 1$ region (min)	Induction time (min)
1200	250	400
1250	90	80
1300	40	50
1400	12	20

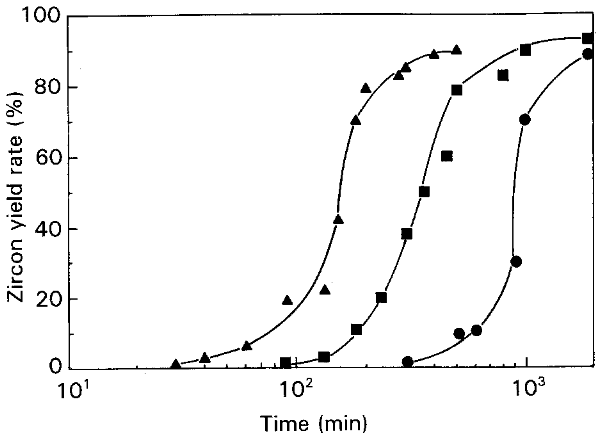

Figure 5 Zircon yield rate as a function of time with 1.5 wt % seeding. Heating rate 1.25 °C min^{-1}. (●) 1200 °C, (■) 1250 °C, (▲) 1300 °C.

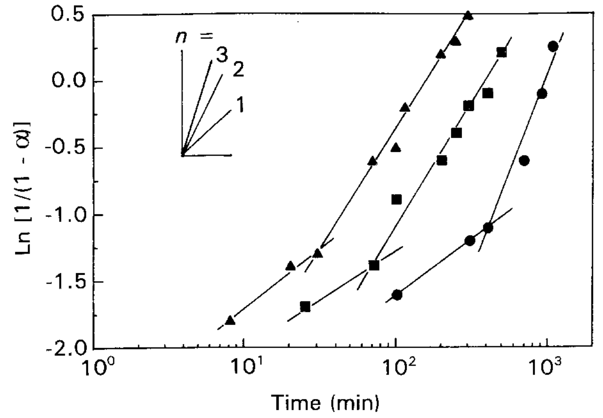

Figure 6 Ln[1/1 − α)] as a function of time with 1.5 wt % seeding. Heating rate 1.25 °C min^{-1}. (●) 1200 °C, (■) 1250 °C, (▲) 1300 °C.

TABLE II Time at the $n = 1$ region and the induction time with 1.5 wt % seeding at various temperatures

Calcination temperature (°C)	Time at $n = 1$ region (min)	Induction time (min)
1200	300	300
1250	45	50
1300	22	30

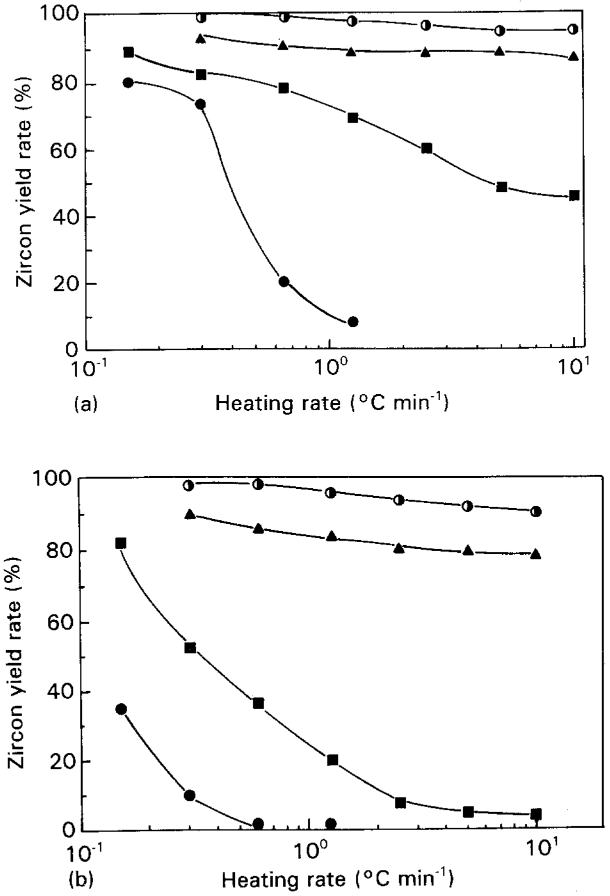

Figure 7 Zircon yield rate as a function of heating rate (a) with 1.5 wt % seeding, and (b) without seeding. Holding time 20 min. (●) 1200 °C, (■) 1250 °C, (▲) 1300 °C, (◑) 1400 °C.

investigated. Fig. 7a shows the relation between heating rate and $ZrSiO_4$ yield rate with the addition of 1.5 wt % $ZrSiO_4$ seed, and Fig. 7b shows the relation between the heating rate and $ZrSiO_4$ yield rate without seeding. From Fig. 7a, a remarkable effect of heating rate appeared at 1200–1250 °C, but there was virtually no effect above 1300 °C. From Fig. 7b, the effect of heating rate is seen to be similar to that of Fig. 7a, but the zircon yield rate depended on heating rate and the slope of the curve was greater than that in Fig. 7a. The $ZrSiO_4$ yield rate was more than 80%, even if the calcination temperature was 1300 °C or less and seeding was not used, when the heating rate was 0.15 °C min^{-1}. From Fig. 7a and b, the difference between seeding and non-seeding is seen to be slight at 1350–1400 °C. As mentioned above, the nucleation increased when the heating rate was slow at 1200–1300 °C, where the $n = 1$ region was wide, and the effect of seeding was remarkable in this case. However, the effect of seeding was only slight at 1350–1400 °C where the $n = 1$ region was narrow. Therefore, it was found that the $ZrSiO_4$ yield rate increased remarkably at 1200–1300 °C without seeding when the heating rate was less than 1 °C min^{-1}. Moreover, the value reached more than 80% at a relatively low temperature (1250 °C).

4. Conclusions

The formation mechanism of $ZrSiO_4$ and the preparation of $ZrSiO_4$ powder from ZrO_2 and colloidal SiO_2 sols was investigated. The following conclusions were drawn from the results.

1. The relation between the holding time and $ZrSiO_4$ yield rate, α_{ZrSiO_4}, showed an "S"-shaped curve with and without seeding. In order to consider the preparation mechanism of $ZrSiO_4$, the Avrami plot was drawn using seeded and unseeded data. The induction time of the $ZrSiO_4$ preparation reaction corresponded to the $n = 1$ region, a simple nucleation region.

2. The $n = 1$ region decreased rapidly with increasing temperature, but it was present over a wide range

at 1200–1300 °C and the nucleation reaction was promoted at these temperatures.

3. The seeding effect disappeared above 1300 °C, because the $n = 1$ region became very narrow above 1300 °C.

4. In the formation reaction of $ZrSiO_4$, the predominant factor affecting this was the nucleation reaction. In particular, the temperature range from 1200–1300 °C, in which the $n = 1$ region of the Avrami plot showed a wide range, was important. It was found that the $ZrSiO_4$ yield rate became very high, even if no seeds were added, when the heating rate was controlled at less than 1 °C min^{-1}.

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