

The zircon thermal behaviour: effect of impurities

Part 1

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The effect of impurities on zircon thermal behaviour is discussed and explained from a thermodynamic point of view. Based on the data obtained from the $ZrO_2-Al_2O_3-SiO_2-TiO_2$ system, previously studied by the authors, the influence of the impurities, normally present in zircon sands, on the dissociation and initial melting temperatures in natural zircon, has been studied.

1. Introduction

Natural zircon constitutes the basis of many traditional ceramic materials. Recently an increased interest has been shown in the literature [1-5] on zirconia toughened materials obtained from reaction sintering of zircon with other ceramic oxides (Al_2O_3 , MgO , etc.). In view of the large technological importance of these kinds of materials, accurate information on the thermal behaviour of zircon is highly desirable. Yet even in the scientific literature there is no general agreement as to the temperature or manner of breakdown of zircon. Table I lists the stability data of various authors where large differences on the thermal behaviour of zircon can be observed.

An analysis of the data shown in Table I indicates that such large disagreements in the thermal behaviour of zircon are due basically to two reasons: (a) the use of zircon minerals with large differences in the nature and proportion of the impurity contents, and (b) a wrong analysis of the experimental results by the authors, since they have not discriminated the decomposition process from the first formation of liquid with partial dissolution of zircon.

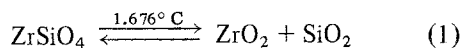
At the present time it seems well established that the mineral zircon, as a chemically pure substance, decomposes in solid state at a temperature of $1676 \pm 7^\circ C$ giving a mixture of tetragonal zirconia and β -cristobalite, as shown in Fig. 1, where the ZrO_2-SiO_2 system by Buttermand and

Foster [23] is represented. This temperature of decomposition agrees closely with that established, from a thermodynamic point of view, by Rosen and Muan [22], when studying the variation of the free energy of zircon with temperature.

2. Thermal behaviour of zircon sands

When considering natural zircon sands, the role of the impurities on the thermal behaviour of zircon must be taken into account. This effect can be analysed from a thermodynamic point of view as follows.

According to the binary system ZrO_2-SiO_2 (Fig. 1):



for this reaction at the dissociation temperature $T = 1949 K$

$$\Delta G = G_z + G_s - G_{zs} = 0$$

At temperatures below T , ΔG will be positive and at temperatures above T it will be negative, as shown in Fig. 2a, where the variation with temperature of the free energies of zircon (G_{zs}) and of the mixture of zirconia (G_z) and silica (G_s) is plotted in a qualitative manner.

Considering the presence of a third component XO (an impurity such as TiO_2 , Al_2O_3 , etc.) and assuming that zirconia and/or silica form stable solid solutions with it (which is highly feasible, since some solid solution is always produced,

TABLE I Data on the thermal stability of $ZrSiO_4$

Investigators	Year	Thermal behaviour	Temperature (° C)
Washburn and Libman [6]	1920	Congruent melting	2550
Matignon [7]	1923	Dissociation	2000
Barlett [8]	1931	Dissociation	1450
Heindl [9]	1933	Dissociation	1800
Zhirnowa [10]	1934	Congruent melting	2430
George and Lambert [11]	1937	Dissociation	~ 1650
Bauer [12]	1939	Dissociation	~ 1650
Geller and Yavorsky [13]	1945	Dissociation	1775
Stott and Hilliard [14]	1946	Dissociation	1550–1750
Curtis and Thomas [15]	1948	Dissociation	> 1740
Geller and Lang [16]	1949	Incongruent melting	1775
McKee and Adams [17]	1950	Dissociation	1800
Curtis and Sowman [18]	1953	Dissociation	1540
Selim [19]	1953/54	Dissociation	1600
Majumdar [20]	1955	Dissociation	1400
Cocco and Schromek [21]	1957	Dissociation	1720 ± 20
Rosen and Muan [22]	1965	Dissociation	1600–1650
Butterman and Foster [23]	1967	Dissociation	1676 ± 7
Anseau et al. [24]	1976	Dissociation	1525–1550

although from a practical point of view it is negligible), their activities will decrease and consequently their partial molar free energy will also decrease since for the above mentioned phases $\Delta G = RT \ln \alpha$ will be negative. Then for the previous temperature of dissociation T :

$$\Delta G = G_z + \overline{\Delta G_z} + G_s + \overline{\Delta G_s} - G_{zs} < 0$$

and since from Equation 1:

$$G_z + G_s - G_{zs} = 0$$

we have:

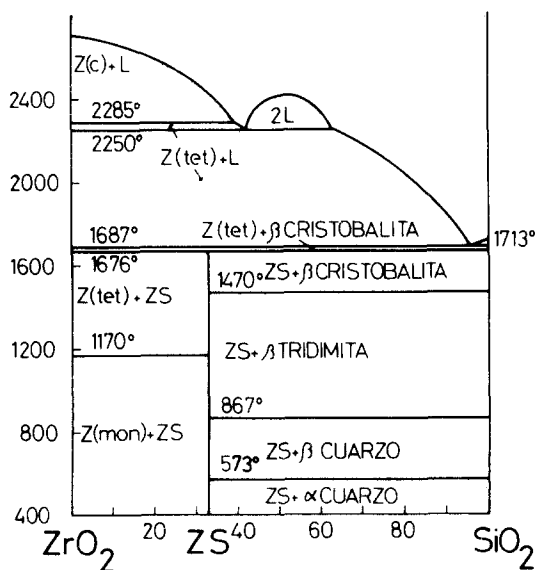
$$\Delta G = \overline{\Delta G_z} + \overline{\Delta G_s} < 0$$

which means that ΔG will now be negative at the previous temperature of dissociation T . However, if temperature is decreased, $G_z + G_s - G_{zs}$ will be made positive (Fig. 2a) and for a given temperature, e.g. T_1 (Fig. 2a), it can be made numerically equal to $\overline{\Delta G_z} + \overline{\Delta G_s}$ so that ΔG will again be equal to zero and, therefore, T_1 will then be the new temperature of dissociation, which is lower to the previous temperature of dissociation in the absence of impurities.

The shape of the equilibrium will be as indicated in Fig. 3 for a hypothetical system ZrO_2 - SiO_2 - XO , where XO forms the α and β solid solutions with ZrO_2 and SiO_2 .

In Fig. 3a, am is the binary eutectic line along which α and β coexist with a liquid. In m , $\alpha + \beta +$ liquid coexist with ZS , so that T_m will be the dissociation temperature of ZS in the presence of a liquid phase (however, the compositions between g and h/k in Fig. 3b will dissociate progressively over a range of temperature).

It should be stressed that point m in Fig. 3a represents the only temperature and composition at which the ternary liquid can exist in equilibrium with ZrO_2 , SiO_2 and ZS . This means that point m is also the higher temperature at which zircon can exist in equilibrium with ZrO_2 , SiO_2 and the ternary liquid and as such it represents the new dissociation temperature of ZS in this hypothetical system.


 Figure 1 ZrO_2 - SiO_2 system [23].

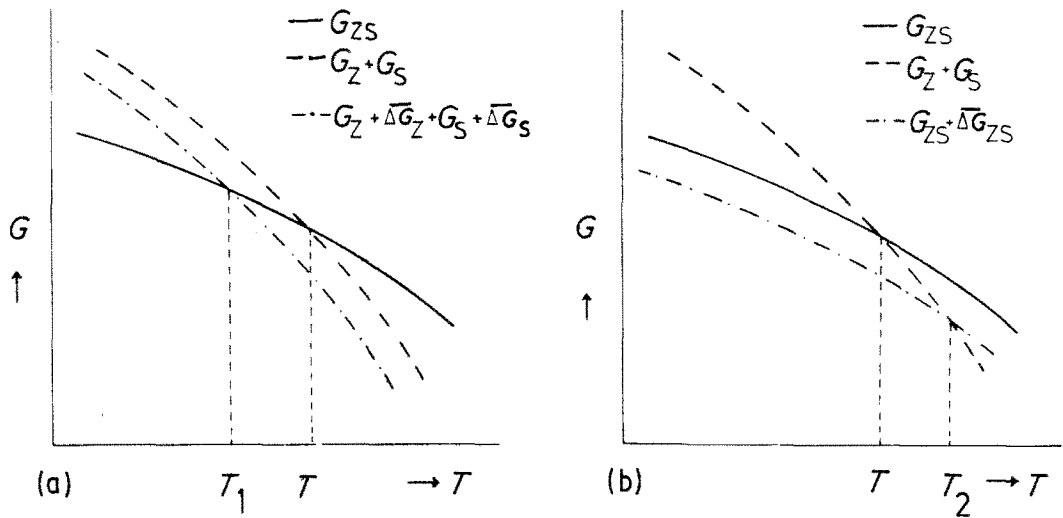


Figure 2 (a) and (b): qualitative variation with temperature of the free energy of ZS (G_{ZS}) and also of the mixture of ZrO_2 (G_Z) and SiO_2 (G_S) without solid solution and alternatively with solid solution of a third compound in the mentioned phases.

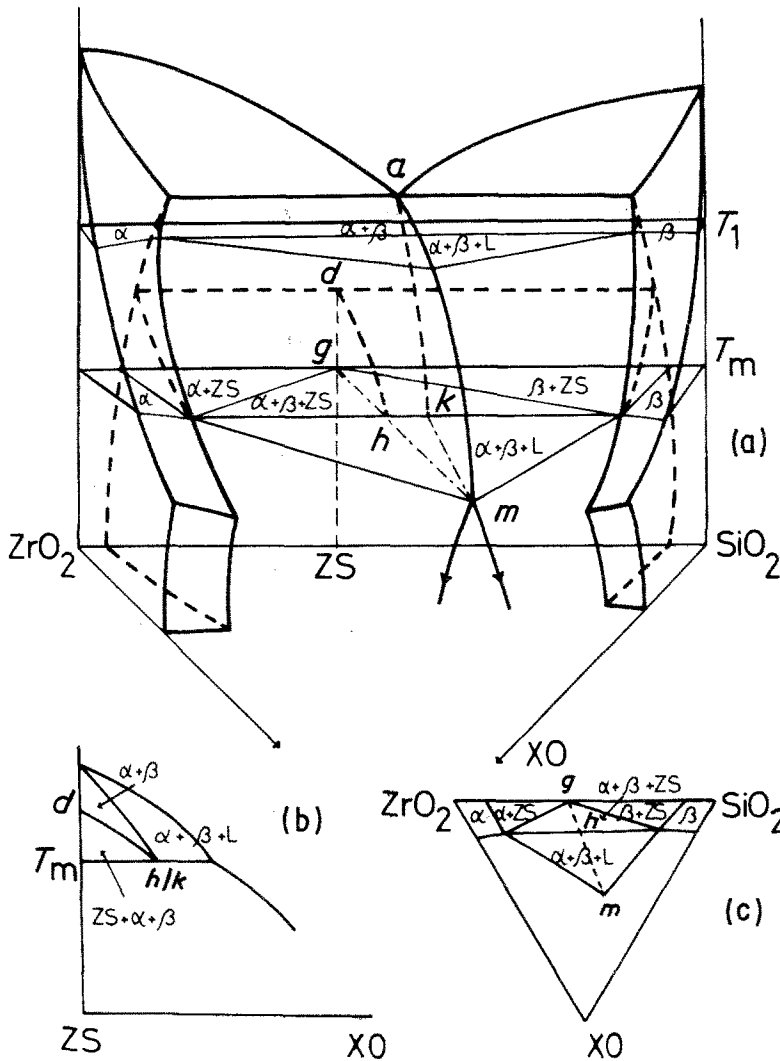


Figure 3 (a) Hypothetical equilibrium diagram for a system ZrO_2-SiO_2-XO with formation of a partial solid solution of XO in the other components and with the existence of a binary compound (ZS) that decomposes in solid state and does not present solid solution. (b) Isoplethal section in the ZrO_2-SiO_2-XO system. (c) Isothermal section on the ZrO_2-SiO_2-XO system at the temperature of the invariant point m .

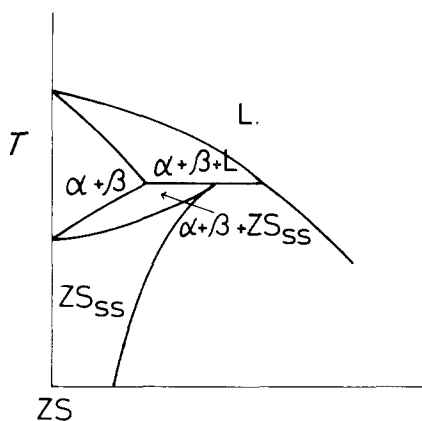


Figure 4 Isoplethal section in the ZrO_2-SiO_2-XO system, showing the possibility that the temperature of decomposition of the ZS phase in the ternary system, could be higher than in the binary system ZrO_2-SiO_2 , due to the presence in the ZS phase of a solid solution higher than in the ZrO_2 and SiO_2 phases.

If instead of considering ZrO_2 and/or SiO_2 form solid solutions with the third component (XO), we assume that zircon (ZS) is forming solid solutions, then following the same argument as above, it can be shown that the temperature of dissociation of zircon will be higher, with the presence of the impurity, than for the case of chemically pure zircon. This is illustrated graphically in Figs. 2b and 4. Consequently there will only be an increase in the temperature of dissociation of zircon with the presence of impurities, if their solid solution in zircon is higher than in zirconia and/or silica. However, with the present knowledge on the systems where zircon is found, this case is very unlikely, and usually the temperature of dissociation will decrease with the presence of impurities.

The above discussion justifies that the presence of impurities in the mineral zircon will bring a decrease of its temperature of dissociation, but it does not indicate the magnitude of such a decrease. Therefore, it can be expected that in zircon sands, the dissociation temperature of zircon will occur always below $1676^\circ C$, which corresponds to the dissociation temperature of chemically pure zircon [23] and will depend on the nature of the impurities.

The main impurities in zircon sands are titania, free silica and alumina. The latter is normally combined with silica in the form of kyanite or andalucite; the rest of impurities only represent 0.05 to 0.3 wt% of the total as it is shown in Table II, where the guaranteed average of the world's main zircon producers, are shown.

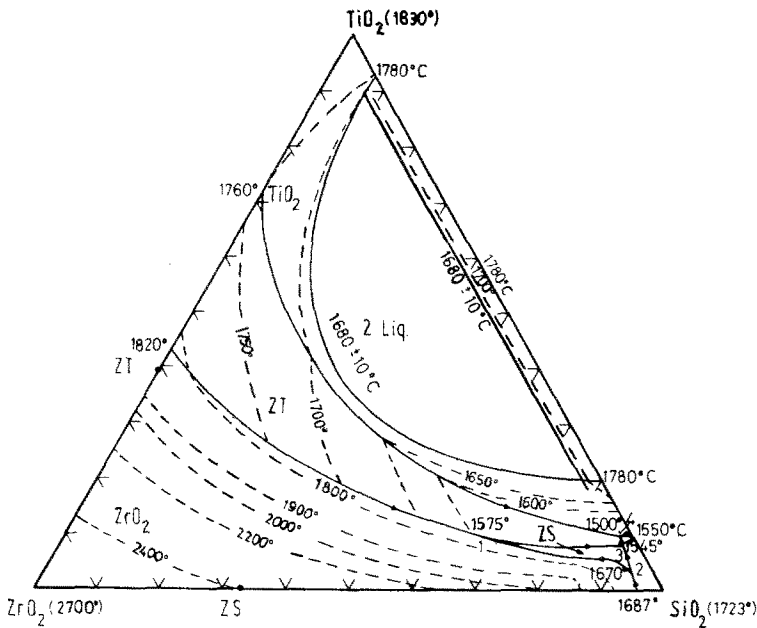
The effect of such impurities on the thermal dissociation of zircon and on the beginning of melting can be quantitatively analysed considering the appropriate published phase equilibrium diagrams.

In the $ZrO_2-SiO_2-TiO_2$ system (Fig. 5a) it can be appreciated that the temperature of dissociation of zircon (point 2 of Fig. 5a) is $1670^\circ C$ which represents a very small decrease in the dissociation temperature of pure zircon ($1676^\circ C$). This one is only decreased slightly more in the presence of alumina as can be appreciated in the system $ZrO_2-SiO_2-Al_2O_3$ (Fig. 5b) where the temperature of dissociation of zircon is reported as $1660^\circ C$. The quaternary system $ZrO_2-SiO_2-Al_2O_3-TiO_2$ (Fig. 6) shows that the combined effect of all indicated impurities, on the thermal dissociation of zircon, is also negligible, since the temperature of dissociation varies from 1660 to $1670^\circ C$, along the eutectic line fe , depending on the wt% Al_2O_3/TiO_2 ratio.

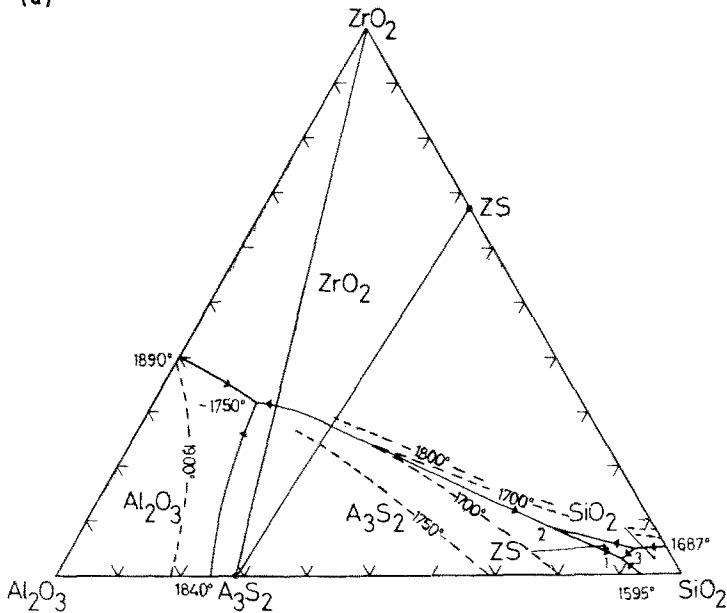
TABLE II Guaranteed average analyses of zircon sands

Wt %	Australia						USA			South Africa	
	East Coast		West Coast		Std.	Prem.	Georgia	Florida		Richard Bay	
	North	South	North	South				Std.	Std.	Prem.	Std.
ZrO_2 min.	65.50	66.00	66.00	66.00	65.00	66.00	65.00	65.00	66.00	65.00	66.00
TiO_2 max.	0.30	0.10	0.20	0.15	0.25	0.10	0.25	0.35	0.20	0.30	0.10
Al_2O_3 max.	0.40	0.30	0.40	0.30	0.30	0.30	0.50	2.00	0.50	0.25	0.08
SiO_2 max.	33.75	33.55	33.35	34.45	34.10	33.33	33.65	33.26	32.55	34.15	33.77
Others max.	0.05	0.05	0.15	0.15	0.15	0.07	0.10	0.04	0.10	0.30	0.05
<i>F</i>	1.93	1.97	1.98	1.97	1.90	1.99	1.94	1.99	2.03	1.90	1.95
Temperature of initial melting	$1450 \pm 10^\circ C$										

Figure 5 (a) $ZrO_2-SiO_2-TiO_2$ system [25]. (b) $ZrO_2-SiO_2-Al_2O_3$ system [26].



(a)



(b)

Although the decrease in the dissociation temperature of zircon is almost negligible with the presence of titania, alumina and silica impurities, the effect is quite different as to the temperature of first formation of the liquid phase.

As observed in Fig. 7, zircon is found in two of the six quaternary subsystems in which the $ZrO_2-Al_2O_3-SiO_2-TiO_2$ system is divided, i.e. $ZS-A_3S_2-ZT-ZrO_2$ and $ZS-A_3S_2-ZT-SiO_2$. Depending on the proportion of titania, silica and alumina, the composition of a zircon sand and will be

located in one tetrahedron or the other. This fact can be expressed by the following relationship:

$$F = \frac{\%ZrO_2 - 1.542 \%TiO_2}{\%SiO_2 - 0.393 \%Al_2O_3} \geq 2.051$$

which has been calculated without considering the existence of solid solutions and taking into account that both possibilities are defined depending on the composition of the sand being located to the right or to the left of the compatibility plane $ZS-ZT-A_3S_2$ (Fig. 7). If $F > 2.051$, the

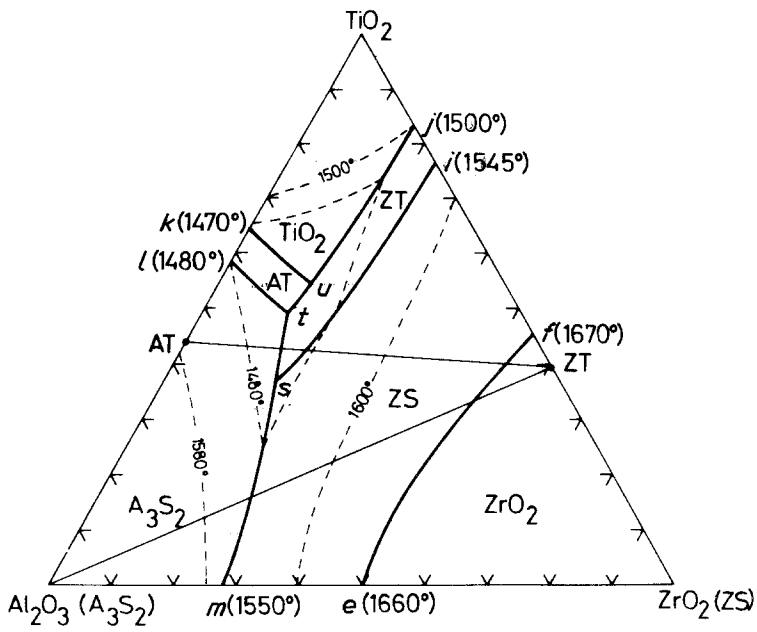


Figure 6 $ZrO_2-Al_2O_3-SiO_2-TiO_2$ system. Projection through SiO_2 onto the opposite face of the quaternary tetrahedron of the boundary surface of the primary phase volume of silica, showing phase boundaries and isotherms [27].

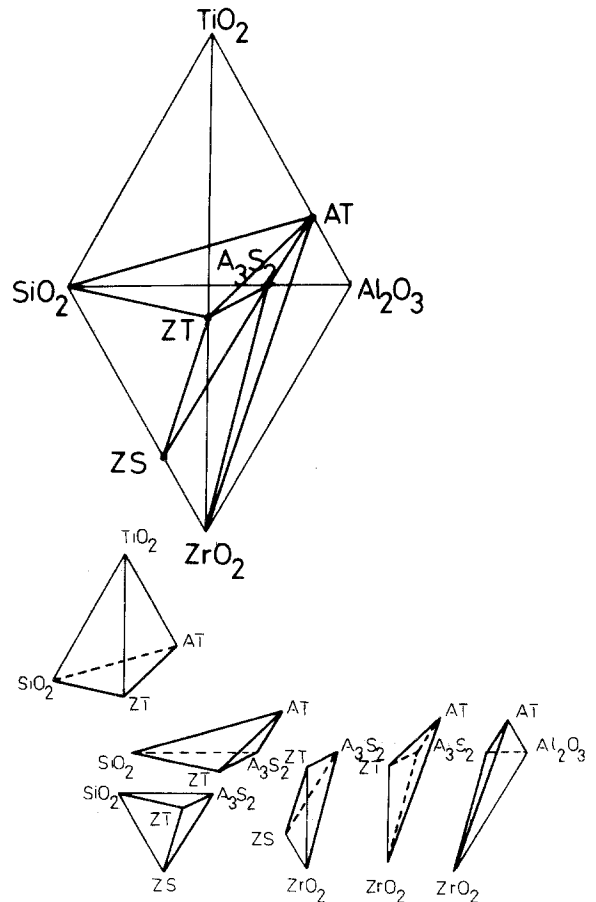


Figure 7 Solid-state compatibility relationship in the quaternary system $ZrO_2-Al_2O_3-SiO_2-TiO_2$. Solid solutions are not represented [27].

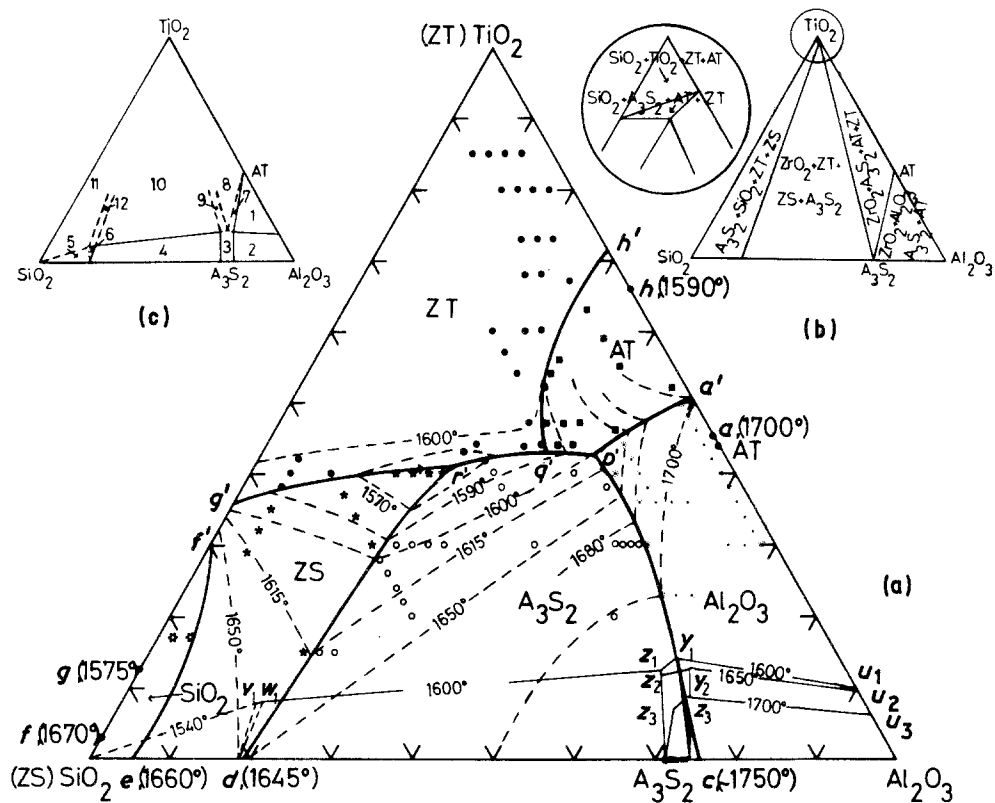


Figure 8 Projection through ZrO_2 -corner showing secondary phases crystallizing during freezing from ZrO_2 - Al_2O_3 - SiO_2 - TiO_2 mixtures containing 60% ZrO_2 [28].

composition of the zircon sand will be within the subsystem $ZS-A_3S_2-ZT-ZrO_2$ and the temperature of first formation of liquid will be $1540^\circ C$, invariant point of that subsystem (point r' , Fig. 8). This temperature is $147^\circ C$ lower than that of the first formation of the liquid phase in a chemically pure zircon (Fig. 1).

If $F < 2.051$, the composition of the sand will be within the subsystem $ZS-A_3S_2-ZT-SiO_2$ and the temperature of first formation of liquid will be $1450^\circ C$ invariant point of that subsystem (point s , Fig. 6). In this case the temperature is $237^\circ C$ lower than those corresponding to the first formation on liquid phase of pure zircon.

For all commercial zircon sands (Table II) $F < 2.051$; consequently the appearance of the liquid phase will take place at the temperature of $1450 \pm 10^\circ C$.

Due to the fact that the location of the quaternary invariant point is very close to the silica corner of the tetrahedron [27], which confirms the low solubility of zirconia in silicate melts, the quantity of liquid formed at the beginning of

melting, for these normal zircon impurity contents, will be very low.

Finally the above discussion suggests that in those reactions where zircon is present, i.e. in the case of the reaction sintering process as zircon-alumina, a transient-liquid phase will appear at temperatures as low as $1450 \pm 10^\circ C$, which will contribute to enhance the rate of reaction as well as the sintering process.

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