JOURNAL OF MATERIALS SCIENCE **24** (1989) 2415–2420

Thermodynamic and crystallographic discussion of the formation and dissociation of zircon

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The mechanism for the formation of zircon from a system of $Si(OC_2H_5)_4$–$ZrOCl_2 \cdot 8H_2O$–C_2H_5OH solution was constituted from the following steps; the formation of sol composed of an equimolar Zr^{4+} located in the neighbourhood of a linear siloxane polymer, deposition of metastable fine (tetragonal) T-ZrO_2 by heating, the tetragonal to monoclinic (T → M) transformation of the fine T-ZrO_2 aggregates separated from the strain energy of grain boundary between two oxide components, the initiation of the interface reaction between T-ZrO_2 and amorphous SiO_2, and the acceleration of the formation by the Hedvall effect caused by the crystallization of SiO_2. The key technology for the synthesis of zircon from the oxide components ZrO_2 and SiO_2 was the mechanochemical activation of the surface layer by milling, the formation of transition phase between the two components by adding the guest element, and the presentation of metamorphic surface state. Zircon dissociated into M-ZrO_2 and SiO_2 glass, and the dissociation temperature was expected to be above 1700° C, which required the correction of the phase diagram for ZrO_2–SiO_2 system used previously.

1. Introduction

The zircon ceramic is an important candidate for high temperature refractory materials, because of its high thermal shock resistance, originating from having a lower thermal expansion coefficient than any other oxide ceramic. But, the thermal dissociation of zircon at higher temperatures is also known. In the presence of impurities, the dissociation temperature is remarkably lowered and the degree of it is elevated [1, 2]. It is said that the impurities showing a high reactivity towards silica have a strong effect on the dissociation phenomena [3].

Butterman and Foster [4] reported that the dissociation temperature was 1676 ± 7° C. Further, in their study of the dissociation and the re-binding of zircon from Florida, Curtis and Sowman [5] reported that the dissociation started at 1540° C and almost all of it had dissociated by 1870° C, with a rapid increase in the rate from 1750° C.

The dissociation phenomena transforming it into monoclinic (M-) ZrO_2 and SiO_2 glass was considerably influenced by the heating time. For example, the dissociation was almost finished by prolonged heating for 6 h at 1760° C. On the other hand, the degree of dissociation is also concerned with an undercooling rate, because of the re-binding of dissociated compounds, which is possible only under a very slow undercooling.

The powders purified from natural zircon sand have been used to investigate the thermal stability and the thermodynamic character of zircon. The natural zircon sand contains various impurities, such as HfO_2, TiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, P_2O_5 [6], but of course, the purified powders are not perfectly free from the impurities. Therefore, it is expected that the dissociation temperature of synthesized zircon is higher than the previously published values [4, 5]. This rise would contribute to the expansion of the application fields of zircon ceramics.

In the synthesis of zircon by the sol–gel method from a $ZrOCl_2 \cdot 8H_2O$–$Si(OC_2H_5)_4$–C_2H_5OH solution system, we previously reported that metastable fine T-ZrO_2 and amorphous SiO_2 powders were obtained by heating and the T-ZrO_2 aggregates gradually transformed into M-ZrO_2 with a decrease in surface energy caused by the temperature increase [10, 11].

Generally, the formation of zircon from ZrO_2 and SiO_2 was studied in view of the additive effect of the impurities being a low melting point such as alkali halide and transition metal oxides. Naturally, the addition of the impurities directly relates to the lowering of the dissociation temperature. In this work, zircon powders were synthesized from ZrO_2 and SiO_2 without reaction promoters, and the thermodynamic and the crystallographic explanation for the formation and the dissociation of zircon were stated.

2. Experimental procedure

2.1. Synthesis of zircon by the sol–gel method

An equimolar solution of $ZrOCl_2 \cdot 8H_2O$ dissolved in hot ethanol and $Si(OC_2H_5)_4$ was mixed using a magnetic stirrer at room temperature. The rotation of stirrer was hindered by the increase in viscosity with an agitation time. Then the gel was allowed to dry in air, and then the dried gel was milled using a teflon ball and pot for 2 days. The milled powders were calcined in an ultra-high temperature electric furnace (Siliconit Co. Ltd Kogyo, Japan) at a heating rate of 300° C h^{-1} under a carrier gas flow of clean air. It was

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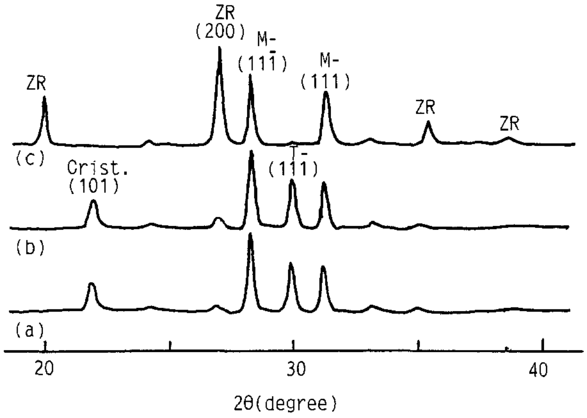

Figure 1 XRD patterns of non-milling ZrO_2–SiO_2 system powders calcined at (a) 1500, (b) 1650, (c) 1700° C. Zr = $ZrSiO_4$; M- = M-ZrO_2; T- = T-ZrO_2; Crist. = crystobalite.

kept for 2 h at the desired temperature, and then cooled in the furnace under an air flow. The resultant powders were characterized by X-ray diffraction XRD (Rigaku Denki Co. Ltd.) using Cu*Kα* radiation.

2.2. Thermal dissociation of zircon

The dissociation was investigated using the commercial zircon powders (Wako Junyaku Co. Ltd) of purity > 90%, manufactured through size reduction, purification and a calcination process of the natural zircon sand. The zircon powders were heated for 2 h at the desired temperatures under an air flow. The resultant powders were similarly characterized by XRD.

3. Results and discussion

3.1. Formation reaction of zircon

Figure 1 shows the representative XRD patterns of non-milling powders synthesized by calcining at 1500, 1650 and 1700° C. The zircon crystal was barely formed at 1500° C, the conspicuous growth of the crystal was unrecognized till 1650° C, and then the zircon formation rapidly advanced by the interface reaction between T-ZrO_2 and crystobalite at 1700° C. It was recognized that the zircon formation by the interface reaction is difficult in the absence of a reaction promoter. This difficulty is easily explained by the crystallographic consideration, as illustrated in Fig. 2, showing a crystal structure of (a) T-ZrO_2 and (b) $ZrSiO_4$.

In a case of T-ZrO_2, the cations are displaced in the face-centred cubic form, and are located in the centre of the cube formed by the anions. The anions exist in the centre of regular tetrahedral formed by cations. The 8-coordination of zirconium is strained in the direction of the little arrows.

If both the movement of Zr^{4+} in the direction of the arrows, and the formation of the island-like lattice of regular tetrahedral SiO_4 by the insertion of the SiO_2 component were permitted, the combination reaction between ZrO_2 and SiO_2, i.e., the zircon formation, was propagated. This crystallographic consideration supports the fact that an activation energy for the combination reaction between ZrO_2 and SiO_2 is kinetically very large, so the combination reaction is permitted only at higher temperatures.

The low reactivity of the interface reaction between ZrO_2 and SiO_2 is also explained by the solubility relationship of the oxides of aluminium and silicon being side by side in the periodic table. The solid solution of SiO_2 in ZrO_2 does not exceed 0.1% SiO_2 according to Lang *et al.* [7]. On the other hand, Alper *et al.* [8] indicated that $<1\%$ ZrO_2 went into solid solution in α-Al_2O_3, and up to $\approx 7\%$ Al_2O_3 could form solid solution with ZrO_2. This solubility limit of the two compound systems let us estimate that the interface reaction of the ZrO_2–SiO_2 system is inferior to that of the ZrO_2–Al_2O_3 system in a reactivity. SiO_2 would be inferior to Al_2O_3 with regard to the activation of a surface layer of ZrO_2. In passing, the eutectic points of ZrO_2–SiO_2 and ZrO_2–Al_2O_3 component systems are 1680, 1820° C, respectively [9] which contradict the reactivity between the solids.

Figure 3 shows (A) representative XRD patterns of milled powders synthesized by calcining at 1583 and 1700° C, and (B) the variation of $I_p/(I_{ZR(200)} + I_{M(11\bar{1})} + I_{M(111)} + I_{T(111)})$ [where P = ZR(2 0 0), M(1 1 $\bar{1}$) + M(1 1 1) or T(1 1 1)] of the powders plotted against calcining temperature.

Here, *I* is the peak intensity of XRD, ZR is $ZrSiO_4$, M- is M-ZrO_2, T- is T-ZrO_2 and (abc) is the index of the crystal plane.

These patterns indicate that unreactive ZrO_2 and SiO_2 remain in the absence of any promoters such as an alkali halide and transition metal, but it also suggests that the zircon formation is remarkably accelerated by the milling of dried powders. This milling effect is probably caused by the mechanochemical activation of the surface layer of dried powders and by the elevated mixing effect. However, we can not get a 100% $ZrSiO_4$ composite powder, because of the topochemical reaction often observed in the reaction between solids. It was estimated from Fig. 3 that the zircon formation is saturated in the temperature region above about 1580° C. Further investigation

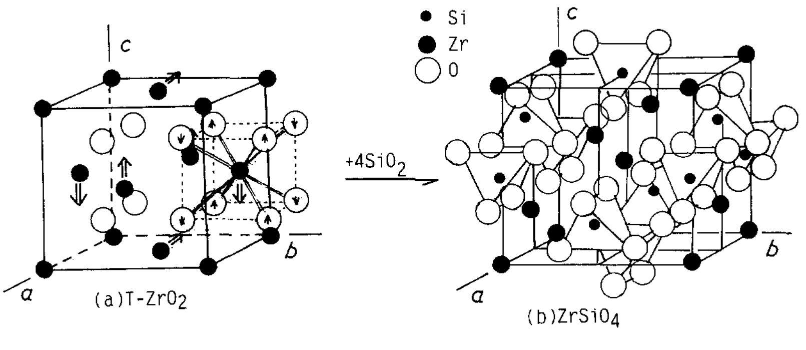

Figure 2 Crystallographic representation of the combination reaction between ZrO_2 and SiO_2, (a) T-ZrO_2, (b) $ZrSiO_4$ (fluorite structure). The little arrows (↑) in the T-structure indicate the displacement of the oxygens from their positions in the c phase. Zirconiums are moved in the direction of (⇑), and then island-like lattice of SiO_4 are formed by the insertion of the SiO_2 component.

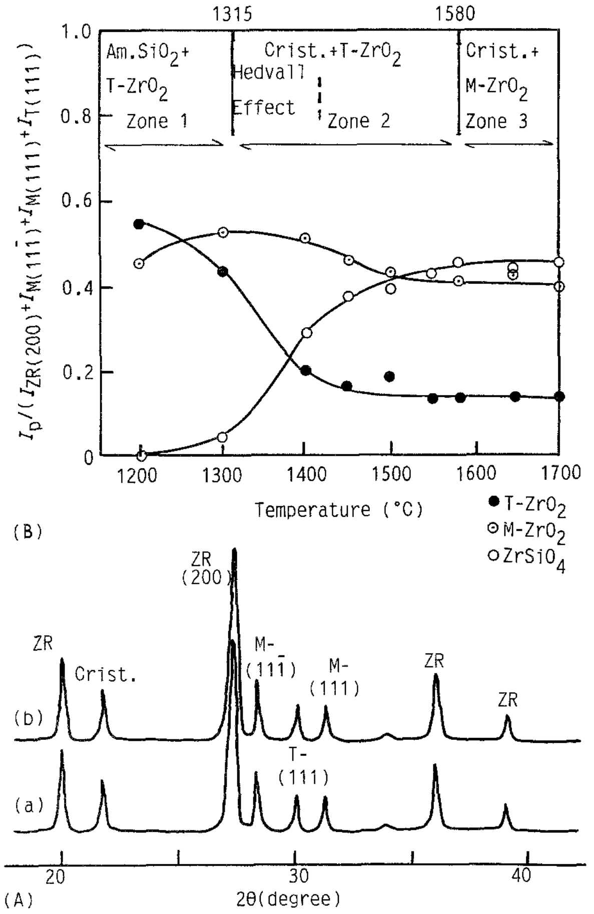

Figure 3 (A) XRD patterns of milled ZrO_2–SiO_2 system powders calcined at (a) 1583, (b) 1700° C. (B) Variation of $I_p/[I_{ZR(200)} + I_{M(11\bar{1})} + I_{M(111)} + I_{T(111)}]$ of the milled powders with calcining temperature. p = ZR(200), M(11$\bar{1}$) + M(111) or T(111); Am = amorphous.

would be needed on the second grinding after the preliminary calcination and the reform of the milling technique in order to get 100% zircon crystal powders without additives.

Fig. 3 also shows the following important item, that is, the zircon formation by the combination between crystobalite and T-ZrO_2 is possible even at 1700° C without the thermal dissociation. Besides, Fig. 1 shows that the change of Gibb's free energy for the formation reaction of zircon at 1700° C is a negative value. This would suggest that the dissociation temperature of zircon is above 1700° C.

In the previous papers [10, 11], we investigated the formation mechanism of $ZrSiO_4$ synthesized from a $Si(OC_2H_5)_4$–$ZrOCl_2 \cdot 8H_2O$–C_2H_5OH system solution in relation to the T → M transformation of ZrO_2 and to the crystallization of SiO_2, where the formation scheme of zircon (zone 1–3), described in Fig. 3B, consisted of four steps; that is, amorphous SiO_2 + T-ZrO_2, crystobalite + T-ZrO_2 (Hedvall effect caused by crystallization of SiO_2), crystobalite + T-ZrO_2, crystobalite + M-ZrO_2* (* estimation) with a temperature increase.

Kadogawa and Yamate [12] synthesized zircon powders (100%) free from residual ZrO_2 and SiO_2 by the sol–gel method from a system of $Si(OC_2H_5)_4$–$ZrOCl_2 \cdot 8H_2O$–H_2O–$Ni(NO_3)_2 \cdot 6H_2O$–HCl (catalyst) in a low temperature region. The zircon formation proceeded from amorphous SiO_2 + T-ZrO_2, then M-ZrO_2 contributed to the formation according to the shortage of T-ZrO_2 consumed, and resulted in zircon powders (100%). This successful synthesis of zircon free from residual oxides is probably due to the effect of transition metal ion standing at the grain boundary between ZrO_2 and SiO_2, for the metallic impurities tend to concentrate to the boundary.

Let us discuss again zone 3 (crystobalite + T-ZrO_2) in Fig. 3. If we want to obtain the zircon powders (100%), the interface reaction between M-ZrO_2 and crystobalite is needed according to the lack of T-ZrO_2 consumed by the zircon formation. This mechanism would be possible by suitable choice of grinding condition of dried powders and/or by twice grinding after preliminary calcination. This speculation is based on the idea that the interface reaction between ZrO_2 and SiO_2 depends on the surface state of two component oxides.

The recombination of dissociated ZrO_2 and SiO_2 has been investigated by many researchers [13, 14], who reported that the recombination is rapidly accelerated from 1450° C. Easy recombination of dissociated ZrO_2 and SiO_2 indicates that the zircon synthesis is readily performed, if the surface state of two component oxides is metamorphic. It is said that the surface structure of the dissociated ZrO_2 and SiO_2 is slightly destroyed, i.e., presents a metamorphic state. Therefore, it is estimated that the synthesis reaction of zircon is strongly affected by the disturbed lattice structure, simultaneously considering the milling effect for the reaction promotion. The dissociation of zircon is remarkably promoted by the penetration of additive oxide components to the interface layer (at a lower temperature) and to the bulk of zircon crystal (at a higher temperature), which means that the formation and the dissociation of zircon is a very sensitive reaction for the surface state.

Next, we will consider the difference in reactivity of

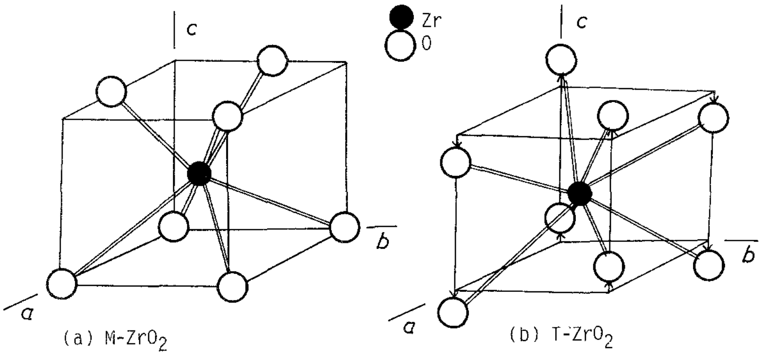

Figure 4 Crystal structure of ZrO_2 polytype (a) M-(7-coordination); (b) T-(8-coordination).

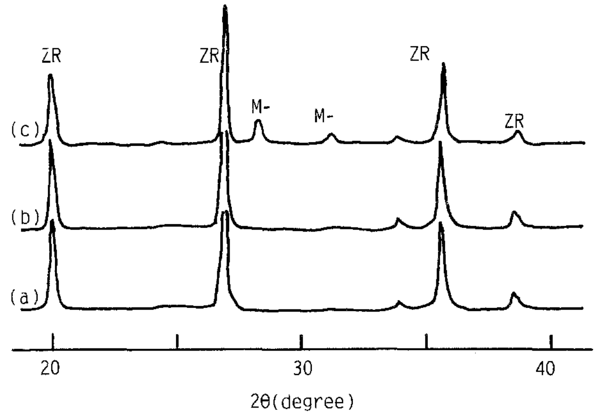

Figure 5 XRD patterns of commercial zircon powders heated at (a) 1500, (b) 1650, (c) 1700°C.

the ZrO_2 polytype against SiO_2 from the crystallographic aspect. Fig. 4 shows the crystal structure of ZrO_2, (a) M-(7-coordination), (b) T-(8-coordination). The 7-coordination of M-ZrO_2 has a directional bonding character. The crystal structure of T-ZrO_2 is strained in the direction of the arrow in Fig. 4b. The coordination number of zirconium in the zircon crystal is 8, therefore it is suspected that T-ZrO_2 having 8-coordination is more favourable for the zircon formation reaction in view of the migration of atoms.

Another geometrical factor, but crystallographic aspect, should be considered on the favourability of T-ZrO_2 for the synthesis reaction of zircon. We formerly reported that the heat-treated powders were a mixture of metastable fine T-ZrO_2 and amorphous SiO_2. The T-ZrO_2 aggregates were then gradually transformed into M-ZrO_2 with an increase in temperature because of the decrease in excess surface energy; the metastable T-ZrO_2 existed in the neighbourhood of SiO_2 as it was stabilized with the aid of the strain energy of grain boundary between SiO_2 and ZrO_2. The fine T-ZrO_2 particles separated from the strain energy tend to aggrolimate, following the T → M transformation [11, 15]. After all, T-ZrO_2 located in the neighbourhood of SiO_2 particles contributes to the formation reaction of zircon at a lower temperature, and M-ZrO_2 perhaps contributes to the reaction at a higher temperature. This is another geometrical reason for the favourability of T-ZrO_2 against the zircon synthesis.

3.2. Dissociation of commercial zircon powder

Fig. 5 shows the XRD patterns of commercial zircon powders heated at 1500, 1650 and 1700° C. The dissociation of zircon did not occur below 1650° C, but the zircon dissociated into M-ZrO_2 and SiO_2 glass at 1700° C. The starting temperature of the dissociation (1650–1700° C) is largely different from the value (1540° C) of Curtis and Sowman [5], but roughly agreed with that (1676 ± 7° C) of Butterman and Foster [4]. This difference may be due to the metallic impurities. The dissociation temperature of zircon powders purified from the natural sand would be further elevated by better techniques for removing the impurities. As the synthesized zircon powders did not dissociate in spite of the 1700° C treatment, there is a possibility that the high performance zircon ceramics suppressed the thermal dissociation.

TABLE I The change in standard Gibb's free energy for the formation of zircon from ZrO_2 and SiO_2 by Rosén and Muan [16]

Temperature (° C)	1180	1242	1300	1366
$-\Delta G_T^0$ (Kcal mol^{-1})	2.38	1.98	1.64	1.29

(1 K cal mol^{-1} = 4.187 KJ mol^{-1})

3.3. Thermochemical analysis of dissociation temperature

In the investigation on stability of zircon in the temperature range 1180 to 1366° C, Rosén and Muan [16] developed an experimental method to determine the change in standard Gibb's free energy ($-\Delta G_T^0$) for the formation of zircon from oxide components ZrO_2 and SiO_2, where the method consisted in equilibrating metallic cobalt, a CO_2/CO ratio of the gas phase, and chosen phase assembles in the system CoO–ZrO_2–SiO_2 and CoO–SiO_2. They gave $-\Delta G_T^0$ as shown in Table I, and estimated that the dissociation temperature was 1600 to 1650° C from an extrapolation of the curve.

From the thermochemical analysis on the basis of calculation of ΔS_T^0, ΔH_T^0, ΔG_T^0 for the reaction (where ΔS and ΔH are the entropy and enthalpy, respectively), Matwejew *et al.* [17] estimated that the dissociation temperature was in the range of 1527–1927° C from the extrapolation method. Where ΔS_T^0 was calculated as follows (using heat capacity values, C_p):

$$\Delta S_T^0 = \Delta S_{298}^0 + \int_{298}^{848} \Delta C_p'/T\,dT + \Delta S_I^0 + \int_{848}^{1478} \Delta C_p''/T\,dT + \Delta S_{II}^0 + \int_{1478}^{T} \Delta C_p'''/T\,dT \tag{1}$$

ΔS_I^0 = heat of $\beta \to \alpha$ quartz transformation divided by 848

ΔS_{II}^0 = heat of M-ZrO_2 → T-ZrO_2 transformation divided by 1478

$$\Delta C_p' = C_{p,ZrSiO_4} - C_{p,M\text{-}ZrO_2} - C_{p,\beta\text{-quartz}},$$

$$\Delta C_p'' = C_{p,ZrSiO_4} - C_{p,M\text{-}ZrO_2} - C_{p,\alpha\text{-quartz}},$$

$$C_p''' = C_{p,ZrSiO_4} - C_{p,T\text{-}ZrO_2} - C_{p,\alpha\text{-quartz}},$$

$$\Delta S_{298}^0 = S_{298,ZrSiO_4}^0 - S_{298,M\text{-}ZrO_2}^0 - S_{298,\beta\text{-quartz}}^0$$

However, the extrapolation done by two groups [16, 17] was too rough. We calculated the dissociation temperature by analysing progressively the $-\Delta G_T^0$ values of these two research groups in the previous paper [18]. As a result, the dissociation temperature was respectively estimated to be 1707° C (in the case of Rosén and Muan) and 1841° C (Matwejew *et al.*). The former value is fundamentally based on experimental data, the latter is due to a typical calculation of the entropy according to Equation 1. Judging from Figs 1 and 3, the dissociation temperature 1707° C is worthy of commendation. The deviation of the latter value (1831° C) is perhaps due to the difference between Equation 1 and the real formation mechanism in Fig. 3.

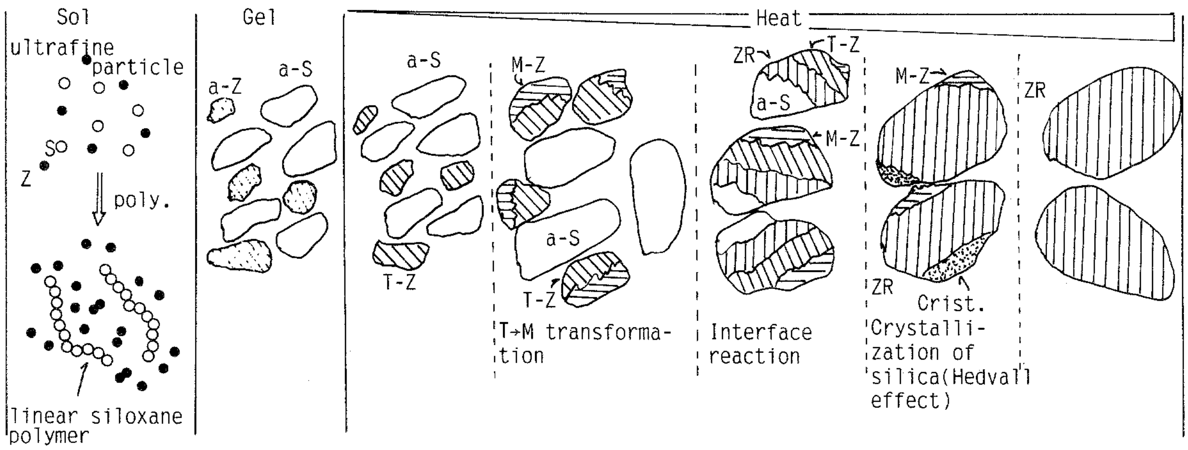

Figure 6 Schematic representation of the formation of zircon from a system of $Si(OC_2H_5)_4$–$ZrOCl_2 \cdot 8H_2O$–C_2H_5OH solution. S = silica; Z = zirconia; a = amorphous; T- = tetragonal; M = monoclinic; ZR = zircon.

Rosén and Muan [16] reported that the ZrO_2 in the phase assemblage, $Co_2SiO_4 + ZrO_2 + 2CO = 2Co + ZrSiO_4 + 2CO_2$, was the T-form and the SiO_2 in the phase assemblage, $Co_2SiO_4 + 2CO = 2Co + SiO_2 + 2CO_2$, was crystobalite. So, the $-\Delta G_T^0$ for the reaction, T-ZrO_2 + crystobalite = $ZrSiO_4$, is calculated from the thermochemical data of three kinds of crystals [19–21], a dissociation temperature of 1609° C was obtained [18]. This value is very low and contradicts the results of Figs 1 and 3. This discrepancy would also arise from a difference of the formation mechanism.

3.4. Calculation of dissociation temperature from the proposed mechanism

Based on the formation mechanism of zircon shown in Fig. 3, the dissociation temperature was calculated as a trial. The heat capacity data [19–21] of the ZrO_2–SiO_2 phase system involved in the formation mechanism is summarized in Table II.

The change in heat capacity, $\Delta C_p = \Delta a + \Delta bT + \Delta cT^{-2}$, for the formation reaction $ZrO_2 + SiO_2 = ZrSiO_4$ was described as follows;

$$\Delta C_{p,\text{zone1}} = 0.30 + 0.24 \times 10^{-3}T - 8.08 \times 10^5 T^{-2} \quad (\sim 1588\,\text{K})$$

$$\Delta C_{p,\text{zone2}} = -0.72 + 1.88 \times 10^{-3}T - 8.08 \times 10^5 T^{-2} \quad (1588 \sim 1853\,\text{K})$$

$$\Delta C_{p,\text{zone3}} = 0.44 + 0.08 \times 10^{-3}T - 4.72 \times 10^5 T^{-2} \quad (1853\,\text{K} \sim)$$

It should be noted that the application region of temperature for the equation $C_p = f(T)$ is not always maintained in a derivation of these equations.

$$\Delta G_T^0 = \Delta H_0 - \Delta aT \ln T - (1/2)\Delta bT^2 - (1/2)\Delta cT^{-1} + yT \quad (2)$$

$$\Delta H_T^0 = \Delta H_0 + \Delta aT + (1/2)\Delta bT^2 - \Delta cT^{-1} \quad (3)$$

By using $\Delta G_{1515}^0 = -1980$, $\Delta G_{1573}^0 = -1640\,\text{cal mol}^{-1}$ in Table I, Equations 1 and 2 are obtained.

$$\Delta G_T^0 = -12\,170 - 0.30T \ln T - 0.12 \times 10^{-3}T^2 + 4.04 \times 10^5 T^{-1} + 8.931T \; (\sim 1588\,\text{K}) \quad (4)$$

$$\Delta H_T^0 = -12\,170 + 0.3T + 0.12 \times 10^{-3}T^2 + 8.08 \times 10^5 T^{-1} \; (\sim 1588\,\text{K}) \quad (5)$$

From Equations 4 and 5, $\Delta G_{298}^0 = -8674$, $\Delta H_{298}^0 = -9359\,\text{cal mol}^{-1}$ and thus $\Delta S_{298}^0 = 2.30\,\text{cal mol}^{-1}\,\text{K}^{-1}$ are obtained. Next, $\Delta H_{1588}^0 = -10\,882\,\text{cal mol}^{-1}$ is calculated from Equation 5. Therefore,

$$\Delta H_T^0 = -12\,620 - 0.72T + 0.94 \times 10^{-3}T^2 + 8.08 \times 10^5 T^{-1} \; (1588 \sim 1853\,\text{K}) \quad (6)$$

From Equation 6, $\Delta H_{1853}^0 = -10\,290\,\text{cal mol}^{-1}$ is calculated, then

$$\Delta H_T^0 = -11\,497 + 0.44T + 0.04 \times 10^{-3}T^2 + 4.72 \times 10^5 T^{-1} \; (1853\,\text{K} \sim) \quad (7)$$

On the other hand, ΔS_T^0 is determined as follows:

$$\Delta S_T^0 = \Delta S_{298}^0 + \int_{298}^{1588} (\Delta C_{p,\text{zone1}}/T)\,dT + \Delta H_{tr}/1588 + \int_{1588}^{1853} (\Delta C_{p,\text{zone2}}/T)\,dT + \int_{1853}^{T} (\Delta C_{p,\text{zone3}}/T)\,dT \quad (8)$$

Here ΔH_{tr} is the crystallization heat for the transformation of amorphous SiO_2 to crystobalite, and it is assumed to be $310\,\text{cal mol}^{-1}$ being the transformation heat of crystabolite. In Equation 8, the transformation heat of ZrO_2 is independent of the change in entropy for the formation of zircon, because M-ZrO_2 already exists as a starting crystal in zone 3, prior to the formation reaction. From Equations 7 and 8, ΔH_{2100}^0 =

TABLE II Heat capacities of the ZrO_2–SiO_2 system substances

Substance	State	$C_p = f(T)$	Temperature (K)
$ZrSiO_4$		$31.48 + 3.92 \times 10^{-3}T - 8.08 \times 10^5 T^{-2}$	(298–1800)
ZrO_2	M-	$16.64 + 1.8 \times 10^{-3}T - 3.36 \times 10^5 T^{-2}$	(298–1478)
ZrO_2	T-	17.8	(1478–1850)
SiO_2	amorphous	$13.38 + 3.68 \times 10^{-3}T$	(298–2000)
SiO_2	crystobalite	$14.40 + 2.04 \times 10^{-3}T$	(523–2000)

M- = monoclinic; T- = tetragonal.

$-10\,170\,\text{cal mol}^{-1}$, $\Delta S^0_{2100} = -3.7855\,\text{cal mol}^{-1}\,\text{K}^{-1}$ are calculated, and so $\Delta G^0_{2100} = -2220\,\text{cal mol}^{-1}$ is determined.

The calculated value of $\Delta G^0_{2100} = -2220$ was so low that we could barely obtain $\Delta G^0_T = 0$, i.e. the dissociation temperature in a higher temperature region than 1831° C described formerly.

The thermochemical trial following the proposed mechanism resulted in failure. The major reason of the failure lay in ignoring the temperature range of application for the equation $C_p = f(T)$. This is the largest problem in the thermodynamics of fine particles. With decreasing the particle size, in general, the surface energy increases the binding energy of the crystal lattice, and the thermal vibration energy is superior to the kinematic one. The thermodynamic function of the fine system accompanying a negligible fluctuation caused by the variation of the surrounding environment should be corrected to some extent. Strictly speaking, the conventional thermodynamic function is valid only in the infinity of the system. Therefore, the determination of the dissociation temperature of the zircon synthesized from the sol–gel process, based on the classical thermodynamics, was unreasonable.

4. Conclusion

The mechanism for the formation of zircon from a system of $Si(OC_2H_5)_4$–$ZrOCl_2 \cdot 8H_2O$–C_2H_5OH solution is schematically summarized in Fig. 6, considering the result described in the previous papers [21–24].

The state of the surface layer of the ZrO_2 and SiO_2 powders was very important in order to advance the combination reaction between two oxide components, and the following items were the most important for the reaction: (1) the mechanochemical activation of the surface layer by milling, (2) the formation of the transition phase between ZrO_2 and SiO_2 by the addition of a guest element, and (3) the presentation of a metamorhic state of the surface.

The calculation for the dissociation temperature should be performed for the zircon powders lacking residual ZrO_2 and SiO_2 and synthesized without additives, but the above calculation was a trial. The thermochemical analysis of the dissociation temperature followed by the proposed formation mechanism of zircon resulted in failure because of the fluctuation of the thermodynamic function generated in the fine system. The dissociation temperature of zircon was estimated to be above 1700° C, and the dissociated zircon transformed into M-ZrO_2 and SiO_2 glass. These speculations led us to the correct form of the phase diagram for the ZrO_2–SiO_2 system (Figs 362 and 2400 of [25]).

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Received 22 March
and accepted 29 July 1988