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Preparation and Characterization of Highly Pure Fine Zircon Powder

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Abstract

The preparation of highly pure fine zircon powders ($ZrSiO_4$) was studied using $ZrOCl_2$ and fumed SiO_2 by the wet chemical method. The gel formation obtained by adding $NH_3 \cdot H_2O$ to the slurry consisting of $ZrOCl_2$ solution and fumed SiO_2 was seeded with zircon sand. The optimum process found to synthesize highly pure fine zircon powder was to calcine the gel at 1400°C for 2 h after preheat treatment at 700°C for 2 h. The powders obtained are composed of submicrometer particles. The relative density of specimens hot pressed at 1650°C for 1 h under 20 MPa reaches 99.2%, and the flexural strength at room temperature is 360 MPa.

Die Herstellung von hochreinem, feinem Zirkonsilikat Pulver ($ZrSiO_4$) wurde unter Verwendung von $ZrOCl_2$ und SiO_2 mit Hilfe einer naßchemischen Methode untersucht. Zu dem Gel, das durch die Zugabe von $HN_3 \cdot H_2O$ zu dem aus $ZrOCl_2$ Lösung und SiO_2 bestehenden Schlicker hergestellt wurde, wurde Zirkonsilikatsand als Keime zugegeben. Der optimale Prozeß zur Herstellung von hochreinem, feinem Zirkonsilikatpulver ist, das Gel nach einer 2stündigen Wärmebehandlung bei 700°C bei 1400°C für 2 h zu kalzinieren. Die hergestellten Pulver bestehen aus submikrometer großen Teilchen. Die relative Dichte der bei 1650°C und einem Druck von 20 MPa 1 h heißgepreßten Proben ergab einen Wert von 99.2%. Die Durchbiegefestigkeit bei Raumtemperatur betrug 360 MPa.

Nous avons étudié la fabrication de poudres de zircon très pures ($ZrSiO_4$) à partir de $ZrOCl_2$ et de poudre de SiO_2, ceci par traitement chimique par voie humide. Le gel obtenu en ajoutant $NH_3 \cdot H_2O$ à la barbotine de $ZrOCl_2$ mélangé à la poudre de SiO_2 a été ensemencé avec du sable de zircon. Nous avons trouvé que le meilleur procédé pour synthétiser de la poudre de zircon fine et très pure est de calciner le gel à 1400°C pendant 2 h après un premier traitement thermique de 2 h à 700°C. On obtient des poudres de taille de grains inférieure au micron. La densité relative des échantillons pressés à chaud 1 h à 1650°C sous une pression de 20 MPa peut atteindre 99.2% et la résistance à flexion à température ambiante est de 360 MPa.

1 Introduction

Zircon ($ZrSiO_4$) is an important material with many unique properties. It has a very low coefficient of heat conductivity (5.1 W/m °C at room temperature and 3.5 W/m °C at 1000°C) and low coefficient of thermal expansion (about 4.1×10^{-6}/°C between 25°C and 1400°C).[1] Its mechanical strength does not degrade even at temperatures higher than 1400°C, and sintered zircon has a thermal shock resistance superior to those of mullite and alumina sintered bodies.[2] These properties make zircon a potential candidate as a useful structural ceramic for high-temperature applications.

The purity of natural zircon sand is often low, with many kinds of impurities such as Al_2O_3, Fe_2O_3, TiO_2 and so on, which will decompose zircon at lower temperatures. Normally, pure zircon decomposes into ZrO_2 and SiO_2 at a temperature of about 1700°C according to the ZrO_2–SiO_2 phase diagram. However, most alkali and alkaline oxides promote the decomposition of zircon at a relatively lower temperature. For example, zircon would react with Al_2O_3 at 1400°C as follows:

$$2ZrSiO_4 + 3Al_2O_3 = 3Al_2O_3 \cdot 2SiO_2 + 2ZrO_2$$

so it is very meaningful to synthesize zircon powder with high purity for its applications, especially at high temperatures.

Highly pure zircon powder is commercially unavailable. In recent years, many studies have been done on the preparation of highly pure fine zircon powder,[1-5] the usual route used in these studies is the sol-gel method starting with $ZrOCl_2$ solution and $Si(C_2H_5O)_4$ (or colloidal SiO_2). For example, Mori *et al* reported the synthesis of fine zircon powder by the sol-gel process from $ZrOCl_2$ and SiO_2 sols,[5,6] obtaining particles of about 0·5 μm in size

In this paper, the preparation of highly pure fine zircon powders by the wet chemical method is reported A small amount of zircon sand was added to the homogeneous gel precipitations as seeds in order to lower the synthesizing temperature of zircon powders and the expected effect was observed The zircon powders obtained were characterized by different methods, including wet chemical analysis, XRD and TEM. The mechanism of lowering the synthesizing temperature is also discussed.

2 Experimental Procedure

Zirconium oxychloride and fumed silica were used as the starting materials. $ZrOCl_2 \cdot 8H_2O$ was dissolved in water and fumed silica was mixed with the solution to obtain a homogeneous slurry The slurry was brought to pH = 10 by adding $NH_3 \cdot H_2O$ solution while under vigorous stirring. The homogeneous gel obtained was thoroughly mixed with a small amount of zircon sand seeds and the mixture was dried at 120°C The dried mixtures were calcined at the proper conditions to obtain highly pure fine zircon powders.

The zircon sand used as seeds was provided by Xianyang Research & Design Institute of Ceramics, the chemical composition of it is listed in Table 1, and the TEM morphology is also shown in Fig. 1, most particles are angular with particle sizes above 0·5 μm

The powders obtained were analysed by the XRD method. The formation rate of $ZrSiO_4$ in the powders obtained was calculated by the following equation:[5-7]

$$\alpha_{ZR} = I_{ZR(200)}/[I_{ZR(200)} + I_{m(111)} + I_{m(111)} + I_{t(111)}]$$

where I is the peak intensity of XRD, ZR is $ZrSiO_4$, m is m ZrO_2, t is t-ZrO_2 and (*abc*) are the crystal plane indices The differential thermal analysis (DTA) curves of homogeneous gel precipitates mixed with zircon sand were taken at a heating rate of 10°C/min to 1500°C. The powders obtained were analysed by wet chemical analysis, transmission electron microscopy (TEM), and infrared spectrophotometry. The specific surface area of the powder was determined by the BET method The particles size distribution of the powder was also determined

The obtained zircon powder was hot-pressed in a graphite die at 1650°C for 1 h under 20 MPa in a nitrogen atmosphere Specimens were cut into 5 mm × 2·5 mm × 30 mm bars without polishing for flexural strength measurement using the three point bending method with a span of 20 mm; the loading rate was 0·5 mm/min The sample density was measured by Archimedes' method

Table 1. Chemical composition of zircon sand

Composition	*Contents (%)*
ZrO_2	62·28
SiO_2	31·17
HfO_2	1·26
Al_2O_3	3·17
TiO_2	0·44
CaO	0·27
Fe_2O_3	0·14
MgO	0·081
Y_2O_3	0·11

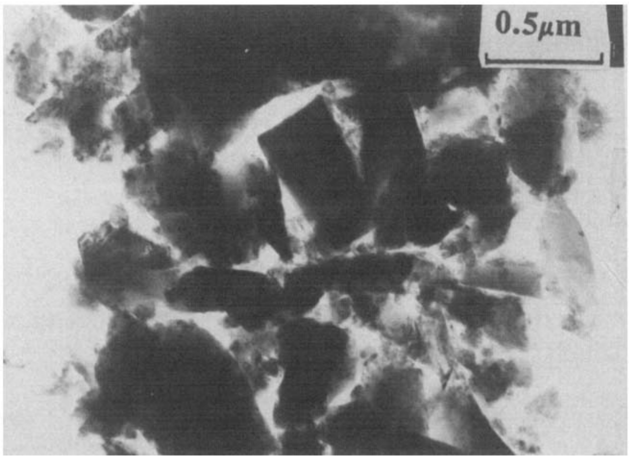

Fig. 1. TEM morphology of zircon sand seeds

3 Results and Discussion

3.1 Formation of zircon without seeds

The relation between the formation rate of $ZrSiO_4$ (α_{ZR}) in gel precipitate without seeds and the calcination temperature is shown in Fig. 2. Zircon can not be formed at temperatures below 1350°C. Zircon formation starts to be observed at a temperature above 1400°C and the formation rate increases remarkably in the temperature range of 1400-1500°C. It can be envisaged that the reconstructive transformation of amorphous silica to cristobalite accelerates the formation reaction of zircon by the so-called Hedvall effect The material gets activated due to volume change at transformation to induce the generation of lattice strain and even fissures.[8]

Moreover, the formation rates of zircon after being preheat treated at 700°C for 2 h (curve 1) is higher than those under the same calcination conditions without heat treatment (curve 2). In the

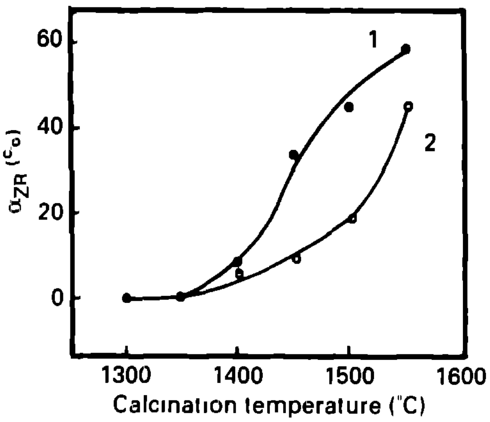

Fig. 2. Formation rate of zircon in gel precipitate without seeds as a function of calcination temperature (holding time 2 h) (1) After heat treatment at 700°C for 2 h, (2) no preheat treatment

report by Mori *et al*, a preheat treatment of the gel was also used before calcination at 1350°C to obtain zircon powders. However, the effect of heat treatment was not discussed in their paper.[5]

Figure 3 shows the IR spectra of gel precipitates. Comparing these two curves, it is found that after heat treatment, the absorption peak at 1400 cm^{-1} disappeared, due to the loss of the bridging OH group. In addition to it there are two weak enhancements of absorption peaks at 880 cm^{-1} (a) and 640 cm^{-1} (b), at which the characteristic absorption peaks of the Zr–O–Si bond are located.[5] The XRD pattern (Fig. 4(a)) of the gel precipitate after heat treatment for 700°C/2 h shows that it is still amorphous and there is a broadened peak at $2\theta = 30.17$ which is characteristic for t-ZrO_2, whereas $Zr(OH)_4$ without fumed SiO_2 becomes m-ZrO_2 after being heat treated under the same conditions (Fig. 4(b)). So it may be argued that after heat treatment, a small amount of SiO_2 may combine with ZrO_2 to form the Zr–O–Si bond and the existence of fumed SiO_2 contributes to the formation and stabilization of t-ZrO_2. This would lead to the formation of zircon.

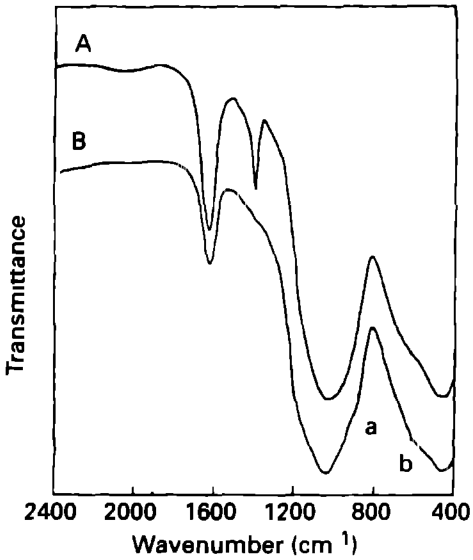

Fig. 3. IR absorption spectra of gel precipitate without seeds (A) No preheat treatment (B) heat treatment at 700°C for 2 h

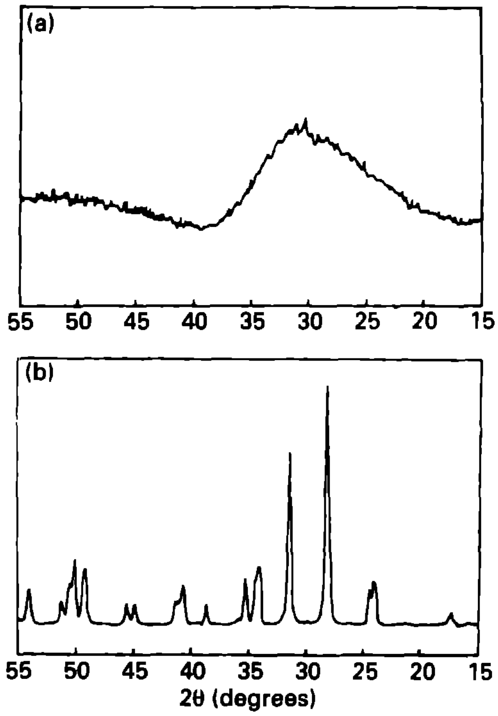

Fig. 4. XRD patterns of (a) gel precipitate without seeds and (b) $Zr(OH)_4$ after treatment at 700°C for 2 h

As it was found to be difficult to fully synthesize highly pure zircon powder from two pure starting materials alone, zircon sand was added to the gel as seeds to promote the formation of zircon.

3.2 Preparation of highly pure fine zircon powder

Figure 5 shows the DTA curves of gel precipitates containing different contents of zircon sand seeds. Their thermal behaviours are the same in the temperature range of room temperature to 1000°C; the large endothermic peak at around 150°C corresponds to the loss of water and the small exothermic peak corresponds to the crystallization of t-ZrO_2. The difference among them is that there is

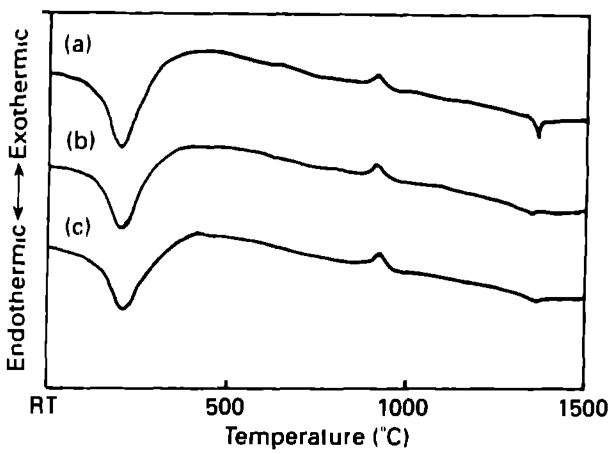

Fig. 5. DTA curves of gel precipitate containing different contents of seeds (a) No seeds, (b) 0.5 mol% seeds, (c) 5 mol% seeds

a small endothermic peak around 1400°C in the no seed sample, representing the reconstructive transformation of amorphous silica, while the same peaks around this temperature almost disappear in seeded gel precipitate curves.

Because of the addition of zircon sand seeds, zircon formation from the gel precipitates will be promoted.[9] Thermodynamic calculations indicate that the formation of zircon is a weak exothermic reaction ($\Delta H = -31$ kJ/mol) It is likely that the heat released from the formation of zircon counteracts the endothermic effect of amorphous silica transformation.

The influences of the amount of zircon sand seed addition on the formation of (α_{ZR}) in the obtained powders have been studied and the results are plotted in Fig 6 The gel precipitates mixed with zircon sand seeds were calcined for 2 h at 1400°C and 1500°C respectively At the first $\frac{1}{2}$% seeds addition, the increase of α_{ZR} formation is dramatic, from less than 20% to nearly 90%. The effect of seed seems to level off at about 1 mol% It can be noticed that preheat treatment at 700°C for 2 h is beneficial to zircon formation, especially at the relatively lower calcination temperature (1400°C). This similar to the results in Fig. 2

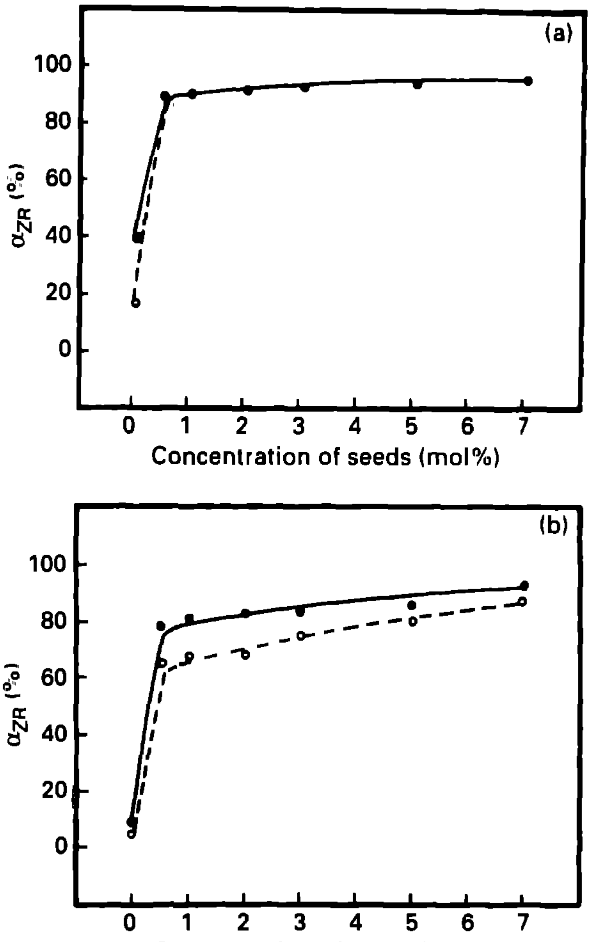

Fig. 6. Formation rate of zircon as a function of seeds addition. ●, After preheat treatment at 700°C; ○, no heat treatment, (a) 1500°C/2 h (b) 1400°C/2 h

The zircon sand seeds can be considered as the second phase particles well-dispersed in the gel. These particles provide a great deal of free surface for heterogeneous nucleation and growth of new zircon particles,[9] and the degree of lattice matching between the seeds and the new formed phase is very important According to the heterogeneous nucleation theory[8]

$$\Delta G_s^* = \Delta G^* \cdot f(\theta)$$

where $f(\theta) = (2 + \cos\theta)(1 - \cos\theta)^2/4$ and ΔG_s^* and ΔG^* are the free energies for heterogeneous and homogeneous nucleations respectively, which show the thermodynamic barriers for nucleation under different conditions The ΔG_s^* decreases with the decreasing θ and tends to be zero as θ approaches zero So the most favourable case is that the seeds are in identical crystalline orientation to the new product to be obtained

The reaction rate constants (K) of no seeded gel precipitate and 7 mol% seeded gel precipitate at different temperatures are calculated based on the formation rates of zircon at different temperatures. The relation between ln K and $1/T$ is plotted in Fig. 7, According to the Arrhenius equation

$$\ln K = \ln A - E/RT$$

where E is the activation energy, the activation energies under different conditions were calculated from the slopes of the two lines in Fig. 7

$$\text{No seed: } E_1 = 390.6 \text{ kJ/mol}$$

$$7 \text{ mol\% seeded } E_2 = 207.7 \text{ kJ/mol}$$

The activation energy drops nearly 50% after seeding with 7 mol% zircon sand and the formation temperature for the same rate of zircon formation drops nearly 200°C

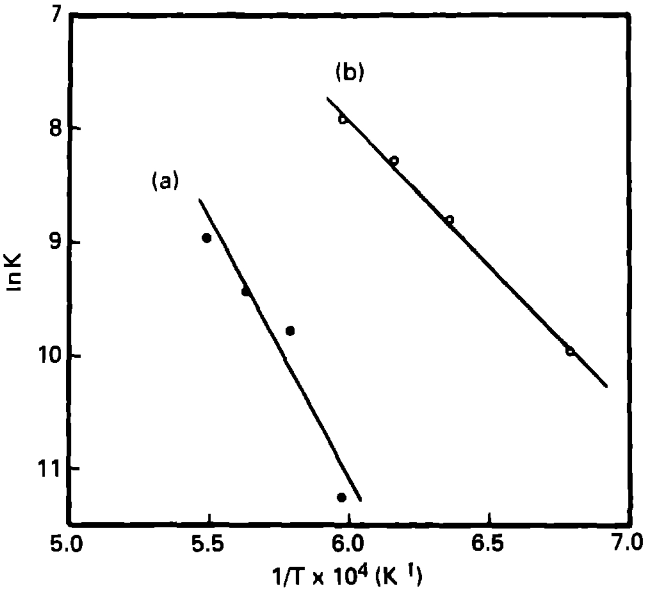

Fig. 7. The relation between ln K and calcination temperature (a) No seeds, (b) 7 mol% seeds

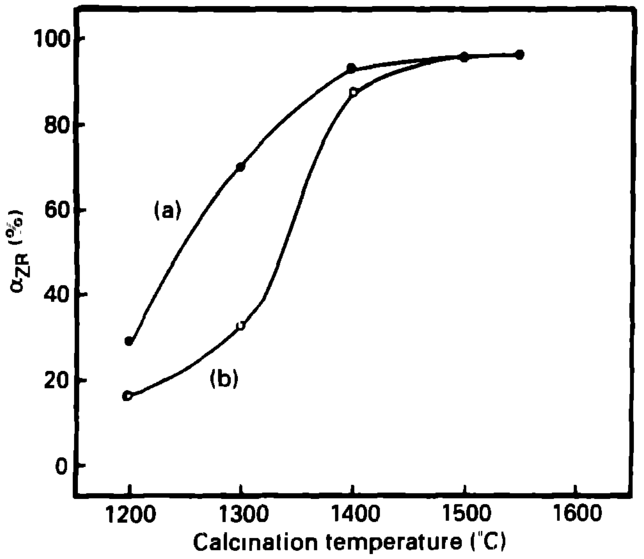

Fig. 8. *Zircon formation in 7 mol% seeded gel precipitate as a function of calcination temperature (holding time 2 h) (a) With preheat treatment at 700°C for 2 h (b) no preheat treatment*

Figure 8 shows the amount of zircon formation under two different preheat treatment conditions when the gel precipitate is seeded with 7 mol% zircon sand. It is clear that heat treatment at 700°C for 2 h fosters the formation of zircon at relatively lower temperatures and the powders obtained are almost completely composed of single zircon phase when the calcination temperature is above 1400°C. The XRD (Fig 9) and IR (Fig. 10) patterns show the

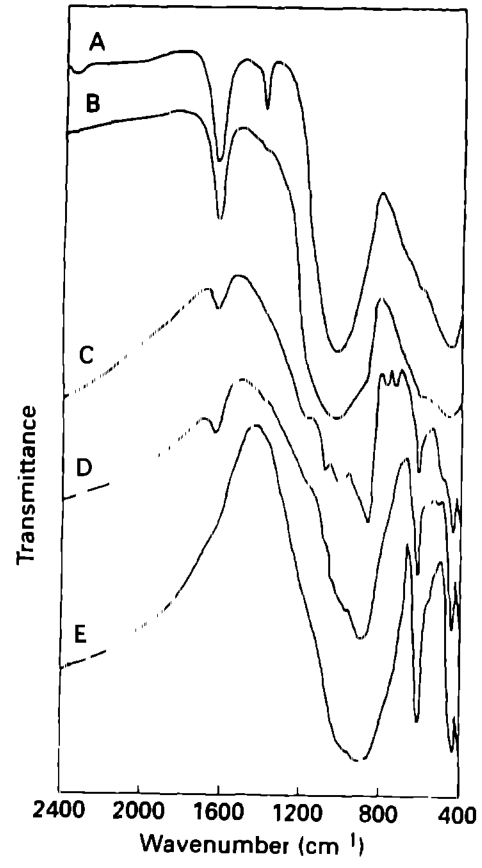

Fig. 10. IR spectra of powders obtained from 7 mol% seeded gel precipitate (A) No preheat treatment, (B) 700°C/2 h, (C) 700°C/2 h + 1200°C/2 h, (D) 700°C/2 h + 1300°C/2 h, (E) 700°C/2 h + 1400°C/2 h

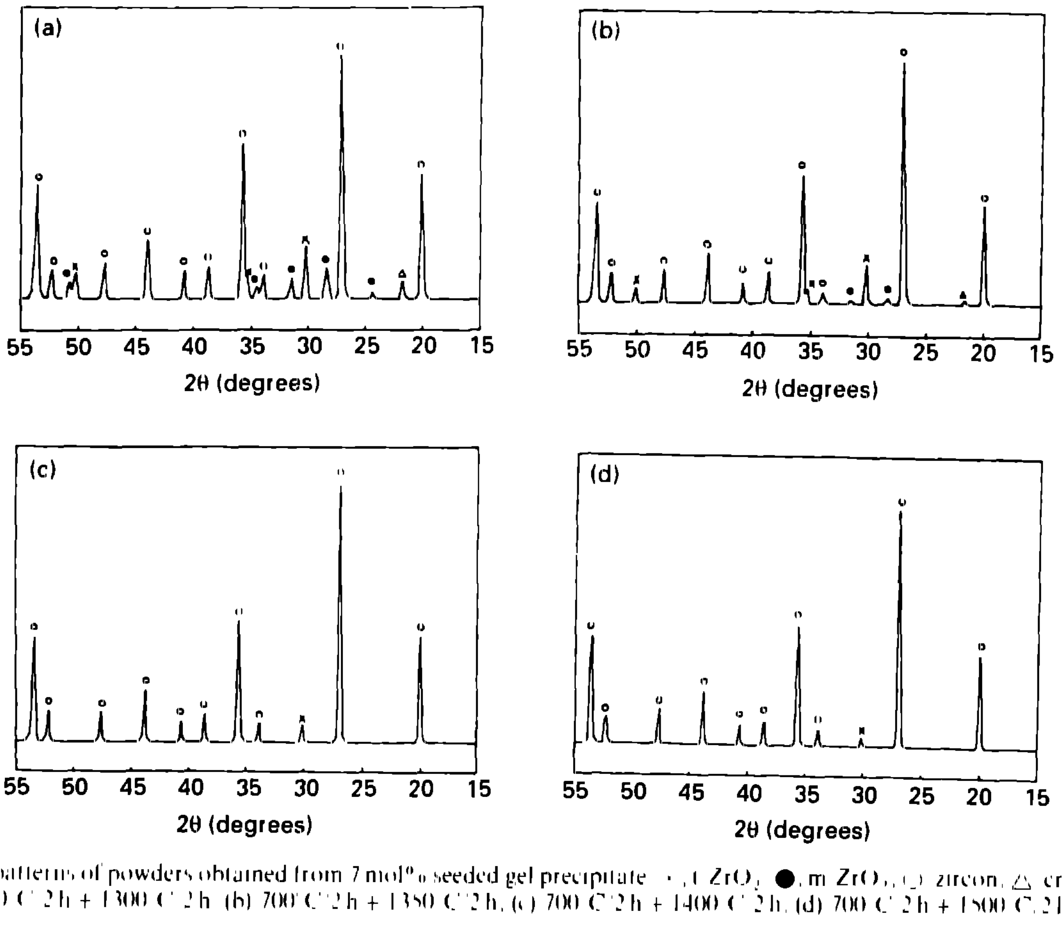

Fig. 9. XRD patterns of powders obtained from 7 mol% seeded gel precipitate ×, t ZrO₂; ●, m ZrO₂; ○, zircon; △, cristobalite (a) 700°C/2 h + 1300°C/2 h (b) 700°C/2 h + 1350°C/2 h, (c) 700°C/2 h + 1400°C/2 h, (d) 700°C/2 h + 1500°C/2 h

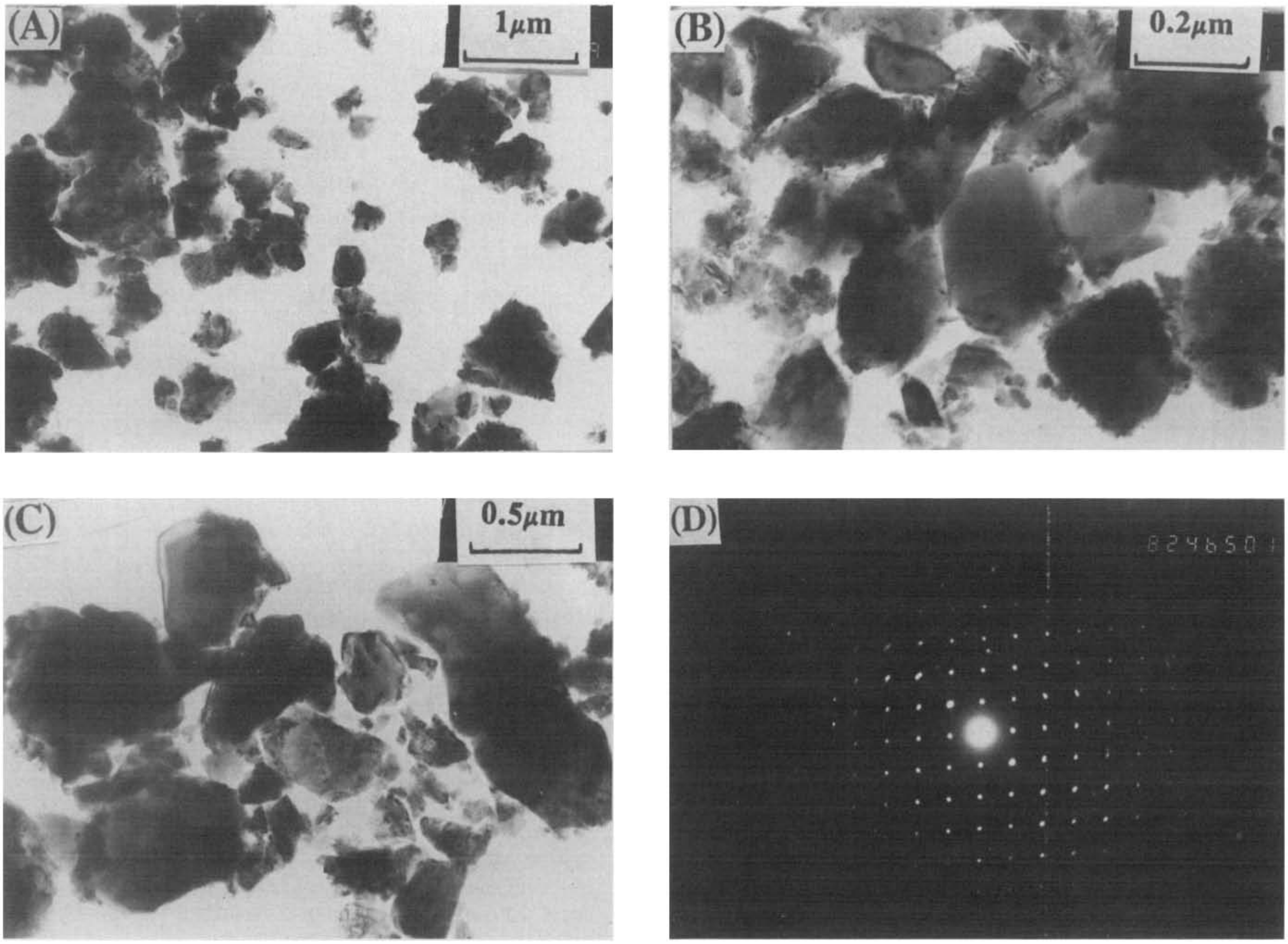

Fig. 11. Transmission electron micrographs of synthesized zircon powders (A) 700°C/2 h + 1400°C/2 h, (B) 700°C/2 h + 1400°C/2 h; (C) 700°C/2 h + 1500°C/2 h, (D) selection area electron diffraction pattern of (A)

same results Both of them show that the formation of zircon begins to be substantial at about 1200°C. The peak of cristobalite in XRD patterns weakens and disappears with increasing temperature, the small peak of t ZrO$_2$ in (C) and (D) is caused by the little overdose of ZrOCl$_2$ used The absorption peaks of IR spectra of zircon (880 cm^{-1} and 640 cm^{-1} [15]) are intensified as the calcination temperature is increased and the pattern (E) is the same as the standard IR pattern of zircon when the calcination temperature reaches 1400°C.

From the results, it is concluded that in the course of processing, it was critical to add proper amount of zircon sand into the precipitate gel as seeds, and the appropriate contents of seeds were more than 1 mol% XRD and IR analysis indicated that zircon formation took place mainly in the temperature range of 1200–1400°C, and preheat treatment had a little favourable affect on the zircon contents in the obtained powder.

3.3 Characteristics of highly pure fine zircon powder

Highly pure fine zircon powder is synthesized under the optimum conditions as already described: seeded with 7 mol% fine zircon sand in the gel precipitate, calcined at 1400°C for 2 h after preheat treatment at 700°C for 2 h

The chemical composition of the powder obtained analysed by wet chemical analysis is shown in Table 2. The total amount of impurities, 0·182 wt%, is much lower than those in normal zircon sand (Table 1). The inpurities in the synthesized powder are caused by the adding of the seeds.

TEM observation (Fig. 11) shows that the synthesized fine zircon powder is composed of particles of about 0·2–0·3 μm (Fig. 11(A) and (B)), much smaller than the original zircon sand powder (Fig. 1) Some agglomerates are observed in Fig. 11(A) A selection area electron diffraction pattern

Table 2. Chemical composition of synthesized zircon powder

Composition	*Contents (wt%)*
ZrO$_2$	66·9
SiO$_2$	31·21
HfO$_2$	1·35
Al$_2$O$_3$	0·15
Fe$_2$O$_3$	0·021
CaO	0·006
MgO	0·005

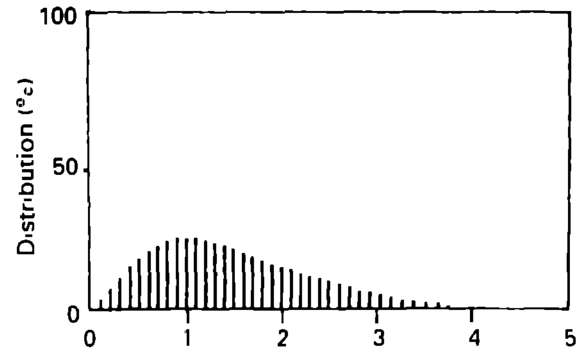

Fig. 12 Particle size distribution of synthesized zircon powder (700°C 2 h + 1400°C 2 h)

(Fig. 11(D)) reveals that the particles are well crystallized zircon. As the calcination temperature rises, the particle size also increases substantially. The average particle size (D_{50}) for powders calcined at 1400°C is determined by particles distribution analysis (Fig. 12) to be 1.59 μm, indicating agglomerates again. The specific surface area is 4.9 m²/g and d_{BET} = 0.27 μm, which corresponds to the TEM observations.

3.4 Primary characteristics of sintered zircon

The bulk density of a specimen hot-pressed at 1650°C for 1 h in a nitrogen atmosphere under 20 MPa is 4.565 g/cm³. Assuming the 4.60 g/cm³ for the theoretical density of zircon, the relative density of 99.2% is obtained. The flexural strength at room temperature is 360 MPa.

4 Conclusions

(1) The wet chemical method was used to synthesize fine zircon powder of high purity starting from $ZrOCl_2$ solution and fumed SiO_2. It is difficult to obtain a high zircon content after high temperature calcination without seed addition.

(2) Addition of zircon sand as seeds, even at very low weight percentages, has a remarkably favourable affect on the formation of zircon with a lowering of the formation temperature which can be explained by heterogeneous nucleation.

(3) The following conditions were chosen from the results of this investigation to synthesize highly pure fine zircon powder: gel precipitate seeded with 7 mol% zircon sand seeds, preheat treated at 700°C for 2 h and then calcined at 1400°C for 2 h after heat treatment at 700°C for 2 h. The particle size of the powders as observed under TEM is about 0.2–0.3 μm, the total content of impurities is less than 0.2 wt%.

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