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Ultrafine particles of the ZrO_2–SiO_2 system prepared by the spray–ICP technique

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Ultrafine powders of the ZrO_2–SiO_2 system prepared by spraying aqueous mixed solutions of $ZrO(NO_3)_2 \cdot 2H_2O$ and silicone oil into an ultrahigh temperature inductively coupled plasma (the spray–ICP technique) have been investigated in connection with particle growth and phase change caused by heat treatment. The prepared powders were composed of roundish ultrafine particles 10 to 20 nm in size, and their components were tetragonal ZrO_2 (t-ZrO_2) and amorphous SiO_2 (a-SiO_2). a-SiO_2 alone did not crystallize below 1400° C, though the particles grew above 900° C. t-ZrO_2 converted to monoclinic ZrO_2 (m-ZrO_2) above 400° C, also followed by particle growth. On the other hand composite powders of t-ZrO_2 and a-SiO_2 exhibited no particle growth below 1200° C. Above 1200° C t-ZrO_2 converted to m-ZrO_2, and its amount decreased with an increase in SiO_2 content. At 1400° C particle growth occurred, and the round particles of ZrO_2 were dispersed in an a-SiO_2 glass medium. These results indicate that ZrO_2 and SiO_2 mutually block particle growth, and that SiO_2 contributes to the quenching of t-ZrO_2 by keeping the particles of ZrO_2 within the critical particle size of t-ZrO_2.

1. Introduction

The spray–ICP technique [1], a modification of the spray–pyrolysis technique with an ultrahigh temperature inductively coupled plasma (ICP), is appropriate for the preparation of ultrafine powders of multi-component oxide systems. If the component oxides do not form a solid solution their particles are well distributed in the powders, because they are precipitated rapidly from the monoatomic gas phase formed at ultrahigh temperature by the complete decomposition of mother metal salts [2]. This gives new chemical and physical properties to the powders.

It was reported previously [3, 4] that powders of the ZrO_2–Al_2O_3 system prepared by this method are composed of the tetragonal type of ZrO_2 (t-ZrO_2) and γ-Al_2O_3, and that the transformation of t-ZrO_2 to monoclinic ZrO_2 (m-ZrO_2) caused by heat treatment largely depends on particle growth. In the present paper the spray–ICP technique has been extended to ZrO_2–SiO_2 system. ZrO_2 and SiO_2 form a compound, namely $ZrSiO_4$. SiO_2 itself has many isomorphs, i.e. amorphous SiO_2 (a-SiO_2), quartz, cristobalite and tridymite [5]. Additionally, the phase of ZrO_2 formed by crystallization from a gel is t-ZrO_2, and the crystallization temperature depends on the amount of SiO_2 [6]. This indicates that SiO_2 has a strong effect on the formation and stabilization of t-ZrO_2 [6]. Accordingly it is interesting to characterize as-prepared and heat-treated powders of the ZrO_2–SiO_2 system prepared by the spray-ICP technique, so as to examine the mutual interaction between ZrO_2 and SiO_2 in the powders.

2. Experimental procedure

Mother solutions were prepared by dissolving guaranteed grades of $ZrO(NO_3)_2 \cdot 2H_2O$ (Kanto Chemical Co) and silicone oil (Shin-Etsu Chemical Co, KF351A) into distilled water in appropriate ratios. They were sprayed through a coaxial type

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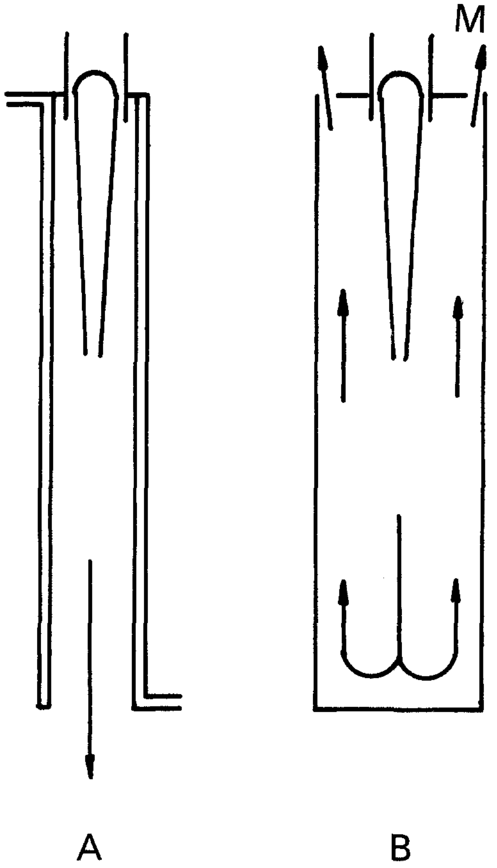

Figure 1 (A): water-cooled collector with an open end (70 mm internal diameter X 500 mm length). (B): collector with a closed end (140 mm internal diameter X 500 mm length): at M particles were collected on a microgrid for TEM.

of nebulizer to form fine droplets of size $< 10\,\mu m$, which were introduced into an argon ICP flame at $5\,m\,sec^{-1}$ with an argon carrier gas. The solutions were filtered beforehand (Millipore filter, pore size $0.22\,\mu m$) to keep the nebulizer from being blocked with dust.

The ICP flame was generated with an oscillator of frequency 6 MHz and maximum power 15 kW, and was stabilized with argon cooling gas flowing at $25\,l\,min^{-1}$. The flame size was 40 mm in diameter and 160 mm long, and the tail flame was about 400 mm long when the solutions were fed in. Further details of this method were reported elsewhere [7].

Powders were deposited into the collectors illustrated in Fig. 1. Collector A is a water-cooled tube (70 mm i.d. x 500 mm length), where the gas flows downwards. Collector B is a quartz tube (140 mm i.d. x 500 mm length) with a closed end and a loose lid. In this type the gas is exhausted through an opening between the tube and the lid. At the place marked M the powders were collected on a microgrid for transmission electron microscopy (TEM).

The prepared powders were ZrO_2 and SiO_2, added to give atomic ratios Zr : Si = 1 : 1, 1 : 2, and 1 : 4 (abbreviated to 1 : 1, 1 : 2 and 1 : 4, respectively). In addition, a mechanical mixture was prepared to compare the effect of heat treatment on the mixture with that on the powders formed by the spray–ICP technique. It was composed of SiO_2 and ZrO_2 obtained separately by the spray–ICP technique (Zr : Si = 1 : 1, abbreviated to 1 : 1 *mix*). The powders were heated in a platinum crucible at $10^\circ\,C\,min^{-1}$ in air and quenched at prescribed temperatures. They were characterized by X-ray powder diffraction (XPD) (Rigaku Denki, Cu$K\alpha$ radiation with nickel filter and diffractometer with graphite single-crystal monochromator) and by TEM (Hitachi HU-11). For XPD measurements the powders were held on a quartz plate which was fabricated so as to give no reflection peak. This is particularly effective in reducing the background, thereby making the XPD pattern clear when the powders contain amorphous oxides.

3. Results and discussion

3.1. Preparation and characterization of the powders

Fig. 2 illustrates XPD patterns of the as-prepared ZrO_2, SiO_2 and 1 : 1, deposited in Collector A. They are characterized as t-ZrO_2, a-SiO_2 and their composite, respectively. 1 : 2 and 1 : 4 were also composites of t-ZrO_2 and a-SiO_2. In the present paper, the mixture of ZrO_2 and SiO_2 prepared by the spray–ICP technique is referred to as a composite so as to differentiate it from the simple mechanical mixture 1 : 1 *mix*. There have been a lot of papers on the stability of t-ZrO_2 at room temperature. The effects of traces of additives such as water or Al_2O_3 [8] and of small particle size related to surface energy [9] appear to contribute to the stability. In a previous paper [3], as-prepared t-ZrO_2 was termed metastable tetragonal ZrO_2 (mt-ZrO_2) to differentiate it from t-ZrO_2 converted from m-ZrO_2 at about 1200° C, and its stability was supposed to come from the presence of water. However, in the case of t-ZrO_2 coprecipitated with SiO_2, it is difficult to discriminate between the as-prepared t-ZrO_2 and t-ZrO_2 quenched from high temperatures, if the

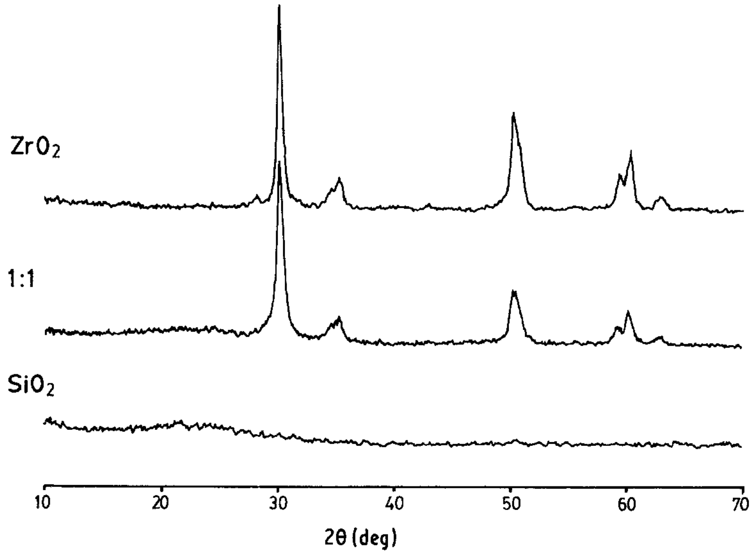

Figure 2 XPD patterns of as-prepared ZrO_2, SiO_2 and 1:1 deposited in Collector A.

as-prepared ZrO_2 is regarded as a high-temperature form of t-ZrO_2 stabilized by the additives or the size effect. In the present paper, they are equally defined as t-ZrO_2, simply because they give indistinguishable XPD patterns.

Fig. 3 shows a transmission electron micrograph of as-prepared 1:1 deposited in Collector A. The particles are roundish and their sizes range from 10 to 20 nm. The other oxides, except a-SiO_2, had almost the same particle size and shape as those of 1:1. The particles of as-prepared a-SiO_2 were 10 to 20 nm in size. However, during observation by TEM, owing to a rise in temperature due to electron bombardment the particles soon grew to about 30 nm as shown in Fig. 4.

Fig. 5 shows TEM of 1:1 collected on the microgrids for TEM at M over Collector B. The collected particles appear to form in the gas phase, and hereafter these particles are the subject of discussion when Collector B is referred to. XPD showed that 1:1 deposited in Collector B was also a composite of t-ZrO_2 and a-SiO_2. Noteworthy in Fig. 5 is that there are small black spots in the transparent particles. As t-ZrO_2 alone gives opaque images in TEM while a-SiO_2 gives transparent ones, the black spots are presumed to be t-ZrO_2 which implies that the small ZrO_2 particles are trapped inside SiO_2 particles. Apparently t-ZrO_2 is formed first, then a-SiO_2 is deposited and covers the particles of t-ZrO_2.

It was reported previously that particles of MgO [7] and Fe_2O_3 [10] deposited in Collector A are roundish, while those in Collector B are cubic and polyhedral respectively. This means that the morphology of ultrafine particles depends on the collectors, in other words on the precipitation

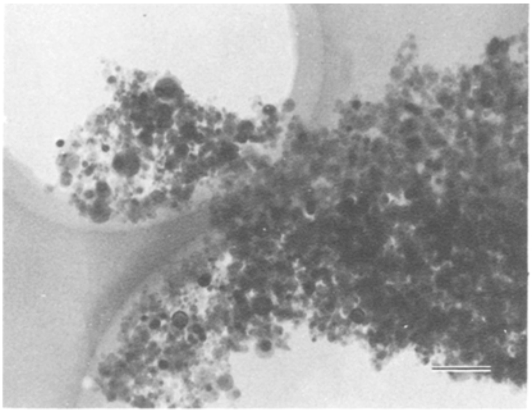

Figure 3 TEM of as-prepared 1:1 deposited in Collector A (bar = 100 nm).

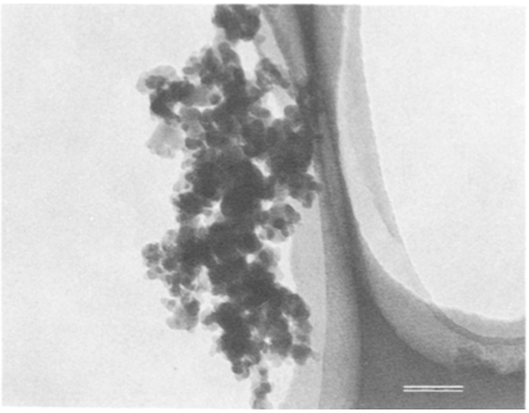

Figure 4 TEM of a-SiO_2, deposited in Collector A; particles grew large during observation (bar = 100 nm).

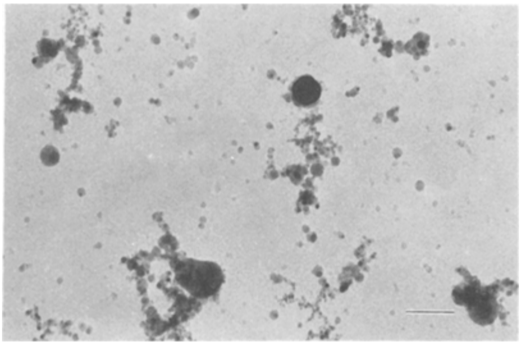

Figure 5 TEM of as-prepared 1 : 1 deposited in Collector B, (bar = 100 nm).

temp.(°C) / powders	as prep.	300	600	900	1200	1400
ZrO_2	tetra	tetra	tetra + mono	tetra + mono	mono	mono
1:1 *mix* *	tetra	tetra	tetra + mono	tetra + mono	tetra + mono	tetra + mono
1:1 *	tetra	tetra	tetra	tetra	tetra	tetra
2:1 *	tetra	tetra	tetra	tetra	tetra	tetra
4:1 *	tetra	tetra	tetra	tetra	tetra + mono	tetra + mono

*atomic ratio Zr:Si

Figure 6 Main phases of ZrO_2–SiO_2 powders quenched from various temperatures; SiO_2 is amorphous over the whole temperature range (tetra = *t*-ZrO_2, mono = *m*-ZrO_2, 1 : 1 *mix* = mechanical mixture).

conditions. It is likely that in Collector A the particles are deposited without further crystal growth owing to rapid quenching, while in Collector B the particles grow large through coalescence because of convection. Accordingly a change in morphology was expected in the present study as well. However, as shown in Fig. 5, the particles of 1 : 1 (also SiO_2 and ZrO_2) deposited in Collector B were also roundish, though their sizes were about five times larger than those in Collector A. Hence the change in morphology of this system was not so large as that of MgO or Fe_2O_3.

In the spray–ICP technique, a low-temperature form of oxide is predicted to deposit predominantly [2]. In a binary oxide system such as ZrO_2–CaO or ZrO_2–MgO, cubic zirconia solid solution is prepared [3]. Moreover, when $SiCl_4$ and Al_2Br_6 are introduced in the tail flame of ICP, mullite is precipitated [11]. The compound is therefore expected to form in the ZrO_2–SiO_2 system. However, the products were actually not $ZrSiO_4$ but composites of ZrO_2 and SiO_2. The formation of *t*-ZrO_2 indicates that the precipitation reaction proceeds below 400° C, because the as-prepared *t*-ZrO_2 was proved to irreversibly transform to *m*-ZrO_2 above 400° C [3]. This is also suggested by the precipitation of low-temperature forms of oxides, i.e. γ-Fe_2O_3 and γ-Al_2O_3 [2]. Consequently once ZrO_2 or SiO_2 is formed, they do not react with each other any more because of the low precipitation temperature. As mentioned above, the deposition of *a*-SiO_2 seems to be preceded by that of *t*-ZrO_2.

3.2. Heat treatment

The main phases of ZrO_2–SiO_2 powders heated to various temperatures and then quenched are summarized in Fig. 6. *a*-SiO_2 does not crystallize over the whole temperature range. Conversion of the as-prepared *t*-ZrO_2 to *m*-ZrO_2 occurred at 400° C, followed by particle growth, and was completed at 1200° C. On the other hand, high-temperature XPD ascertained that *t*-ZrO_2 was retained while heated at 900° C for 1.5 h. These observations clearly indicate that the conversion of *t*-ZrO_2 to *m*-ZrO_2 occurs in the cooling process. For 1 : 1 and 2 : 1, *t*-ZrO_2 is maintained below 1400° C, though an increase in ZrO_2 content (4 : 1) results in the formation of *m*-ZrO_2 even at 1200° C. Compared with a powder of the ZrO_2–Al_2O_3 system having an equivalent molar oxide ratio, SiO_2 retains *t*-ZrO_2 more strongly than Al_2O_3, because in the case of a powder having $ZrO_2 : Al_2O_3 = 1 : 1$ (corresponding to 2 : 1 of the ZrO_2–SiO_2 system) a large amount of *t*-ZrO_2 converts to *m*-ZrO_2 when heated to 1380° C [3].

The process of particle growth, as well as the state of particle dispersion, seems to play an important role in the stability of *t*-ZrO_2. *a*-SiO_2 alone caused particle growth above 900° C and *t*-ZrO_2 alone above 400° C, while particle growth of the composite powders did not occur even at 1200° C. This indicates that ZrO_2 and SiO_2 block the particle growth mutually. Fig. 7 shows TEM of 1 : 1 heated at 1400° C. This gives almost the same particle images as those of plasma-dissociated zircon [12]. The particles of *t*-ZrO_2 (black spots of size 40 to 50 nm) are dispersed homogeneously in *a*-SiO_2 (the transparent part) and are separated completely by SiO_2. This hinders particle growth and keeps the particle size of ZrO_2 within the critical size of *t*-ZrO_2 [13], which readily explains the stability of *t*-ZrO_2 in the presence of SiO_2.

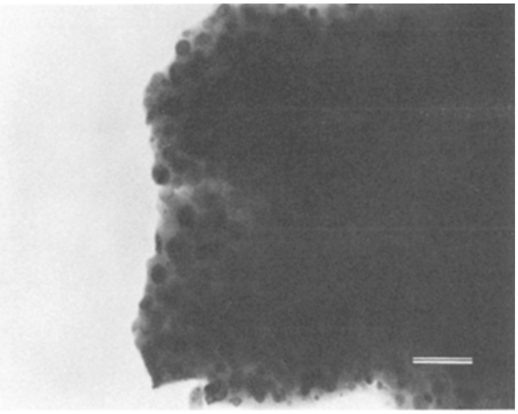

Figure 7 TEM of 1 : 1 heated at 1400° C (bar = 100 nm).

Further heat treatment of 1 : 1 at 1500° C for 2 h resulted in the formation of cristobalite, while *t*-ZrO_2 was maintained unchanged. After 7 h heating some *t*-ZrO_2 reverted to *m*-ZrO_2, and the particles of ZrO_2 grew to 150 to 200 nm. Consequently the critical size of *t*-ZrO_2 in SiO_2 is about 200 nm.

t-ZrO_2 of 1 : 1 *mix* transformed to *m*-ZrO_2 at low temperatures, as in the case of the as-prepared ZrO_2 alone. However, a small amount of *t*-ZrO_2 is quenched at 1200 and 1400° C, which is the effect attributed to SiO_2. Clearly SiO_2 in composite powders prepared by the spray–ICP technique obstructs the phase change of *t*-ZrO_2 more strongly than that of the mechanical mixture. These findings suggest that the as-prepared composites are not simple mechanical mixtures of ZrO_2 and SiO_2, but are mixtures having a strong mutual interaction between ZrO_2 and SiO_2.

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