The zircon thermal behaviour: effect of impurities

Part 2

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The influence of the impurities, usually present in zircon sands, on the initial melting temperature and thermal dissociation of zircon has been experimentally studied by SEM and KEVEX-microanalysis. The results have shown that a liquid phase is developed in zircon sands at temperatures as low as 1500° C. The data agree with the thermodynamics considerations previously reported by the authors.

1. Introduction

In a previous work the authors have studied, from a thermodynamics point of view and on the basis of the data obtained from the ZrO_2–Al_2O_3–SiO_2–TiO_2 system, the thermal behaviour of the main commercial zircon sands [1]. In that study they reached the conclusion that a liquid phase will appear in zircon sands at a temperature of $1450 \pm 10°$ C.

The purpose of the present work is to provide experimental data that support the previous thermodynamics statement.

2. Experimental procedure

The starting material was a high purity Australian zircon sand (> 99 wt %). The chemical analysis is given in Table I. The main impurities were rutile (TiO_2), quartz (SiO_2), kyanite, sillimanite and felspar.

Zircon sands were pressed into pellets ~ 5 mm diameter and 4 mm thick. These pellets were axial pressed using an organic binder at $60 \, \mathrm{MN \, m^{-2}}$. The specimens were settled into Pt-foil crucibles and heat treated, at temperatures ranging from 1500 to 1650° C, in a molybdenum furnace with an electronic temperature controller ($\pm 1°$ C). After a period of 24 h, at each selected temperature, the samples were then air-quenched by being withdrawn from the furnace, and then polished by conventional methods.

The microstructure of the specimens were observed by reflected light microscopy and SEM using a Super 3A ISI Co.

Energy-dispersive X-ray (EDX) microanalyses have been performed on the polished samples sections by a SEM–EDX equipment (Kevex 7077). The calibration was carried out with $ZrTiO_4$ (titanium and zirconium), ZrO_2, SiO_2, and

TABLE I Typical analysis of zircon sand

	(wt %)
ZrO_2	67.17
SiO_2	32.10
Al_2O_3	0.30
TiO_2	0.15
Minor amounts	0.28

TABLE II Typical microanalysis of zircon

Selected zircon grains (KEVEX–EDX)		Theoretical zircon	
	(wt %)		(wt %)
SiO_2	32–33	SiO_2	32.74
ZrO_2	64–66	ZrO_2	67.25
HfO_2	3– 1	–	

potash feldspar (BCS 376) as reference materials. Weight percentage was calculated from measured net intensities with a program correcting the influence of atomic number, absorption and fluorescency (Quantex ZAF corrections via MAGIC V). The relative counting error ϵ_N has been calculated as $\epsilon_N = (N^{1/2}/N) \times 100$ (N = accumulated counts) with a probability of 98.5%.

3. Microstructure and microanalysis of the treated zircon samples

The specimens treated in the temperature range 1500–1600° C for 24 h show a similar kind of microstructure. Almost all the samples are formed by coarse round grains of zircon, some of them broken, without any sign of reaction (Fig. 1). The average microanalysis of the zircon grains are shown in Table II. However, it was possible to detect few and small areas of inclusions, dispersed on the samples, where reaction was significant, even at temperatures as low as 1500° C. Fig. 2 shows the back scattered electron image of a typical area, where reaction has taken place, and the titanium, silicon and zirconium X-ray spectra is several points of it.

A reaction zone, between the zircon grains (ZS) and the intergranular rutile (T) inclusion can be appreciated. Fig. 3 shows a detail of the same
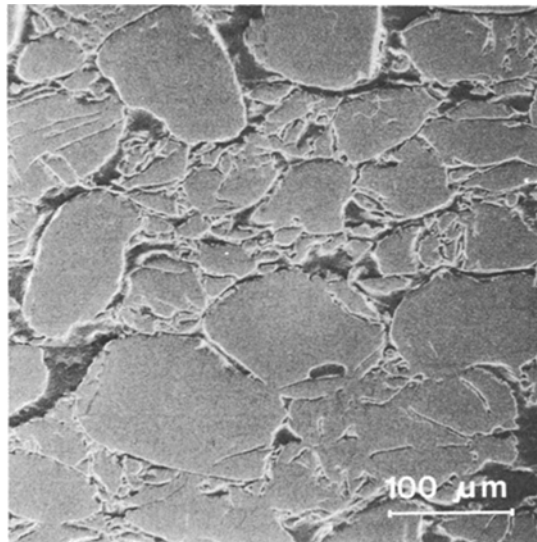

Figure 1 SEM micrograph of zircon sand (1500° C/24 h). Black ares are Araldyte.

area with the corresponding mapping image of titanium distribution. Results of Kevex microanalysis on a similar reaction zone (Fig. 4) are shown in Table III.

Most of the impurities are mainly intergranular, located between the zircon grains and, only in a few cases, it was possible to observe other reactions zones within the zircon grains. Fig. 5 shows the back scattered electron image of a reaction area within a zircon grain. Kevex microanalyses of this zone (Table IV) suggest that the inclusion was constituted by a feldspar.

Inclusions within the zircon grains, where no reaction has been detected, even at the highest temperature tested (1650° C), were also observed

TABLE III KEVEX–EDX microanalysis of the areas labelled 1, 2 and 3 in Fig. 4

Area	wt % ± σ			Phase
	SiO_2	ZrO_2	TiO_2	
1	33.5	66.5	–	Zircon
2 dark phase	11.3 ± 0.2	67.3 ± 0.5	21.4 ± 0.2	?
2 white phase	Traces	68.5 ± 0.5	31.5 ± 0.2	$ZrTiO_4$ ss
3 dark phase	64.3 ± 0.2	16.1 ± 0.3	19.6 ± 0.2	Glass
3 white phase	2.5 ± 0.2	17.3 ± 0.3	80.2 ± 0.2	TiO_2 ss

TABLE IV KEVEX–EDX microanalysis

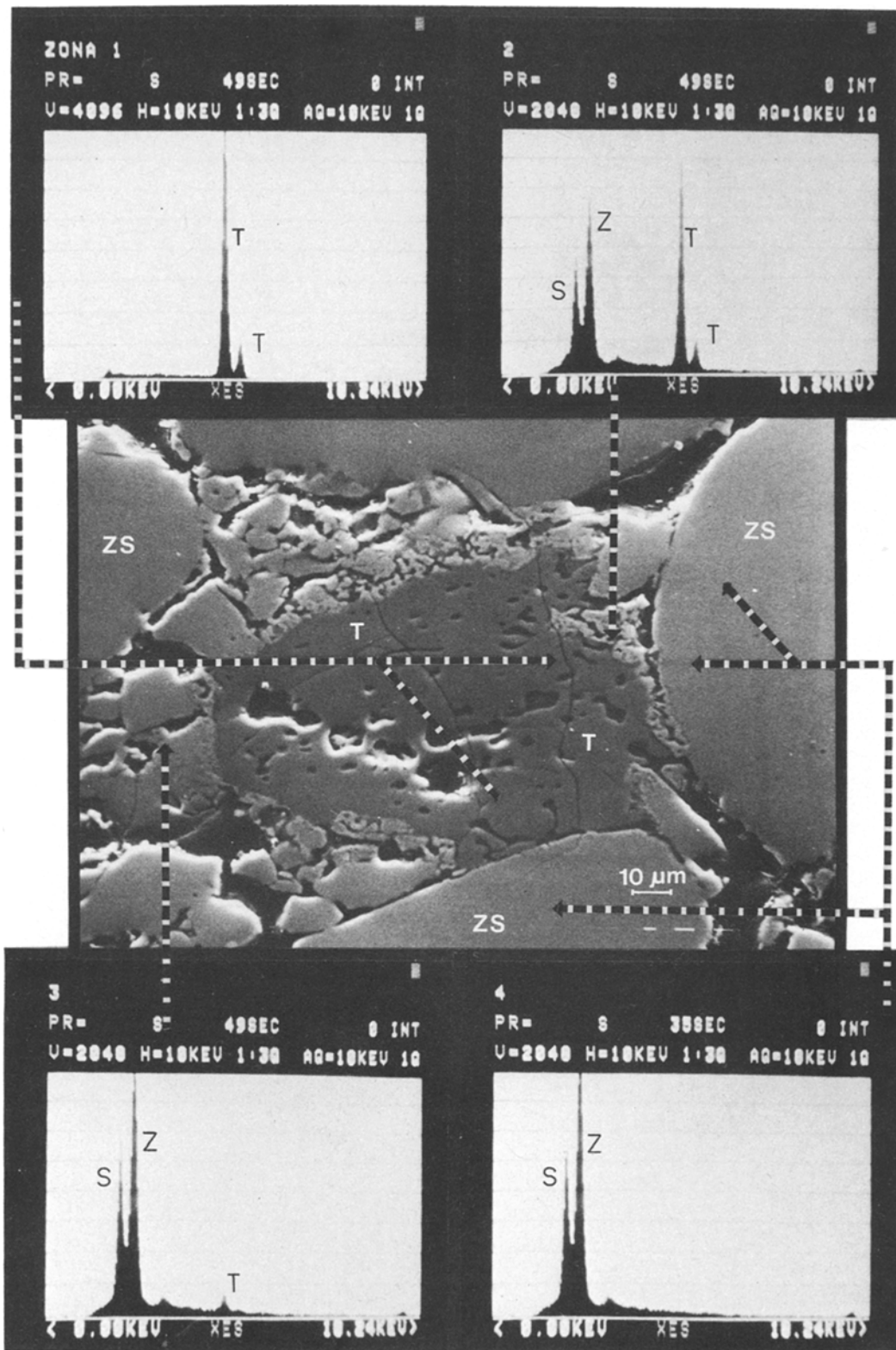| Area	wt % ± σ				Phase
	Al_2O_3	SiO_2	ZrO_2	K_2O	
Black	11.5 ± 0.3	86.6 ± 0.5	–	1.8 ± 0.2	Glass
White	–	–	100	–	ZrO_2
Grey	–	32.3 ± 0.5	67.7 ± 0.5	–	Zircon

Figure 2 Back-scattered electron image of a polished sample of zircon sand treated at 1500°C for 24 h, showing a typical reaction area. Titanium, Silicon and zirconium X-ray spectra in several points of it are also shown. (ZS = zircon; T = rutile).
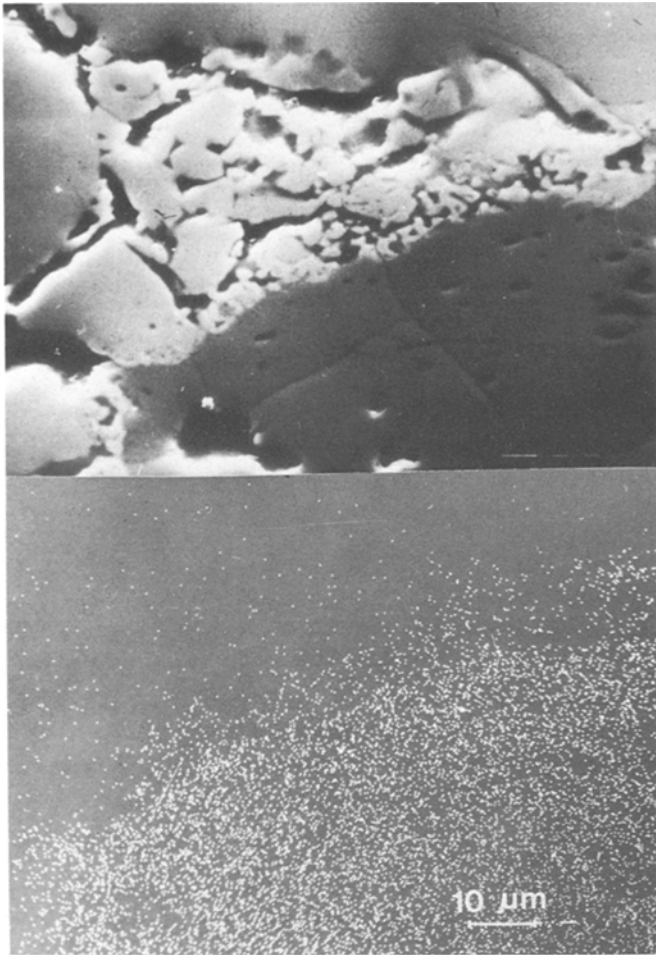
(Fig. 6). Kevex microanalysis of these inclusions shows them to be silica in all cases.

4. Discussion

According to the experimental results the impurities found in commercial zircon sands [1], as rutile, sillimanite of kyanite, free silica and feldspar, etc., can originate local equilibrium reactions with partial dissolution of zircon at temperatures which will depend of the nature of
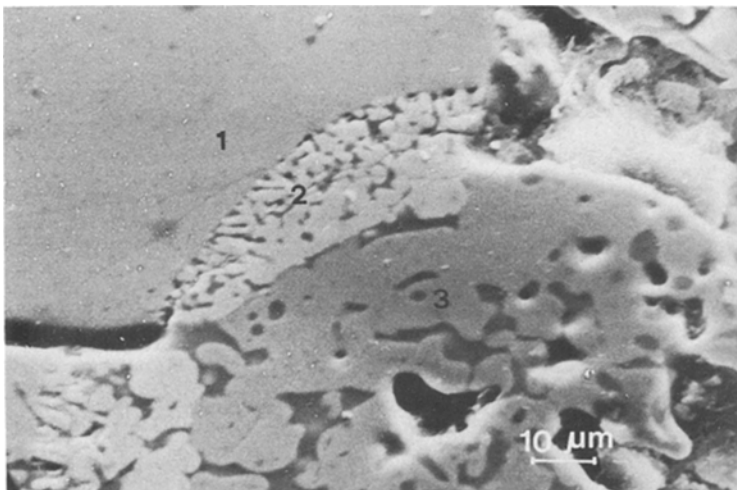

Figure 4 Back-scattered electron image of a polished sample of zircon sand treated at 1600° C for 24 h, showing a typical reaction area.
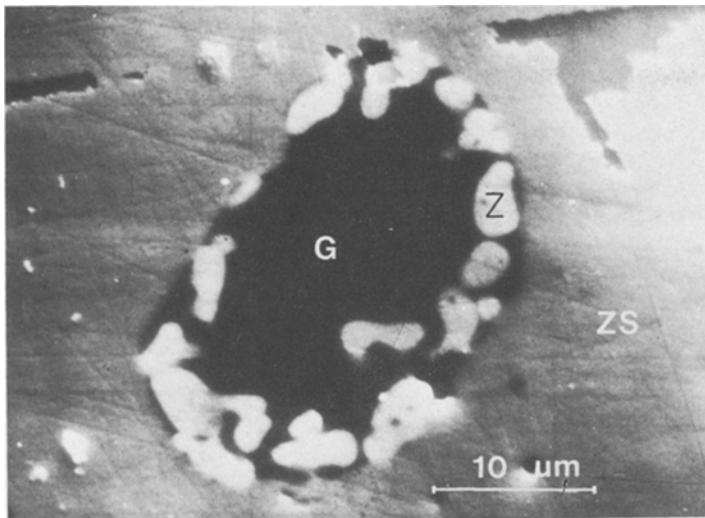
Figure 5 Back-scattered electron image of a polished sample of zircon sand treated at 1550°C for 24 h, showing a reaction area within a zircon grain. (ZS = zircon; Z = zirconia; G = glass).

these impurities but always lower than 1676°C temperature of dissociation of chemically pure zircon [2].

That is the case of rutile which is the most important impurity in zircon sands, as can be appreciated in Figs. 2 to 4. In this case, according to the ternary system ZrO_2–SiO_2–TiO_2, (Fig. 7) and due to the relative proportion of zircon and rutile in the area considered at the beginning of reaction, a liquid phase will be formed at a temperature of 1500°C which corresponds to the lower invariant point of the system. As temperature goes up the reaction area becomes rich in zircon and the liquid will move approximately in

Figure 6 Back-scattered electron image of a polished sample of zircon sand treated at 1650°C for 24 h, showing a silica inclusion within a zircon grain. (ZS = zircon; S = silica).

the direction of zircon composition. At a temperature of 1600°C the coexisting phases will be zircon, zirconium titanate and liquid which is in agreement with the previously related experimental results. The micrographs 2 to 4 show that this sequence took place during heating in all those areas where rutile is present and the Kevex microanalysis (Table III) are also in total agreement with the equilibrium data.

A similar behaviour has been observed in the case of feldspar impurities. Unfortunately the system ZrO_2–Al_2O_3–SiO_2–K_2O is not as well known as the system ZrO_2–SiO_2–K_2O. However, based on the similitude, which is expected to exist, between the system ZrO_2–SiO_2–K_2O and the system ZrO_2–SiO_2–Na_2O established by Sircar and Brett [4] it is possible to estimate that a liquid phase will appear at a temperature near 1100°C. As temperature is increased the liquid composition will move depending on the zircon/feldspar ratio. For very small amounts of feldspar and at a temperature of 1550°C the liquid composition will probably lie on the eutectic line which separates the primary phase fields of zircon and circonia. This is an agreement with the results of Yamaguchi and Kato [5] in their study on reaction of zircon refractories and potassium salt varpours and with the results shown in Fig. 5 and Table IV.

No sillimanite or kyanite were detected in the samples studied. However, it is possible to predict that in these areas a liquid phase will appear at a temperature of 1555°C invariant point of the subsystem zircon, mullite, silica [6].
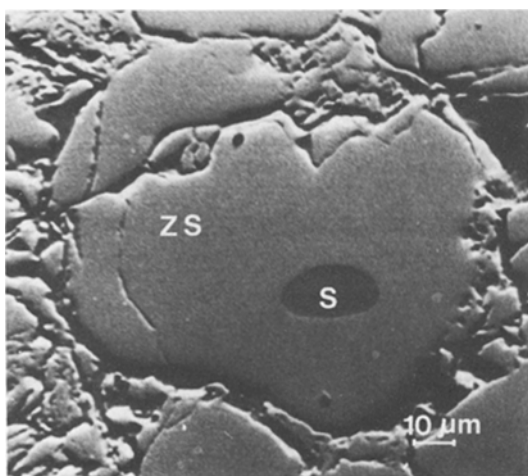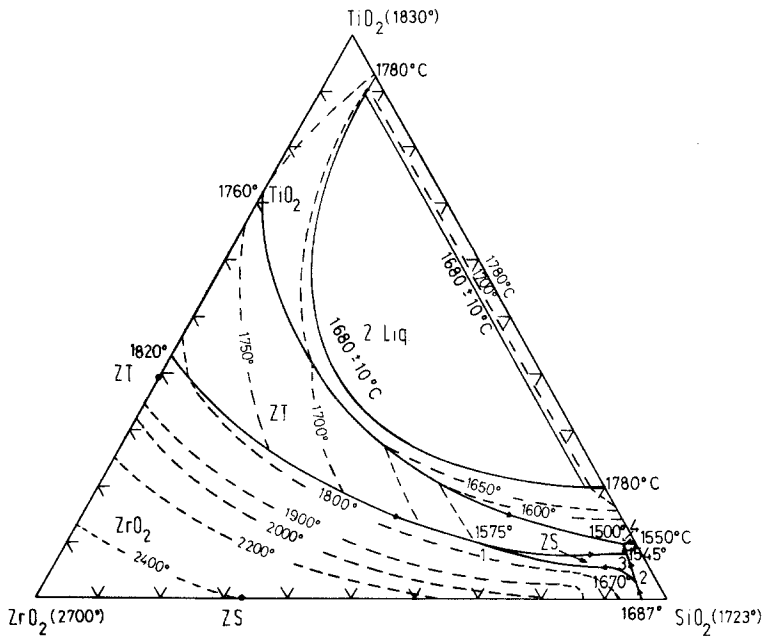
The silica inclusions detected, in this study, requires special mention. In all of them no reaction was observed between zircon and silica (Fig. 6) even at the highest temperature tested (1650° C). This fact seems to confirm that, in the system ZrO_2–SiO_2 zircon dissociate in the solid state [2] or peritectically [7, 8] at a temperature higher than 1650° C which contradicts the work of Curtis and Sowman [9] and Anseau *et al.* [10] who state that zircon dissociates in the solid state at 1550° C.

Being rutile the most important impurity in zircon sands, the temperature of the first significant liquid phase formation should be taken as 1500° C. This result agrees closely with the previous theoretical prediction of the authors [1]. Due to the location of the primary phase field of zircon, close to the silica corner, in all the ternary and quaternary system known where zircon is found, the quantity of liquid, at the beginning of melting, will be very low whichever is the impurity considered.

Due to the actual high technological importance of zircon for obtaining toughened materials by reaction-sintering, i.e. zircon–alumina based bodies, it is easily deduced, from the present work, the important role that the impurities, present in zircon sands, can play in order to evaluate processing parameters as densification rate, kinetics of reaction, etc. For example, recent research [11, 12] state that a complete reaction

is obtained in 3/2 molar ratio zircon–alumina mixtures at temperatures between 1420–1570° C. This fact can be explained from the present work, considering the appearance of a transient liquid phase which enhances the reaction sintering process [13].

Finally the appearance of this kind of liquids can play an important technological role in all those reactions where zircon sands are employed.

Acknowledgements

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