JOURNAL OF MATERIALS SCIENCE 25 (1990) 1987–1990

Stability of metastable tetragonal ZrO_2 in compound powders and nucleation arguments

YOSHINORI KANNO
Department of Chemistry, Yamanashi University, Takeda, Kofu 400, Japan

ZrO_2–SiO_2 (1:1) mixtures and ZrO_2 particles were prepared by a sol–gel method from the solutions of $ZrOCl_2 \cdot 8H_2O$ (ZOC) + $Si(OC_2H_5)_4$ (TEOS) + C_2H_5OH and ZOC + C_2H_5OH + H_2O + NH_4Cl systems, respectively. Quantitative changes of phase crystallized by heating were compared with those of ZOC + TEOS + H_2O and/or $ZrO(NO_3)_2 \cdot 2H_2O$ + H_2O systems, respectively. The stability of metastable tetragonal (mt)-ZrO_2 particles depends on the Young's modulus of the SiO_2 matrix. Transition metal oxides existing on the interface assisted in stabilizing mt-ZrO_2. The order of the assistance agreed with that of the relative field strengths of their oxides. A relationship between the ionic radius and the volatility of anionic groups, and the difficulty of nucleation for the martensitic transformation accompanying a shear stress, is suggested.

1. Introduction

There has been much effort recently to elucidate the stability of metastable tetragonal (mt)-ZrO_2 particles in ceramic matrices with particular reference to Al_2O_3–ZrO_2 composites (ZrO_2-toughened Al_2O_3) and to partially stabilized ZrO_2 [1–3]. It is known that particles above a critical size transform martensitically from tetragonal (T) to monoclinic (M) type on cooling; the critical factors that could affect the size dependence of the transformation temperature are surface and strain energies, the chemical free energy driving force, and the difficulty of nucleating the martensitic transformation [4].

On the stability of the mt-ZrO_2 phase in ultrafine ZrO_2 and/or ZrO_2-containing mixtures, however, the surface and strain energies have, oddly, been argued without consideration of the other factors described above [5, 6]. Here we discuss stability from the angle of topochemical reactions for inorganic solid materials.

In studying the matrix effect on the stability of mt-ZrO_2 within ZrO_2–MO_x (MO_x = SiO_2, Al_2O_3) system, we suggested from elementary kinetics that the transformation reaction of mt-ZrO_2 was composed of four terms: the chemical factors for the interface between two oxide particles (f_c) and for the bulk property such as Young's modulus of the matrix (f_y); the geometrical factor for the dispersive state (inter- or intragranular) (g); the content of ZrO_2 in the binary system [C_{ZrO_2}]; and the typical function of the mobility of ZrO_2 particles with a temperature-dependency, $\mu(T)$ [7]. From the equation proposed in the report [7], we stated that the phase transformation of mt-ZrO_2 in the compound powder system could be conveniently explained. In the present work, we report about the role of f_c and f_y on the stability of mt-ZrO_2 in detail, and deal with the nucleation arguments for martensitic transformation.

2. Experimental procedures

ZrO_2–SiO_2 (1:1) mixtures were prepared by a sol–gel process. The equimolar solution of $ZrOCl_2 \cdot 8H_2O$ (ZOC) dissolved in hot ethanol and $Si(OC_2H_5)_4$ (TEOS) was mixed by magnetic stirrer agitation at room temperature. Finally the rotation of the stirrer was terminated due to the increase in viscosity with agitation time. The gel was allowed to air-dry, and then dried to a powder and calcined at the raising rate of 300° C h^{-1} with a clean air carrier, kept for 2 h at the desired temperatures, and then cooled in the furnace under air flow. ZrO_2 powders were also prepared by the sol–gel method from hydrolysis of a system of ZOC + C_2H_5OH + H_2O + NH_4Cl (catalyst) solution. The heat-treated powders were characterized by XRD (Rigaku Denki Co.) using CuK_α radiation.

3. Results and discussion

3.1. Stability of mt-ZrO_2 in the ZrO_2–SiO_2 system

Table I shows the relation between the crystal phase of ZrO_2–SiO_2 (1:1) system powders and calcination temperatures, where the data [8] of Kadogawa and Yamate, obtained by the sol–gel process using a solution of ZOC + TEOS + H_2O, are included in order to account for the behaviour differences.

In the ZOC + TEOS + C_2H_5OH system, the heat-treated powders were mixtures of T-, M-ZrO_2 and amorphous SiO_2 (a-SiO_2) at 500° C; the content of T-ZrO_2 decreased gradually with an increase of temperature in contrast with increasing M-ZrO_2. The variation of the relative content of T-, M-ZrO_2 was due to the crystallization as α-cristabalite from the amorphous state at 900° C. Further, not much change in the relative content was caused by heating to 1350° C.

From these results, we may conclude that the T → M phase transformation reaction proceeds as far

0022-2461/90 $03.00 + .12

TABLE I Main phases of ZrO_2–SiO_2 (1:1) powders quenched from various temperatures

Procedure	Temperature (° C)					
	320	500	800	900	1200	1350
TEOS + ZOC		T-	▬	T- ▬	const. ▬	T-
+ C_2H_5OH		M-	▬	M- ▬	const. ▬	M-
		a-S		α-C	const.	α-C
TEOS + ZOC	T-		T- ▬	▬	▬	T-
+ H_2O [8]			M- ▬	▬	▬	M-
					a-S	α-C

TEOS = $Si(OC_2H_5)_4$, ZOC = $ZrOCl_2 \cdot 8H_2O$, T- = T-ZrO_2, M- = M-ZrO_2. a-S = amorphous silica, α-C = α-cristobalite, const. = constant.

as the a-SiO_2 matrix with a smaller Young's modulus, and terminates with an increase of strain energy caused by the increase of the modulus of the matrix, f_y, due to crystallization. This clearly indicates that the strain energy contributes to the stabilization of fine mt-ZrO_2 particles.

Garvie [5] has reported the critical diameter of mt-ZrO_2 with a free surface to be about 30 nm, but we suggest that the diameter of mt-ZrO_2 within binary system powders cannot be defined, because of the particle morphology and Young's modulus of the matrix.

In the ZOC + TEOS + H_2O series, on the other hand, the T → M phase transformation reaction in ZrO_2–SiO_2 (1:1) powders took place from 800° C and propagated to 1350° C, whence a-SiO_2 crystallized as α-cristobalite. From a comparison with the results of two series, it is reconfirmed that the strain energy caused by the bulk property of the matrix at the boundary affects the reaction.

As described in previous papers [9–11], the difference of starting temperatures for the phase transformation of ZrO_2 and the crystallization of SiO_2 was influenced by the solvents (H_2O, C_2H_5OH), that is, by the difference in type or shape of the siloxane polymers (linear or three-dimensional), because the hydrolysis reaction of TEOS is strongly dependent on the molar ratio of water.

3.2. Effect of transition metal ions on the stability of mt-ZrO_2

Kadogawa and Yamate [8] have synthesized $ZrSiO_4$ powders which were free of residual ZrO_2 and SiO_2 by the sol–gel method from a solution of TEOS + ZOC + H_2O + HCl (catalyst for the hydrolysis of TEOS) plus a small amount (~ 3.2 mol %) of transition metal salts at comparatively low temperatures. This promotes the formation of $ZrSiO_4$, $CoCl_2$, $CuCl_2$, $Fe(NO_3)_3$, $MnCl_2$ and $Ni(NO_3)_2$.

In their report [8], they presented the XRD patterns of powders obtained by heating the gel with these additives at 1000° C. The patterns indicate that T → M phase transformation is strongly dependent on the kind of additive metal ions. On the variation of peak intensity, Table II summarizes the effect of transition metal ions on the stability of mt-ZrO_2 in the ZrO_2–SiO_2 mixture. In Table II, $CoCl_2$ resulting in the successful formation of $ZrSiO_4$ at 1000° C is an exception.

TABLE II Effect of small amount of additives (transition metal salts) on stability of mt-ZrO_2 in ZrO_2–SiO_2 (1:1) powders

$Ni(NO_3)_2 > CuCl_2 > Fe(NO_3)_3 > MnCl_2$

TABLE III Lowest temperatures to form the liquid phase between SiO_2 and transition metal oxides, and relative field strengths (Z/a^2) of the metal ions

	–NiO	–CuO	–FeO	–MnO
Temperature (° C)	1650 ± 10	1050	1175	1251
Z/a^2	0.55	0.53	0.52	0.48

Z, charge of cation; a, distance between cation and anion.

The order summarized in Table II teaches us the factors involved in the stability of mt-ZrO_2 particles. In order to extract the factors, we summarize in Table III the lowest temperatures to form the liquid phase between SiO_2 and transition metal oxides [12], and relative field strengths of metal ions [13]. The field strength is regarded as a measure of the force of metal ions attracting the electron cloud of oxygen. Although the $Fe(NO_3)_3$ used is trivalent, the cations listed in Table III are divalent.

The thermal decomposition (or melting) temperatures of transition metal salts used are: $Ni(NO_3)_2$, mp = 105 to 110° C; $CuCl_2$, mp = 498° C; $MnCl_2$, mp = 650° C; $Fe(NO_3)_2$ < $FeSO_4$, mp = 170° C; $Fe_2(SO_4)_3$, 480° C [14]. These values indicate that the effect of anion groups on the stabilization of mt-ZrO_2 by heating at 1000° C may be ignored. Therefore, the above order can be interpreted as a behaviour for transition metal oxides. From a comparison of Tables II and III, it is clear that the order of relative field strength agrees with the stabilization order.

Therefore we may conclude that transition metal ions existing on the interface between fine mt-ZrO_2 particles and SiO_2 matrix play an important role in assisting in stabilizing the mt-ZrO_2 phase against transformation during cooling. Generally, cations with a high relative field strength attract stronger mt-ZrO_2 particles and restrict the mobility (freedom) of the particles. However, it should be noted that these arguments are limited in the interactions between the pair of acidic oxides.

In their study of the role as a solute stabilizer of impurities (e.g. CaO, 0.2 wt %; MgO, 0.12 wt %) by using X-ray microanalysis of ZrO_2 particles in ZrO_2-toughened Al_2O_3, Butler and Heuer [15] clarified that solute levels in ZrO_2 particles can differ significantly. However, these solute differences do not appear to affect significantly the particle-size dependence of the transformation temperature or its variation with particle size. However, the dopant above a few mol % would presumably show the chemical effect significantly against the stabilizing of mt-ZrO_2.

The amount of transition metal ions added, ~ 3.2 mol %, can be incorporated in solid solution in mt-ZrO_2 at the boundaries, and would assist in stabilizing this phase. (This factor corresponds to the term f_c in our previous paper [7].)

3.3. Nucleation discussion on the stability of isolated mt-ZrO_2 particles

It is generally held that the most important factors determining the phase transformation of fine particles have been shown to be particle size, particle shape, and manufacturing process (concerning the kind and concentration of lattice defects, or imperfections of crystal).

The relationship between the crystallized phase of isolated ZrO_2 particles produced by the sol–gel method and the heat-treatment temperature is summarized in Table IV. The data of ultrafine particles of ZrO_2 prepared by the spray-inductively coupled plasma (ICP) technique carried out by Ono *et al.* [16] are also referred to, in order to account for the effect of starting mother salts on the phase transformations.

The particles produced by the sol–gel method exhibited a phase transformation reaction at 500° C with diminishing content of T-form with higher temperatures, and the reaction terminated at 1500° C.

In the spray ICP particles, the transformation finished at 1200° C, the reaction propagating gradually from 400° C. The temperature deviation on the transformation observed between these two methods may be interpreted with the aid of nucleation arguments. The T → M transformation of ZrO_2 is displacive, and a rapid transition. Deformation twins accompanying the shearing strain of the crystal, and unnecessary diffusion of the atom, were often observed in the transformed crystals [17, 18].

In fine crystal, it is thought that the displacive transformation takes place because of the shortage of dislocations which are nuclei of transition, and/or the low mobility of dislocations leading to repression of nucleation and growth. Therefore, the quantity of dislocations is largely concerned with the T → M transformation.

According to Moriyoshi *et al.* [19], high voltage electron microscope observations have revealed that ZrO_2 particles in calcined powders prepared from dried mixture of Al_2O_3 powders and ZOC solution had no dislocations and stacking faults.

In their study on crystallization and phase transformation of ZrO_2 particles produced by direct calcination of zirconyl nitrate and zirconyl chloride, Murase *et al.* [20] showed that the former induced the T → M transformation at a lower temperature than the latter. Therefore we expect that ZrO_2 particles derived from a nitrate easily, propagate the transformation.

In terms of topotaxy between mother material and oxide transmitted, compare $ZrO(NO_3)_2$ and $ZrOCl_2$. Zirconyl, having the rotational atomic group of NO_3^- with a larger ionic radius than that of Cl^-, a shear stress tends to appear in its structure on desorption of anionic groups accompanying a violently thermal vibration.

TABLE IV Main phases of isolated fine ZrO_2 powders quenched from various temperatures

Mother solution	Temperature (° C)				
	300	400	500	1200	1500
ZOC + H_2O + NH_4OH (catalyst) (sol–gel)		T-	T- M-		M-
$ZrO(NO_3)_2 \cdot 2H_2O$ + H_2O [16] (spray ICP)	T-	T- M-		M-	

ZOC = $ZrOCl_2 \cdot 8H_2O$.

It is generally held that the formation of twin crystals propagates rapidly only if the elastic energy stored in the crystal reaches a limit. From the mechanism of martensitic transformation, the structural body rich in shear stress, which is consumed as energy for the atomic deformation, tends to advance T → M transformation of ZrO_2.

The second argument is the difference in desorption temperatures of NO_3^- and Cl^- ions. (That of the former is expected to be lower than that of the latter.) Anionic impurities remaining in the metastable phase tend to condense into the dislocations and boundaries, and operate as stabilizers of lattice imperfections contributing to nucleation for the transformation. By heating the sample, the volatility of NO_3^- groups takes place with decreasing the restraint force against the dislocations and the boundaries from a lower temperature, and results in the isothermal transformation of the metastable phase. Furthermore, there is a possibility that easily volatile NO_3^- ions produce the excess vacancies above thermal equilibrium concentration within the crystal, and these vacancies result in the formation of secondary defects which are useful for the transformation. As a feature of the spray ICP technique, the argument about the super-cooling process is needed, because the process is liable to produce lattice imperfections.

4. Conclusions

The stability of mt-ZrO_2 particles depends on the Young's modulus of the SiO_2 matrix. Transition metal oxides existing on the interface with the SiO_2 matrix assisted in stabilizing mt-ZrO_2. The order of assistance agreed with that of the relative field strengths of their oxides.

It has been argued that the rotational atomic group of NO_3^-, with a larger ionic radius, shows a shear stress in its structure on desorption, and this stress assists in the martensitic transformation of ZrO_2. It is suspected that the volatility of NO_3^- groups decreases the restraining force against dislocations and results in the progress of phase transformation.

References

1. N. CLAUSSEN, *J. Amer. Ceram. Soc.* **61** (1978) 85.
2. E. P. BUTLER and A. H. HEUER, *ibid.* **65** (1982) C-206.
3. M. KOMATSU, H. FUJITA and S. TAKENO, *Yogyo-Kyokai-shi* **94** (1986) 748.
4. A. H. HEUER, N. CLAUSSEN, W. N. KRIVEN and M. RÜHLE, *J. Amer. Ceram. Soc.* **65** (1982) 642.
5. R. C. GARVIE, *J. Phys. Chem.* **69** (1965) 1238.
6. Y. MURASE, E. KATO and K. DAIMON, *J. Amer. Ceram. Soc.* **69** (1986) 83.
7. Y. KANNO and T. SUZUKI, *J. Mater. Sci. Lett.* **8** (1989) 41.
8. Y. KADOGAWA and T. YAMATE, *Yogyo-Kyokai-shi* **93** (1985) 338.
9. Y. KANNO and T. SUZUKI, *Hyomen Kagaku* **9** (1988) 434.

10. Y. KANNO, *J. Mater. Sci.* **24** (1989) 2415.
11. *Idem, Hyomen Kagaku* **9** (1988) 207.
12. E. M. LEVIN, C. R. ROBBINS and H. F. McMURDIE, "Phase Diagrams for Ceramists" (American Ceramics Society, 1964) pp. 59, 65, (1969) pp. 32, 90.
13. B. C. WEBER, H. J. GARRETT, F. A. MAUER and M. A. SCHWARTZ, *J. Amer. Ceram. Soc.* **39** (1956) 197.
14. Nippon kagaku kai ed. "kagaku Binran" (maruzers) (1966) pp. 60, 62, 92, 136.
15. E. P. BUTLER and A. H. HEUER, *J. Amer. Ceram. Soc.* **65** (1982) C-206.
16. T. ONO, M. KAGAWA and Y. SYONO, *J. Mater. Sci.* **20** (1985) 2483.
17. J. E. BAILEY and M. RÜHLE, *Prog. Ray. Soc.* **279A** (1964) 395.
18. E. BISCHOFF and M. RÜHLE, *J. Amer. Ceram. Soc.* **66** (1983) 123.
19. Y. MORIYOSHI, Y. CHIDA, T. IKEGAMI, H. YAMAMURA and A. WATANABE, *Zirconia Ceram.* **1** (1983) 97.
20. Y. MURASE, E. KATO and H. MATSUMOTO, *Nippon Kagaku Kaishi* (1972) 2329.

Received 9 January
and accepted 23 August 1989