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Wet Chemical Synthesis of ZrO_2–SiO_2 Composite Powders

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Abstract

Gels of composition $xZrO_2(1-x)SiO_2$, *with* x = *10, 20, 30 and 40 vol%, have been prepared by a wet chemical method using fumed silica and zirconyl chloride as precursors. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) show that weight loss is caused by release of the absorbed water and decomposition of the* $Zr(OH)_4$ *gels. Gels were heat-treated for 2 h at 500, 700, 900, 1100 and 1350°C, and the products examined using infra-red (IR) spectroscopy. The increasing intensity of the peak at 800* cm^{-1} *in the IR spectra with increasing temperature is attributed to the formation of Si–O–Si bonds among different* SiO_2 *particles, which means that the* SiO_2 *particles grow bigger with increasing temperature. The DTA exothermic peak as well as the IR results reveal that the crystallization of tetragonal zirconia* (t-ZrO_2) *begins at about 900°C, which is confirmed by X-ray diffraction (XRD). XRD curves also suggest that the silica matrix contributes to the thermal stability of* t-ZrO_2. *The stability of* t-ZrO_2 *is interpreted by the particle-size effect. © 1996 Elsevier Science Limited.*

1 Introduction

The discovery of the strength and toughness of CaO-TZP by Garvie *et al.*[1] and the role of tetragonal zirconia (*t*-ZrO_2) have stimulated world-wide interest in these ceramics. Tetragonal ZrO_2 is incorporated into ceramics both as precipitates and as dispersed particles. On the other hand, in the field of glass technology, zirconia has been used extensively as a nucleating agent and/or as an alkali-resistant agent in glass-ceramics. More recently, the preparation of ZrO_2-transformation-toughened glass-ceramics containing up to 20 to 30 wt% ZrO_2 was reported.[2] Generally, it is difficult to melt glasses containing high amounts of ZrO_2 because it requires a high temperature. The sol–gel method enables glass-ceramics with high ZrO_2 content to be fabricated at a lower temperature.

To date ZrO_2–SiO_2 monolithic glasses[3] and powders[4] have been prepared by means of the sol–gel process. However, the sol–gel method is time-consuming and the alkoxide precursors are expensive; moreover, supercritical conditions are needed to deal with the gels, otherwise monolithic glass cannot be obtained. The present work concerns the preparation of ZrO_2–SiO_2 composite powder by a co-precipitation approach using fumed silica and zirconium oxychloride octahydrate as raw materials. We have successfully obtained homogeneously dispersed ZrO_2–SiO_2 powders. The powders obtained were characterized by differential thermal analysis (DTA), thermogravimetric analysis (TG), X-ray diffraction (XRD), infra-red (IR) spectroscopy and transmission electron microscopy (TEM).

2 Experimental Procedure

Gels in the composition range $xZrO_2$–$(100-x)SiO_2$, x = 10, 20, 30 and 40 vol%, were prepared from fumed silica and zirconyl chloride solution as starting materials. The fumed silica was first dispersed in distilled water, then $ZrOCl_2$ solution was added under stirring. Next, concentrated ammonia was added dropwise to the homogeneous slurry obtained above, under vigorous stirring. To ensure complete reaction, an excess of ammonia was used and the pH value of the mixed solution was maintained above 10 during precipitation.

The resulting gels were filtered and thoroughly washed with distilled water several times. Finally the gels were washed with ethyl alcohol and dried at 120°C for 24 h. The as-dried gels were then calcined in air for 2 h at 500, 700, 900, 1100 and 1350°C. A Netzsch STA429 thermal analyser was employed to detect the thermal evolution of the as-dried gels, at heating rate of 10°C min^{-1}. The calcined powders

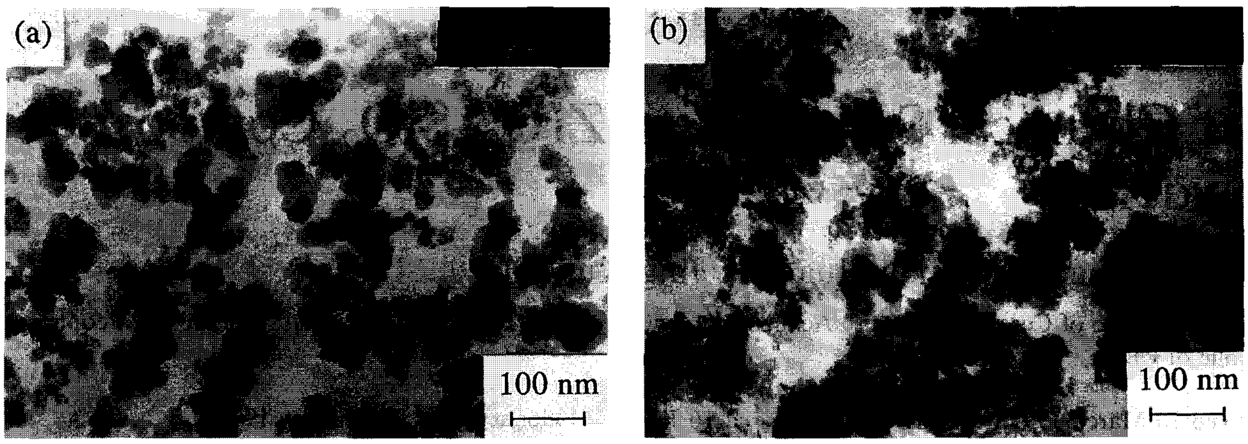

Fig. 1. TEM micrographs of (a) fumed silica after being dispersed in water and then dried, and (b) ZrO_2–SiO_2 composite powder (20ZR) heat-treated at 700°C for 2 h.

were characterized by XRD (RAX-10 diffractometer) using CuK_α radiation. Transmittance spectra were acquired with an IR spectrophotometer in the range 400–2000 cm^{-1}. The morphology, particle size and distribution of the powders calcined were observed by TEM using a JEM-200cx instrument.

3 Results and Discussion

3.1 TEM observations

The particle size of the fumed silica was determined to be about 20 nm, and some agglomerates were also found by transmission electron microscopy [Fig 1(a)]. Figure 1(b) shows the morphology of the 20 vol% ZrO_2–80 vol% SiO_2 sample (abbreviated as 20ZR) after calcination at 700°C for 2 h. It can be seen that the ZrO_2 agglomerates take on a sponge-like form and that the ZrO_2 agglomerates and SiO_2 particles overlap. SiO_2 agglomerates without the cover of the ZrO_2 sponge-like body can be seen in the middle of Fig. 1(b).

3.2 DTA–TG analysis

All DTA curves (Fig. 2) show an endothermic band attributed to water desorption at 100°C and an exothermic band (at 300–500°C) attributed to decomposition of the $Zr(OH)_4$ gels. These assignments are based upon the observation that both features are associated with a weight loss in the TG curve [Fig. 2(a)]. According to the thermochemical calculation, the enthalpy change of the reaction $Zr(OH)_4(s) = ZrO_2(s) + H_2O(g)$, i.e. $\Delta H = -93{\cdot}6$ kcal mol^{-1}, suggests that the decomposition of $Zr(OH)_4$ is responsible for the exothermic peak in the range of 300–500°C. Another weak exothermic peak appears at 900°C that does not correspond to a weight change and becomes stronger with increasing content of ZrO_2 (from 20ZR to 40ZR), indicating the crystallization of t-ZrO_2 from the amorphous state. This was corroborated by the XRD results (Fig. 3). A similar phenomenon was reported by Palladino *et al.*[3] who observed that the crystallization peak of t-ZrO_2 appears at 910–980°C in the formation of ZrO_2–SiO_2 glass-ceramics by the sol–gel route. For the pure ZrO_2 gel, however, metastable tetragonal ZrO_2 began to crystallize at 500°C.[5] We assume that the temperature differences of the crystallization of t-ZrO_2 are related to the different preparing methods, and to the situation around the ZrO_2 particles. In the ZrO_2–SiO_2 system, the crystallization of t-ZrO_2 at higher temperatures may be ascribed to the constraint of the SiO_2 matrix.

3.3 XRD results

ZrO_2–SiO_2 composite powders obtained from the co-precipitated method were amorphous to XRD (taken on sample 20ZR as an example). After calcination at 500°C for 2 h, the powder remained

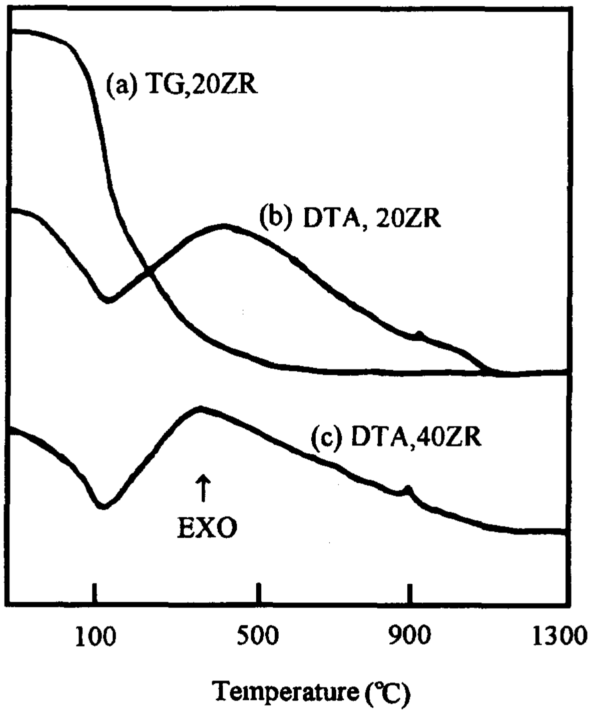

Fig. 2. DTA–TG curves of as-dried ZrO_2–SiO_2 gels.

amorphous [Fig. 3(a)]. The broad band at $2\theta = 30°$ suggests the ordering of small amounts of *t*-ZrO_2 for the sample calcined at 700°C for 2 h [Fig. 3(b)]. XRD on 20ZR powder heat-treated at 900°C identified the tetragonal phase, with four major peaks corresponding to the 1 1 1, 2 0 2, 1 3 1 and 2 2 0 planes in decreasing intensity [Fig. 3(c)]. This result is in consistent with that of Saha and Pramanik.[4] The increasing sharpness of the XRD peaks with increasing temperatures [Figs 3(d) and (e)] indicate the gradual ripening of the *t*-ZrO_2 phase and gradual growth of *t*-ZrO_2 particles. The formation of cristobalite or the trace of $ZrSiO_4$ was not observed in the XRD spectrum from the sample calcined at 1350°C [Fig. 3(e)]. The most striking feature of the XRD curves with increase of calcining temperature is that no evolution of monoclinic phase from *t*-ZrO_2 is detected in the present experiment. According to Ramamurthi *et al.*[5] the monoclinic phase gradually evolves with increasing temperature above 700°C for the pure ZrO_2 gel. For the Y-TZP powders co-precipitated by Xu,[6] the *m*-ZrO_2 phase emerged in the XRD spectra after the powders were calcined at 750°C for 2 h. Thus, the absence of *m*-ZrO_2 in the ZrO_2–SiO_2 system reveals that silica has the ability to stabilize the tetragonal zirconia phase.

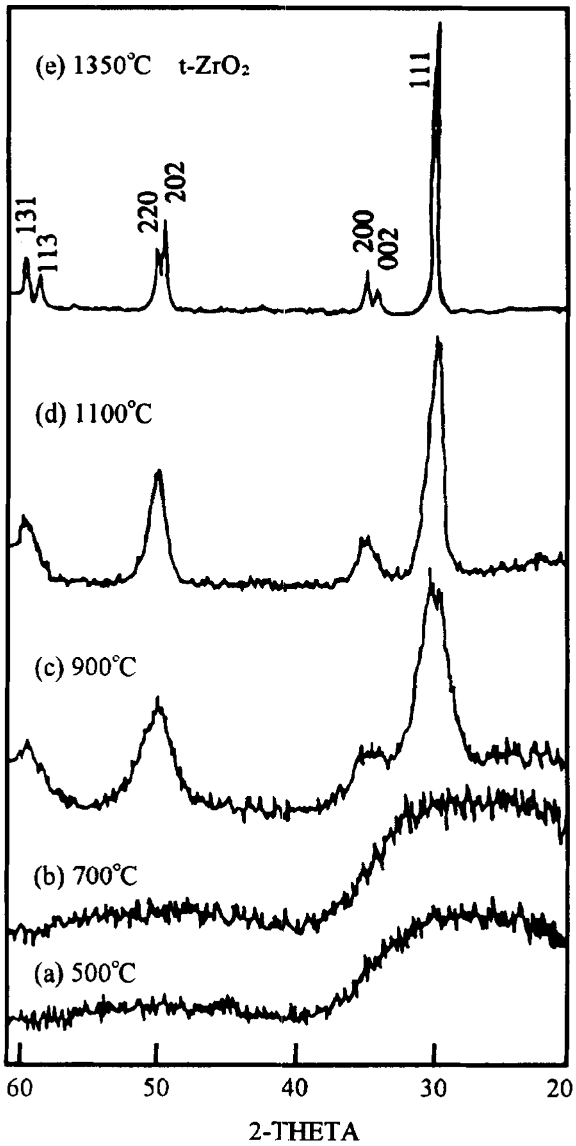

Fig. 3. XRD patterns of ZrO_2–SiO_2 gel (20ZR) calcined at different temperatures for 2 h.

According to the literature, the stabilization of the tetragonal phase in zirconia may be ascribed to the particle-size effect reported by Garvie:[7] i.e. the smaller the particle size of the *t*-ZrO_2 phase, the more stable it is at low temperature because of its larger specific area. The SiO_2 grains grow rapidly with increasing temperature, reaching 0·4–0·6 μm in size when the calcining temperature was raised to 1350°C (Fig. 4). At the same time ZrO_2 grains were encased in silica grains and, since the ZrO_2 particles were embedded in the silica matrix, grain growth of ZrO_2 was impeded. After calcining at 1350°C for 2 h, the average size of *t*-ZrO_2 particles was about 50 nm (Fig. 4, the dark round phase was zirconia particles). It has been reported that the critical size of free *t*-ZrO_2 particles is around 30 nm, while that of ZrO_2 particles in an Al_2O_3 matrix is larger, typically 600 nm.[7] It is suggested that the critical size of *t*-ZrO_2 grains has different values when the ZrO_2 grains are dispersed in different matrices. Therefore, the stability of 50 nm *t*-ZrO_2 grains is attributed to its smaller particle size than the critical size of *t*-ZrO_2 in the present system.

3.4 IR Spectra

From the IR spectra (Fig. 5) for the 20ZR sample calcined at different temperatures, it is easily seen that the observed frequencies of the vibration at 1200, 1100, 800 and 460 cm^{-1} for the Si–O–Si bond are in good agreement with the values reported by Phillippi and Mazdiyasni[8] and Nogami.[9] The bands at 1200 and 1100 cm^{-1} are assigned to the Si–O–Si asymmetric bond stretching vibration. The bands at 800 and 460 cm^{-1} are associated with the network

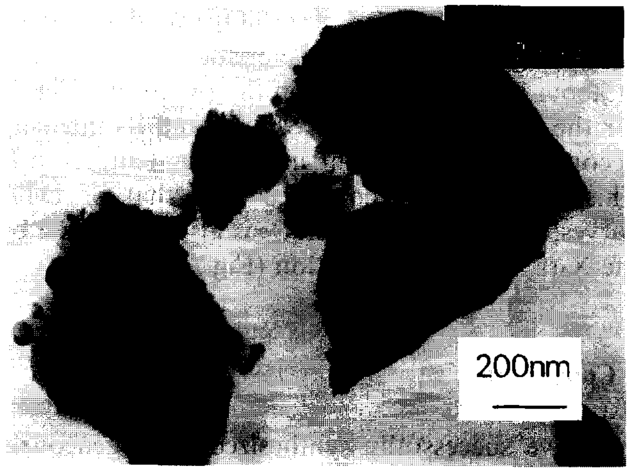

Fig. 4. TEM micrograph of ZrO_2–SiO_2 gel (20ZR) calcined at 1350°C for 2 h (the dark, round, embedded phase is zirconia particles).

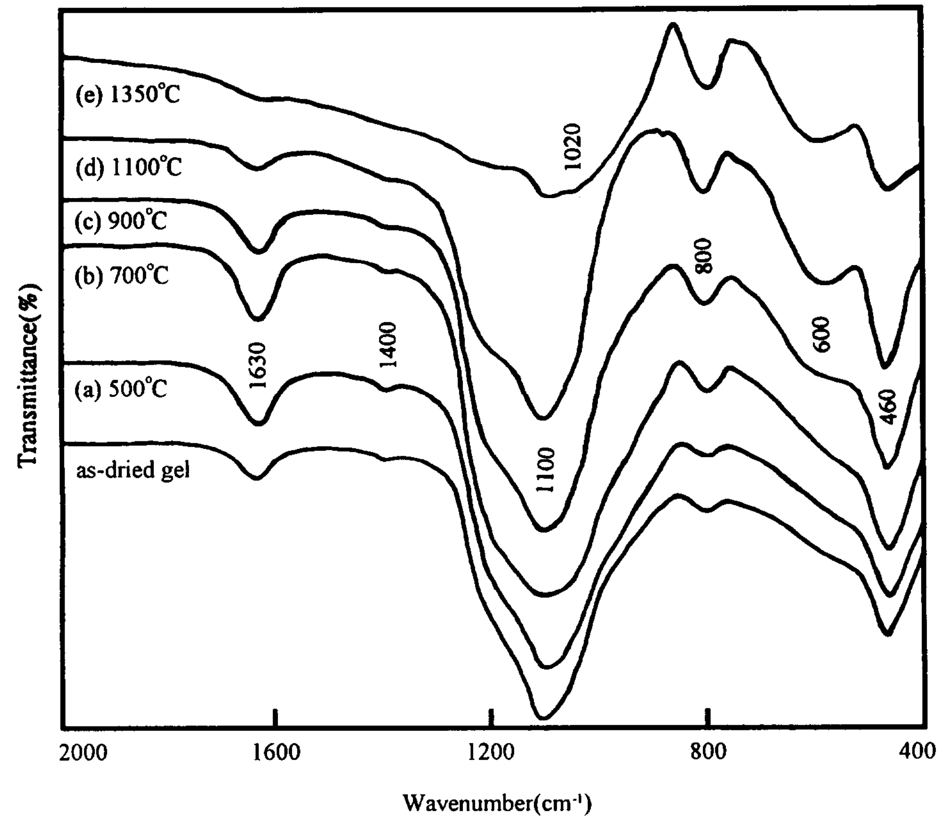

Fig. 5. IR spectra of ZrO_2–SiO_2 gel (20ZR) calcined at different temperatures for 2 h.

Si–O–Si symmetric bond stretching vibration and bond bending vibration, respectively. The increasing intensity of the 800 cm^{-1} peak with temperature indicates the formation of Si–O–Si bonds among the different SiO_2 particles. That is, the SiO_2 grains grow bigger with increasing temperature. The absorption peak at 1630 cm^{-1} is attributed to the coordinated and absorbed water and the peak at 1400 cm^{-1} is attributed to the bridging OH group in the $Zr(OH)_4$ gels, both of which decrease with increasing temperature. It is clear that the structurally coordinated water and the bridging OH group can survive higher temperatures. The weak absorption peak around 1020 cm^{-1} for the sample calcined at 1350°C suggests that a few Zr–O–Si bonds are formed,[10] but no trace of $ZrSiO_4$ was detected by XRD [Fig. 3(e)]. The characteristic band of t-ZrO_2 at about 600 cm^{-1} emerges on the IR profile (Fig. 5) for the sample calcined at 900°C, and its intensity becomes stronger with increasing temperature. This result is in accordance with that of DTA curves; the presence of t-ZrO_2 is also confirmed by the X-ray powder diffraction (Fig. 3).

4 Conclusion

We have successfully synthesized homogeneously dispersed ZrO_2–SiO_2 composite powders adopting fumed silica and zirconyl chloride as starting materials. The DTA–TG results show that the decomposition of $Zr(OH)_4$ gels is achieved below 500°C, accompanied by an exothermic phenomenon. The DTA exothermic peak at higher temperatures and the emergence of the band at about 600 cm^{-1}on the IR profiles reveal that the crystallization of t-ZrO_2 begins at about 900°C, which is confirmed by the X-ray diffraction. XRD curves also suggest that the silica matrix contributes to the thermal stability of the tetragonal zirconia. The t-ZrO_2 grains with smaller size, due to their encasement in the silica matrix, result in the survival of t-ZrO_2 in the ZrO_2–SiO_2 gels after calcination at elevated temperatures. The formation of Si–O–Si bonds among different SiO_2 particles means that the SiO_2 particle size grows bigger with increasing temperature.

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