

Decalcification of Stabilized Zirconia by Silica and some other Oxides

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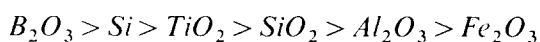
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Abstract

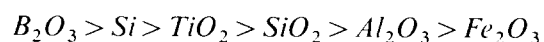
Calcium-stabilized cubic zirconia may react with different oxides, susceptible to combining with calcium, and be transformed into the monoclinic modification with undesirable consequences. The reaction with silica has been investigated, and the kinetics recorded by X-ray quantitative diffraction; the data have been fitted to the Jander equation, yielding the rate constant and the activation energy; comparison has been made with the action of silicon and some current oxides, allowing the following classification from the most to the least active:



These data have been rationalized by the Polanyi relationship, which correlates the kinetics to the formation enthalpy of ternary calcium oxides like $CaSiO_3$. The reaction interface is complex with three different layers: an ill-organized one in contact with cubic zirconia, a second layer with monoclinic calcium-free zirconia particles, and a third with silicates: $CaSiO_3$, $ZrSiO_4$ and $Ca_2ZrSi_4O_{12}$. The diffusion and nucleation are discussed; it seems that silicon plays a preponderant role in these processes.

Durch Kalziumoxide stabilisiertes Zirkoniumdioxid kann mit verschiedenen anderen Oxiden reagieren, wobei es sich mit Kalziumoxid verbindet und mit nachteiligen Folgen zur monoklinen Modifikation umgewandelt wird. Es wurde die Reaktion mit Siliziumdioxid untersucht und die Reaktionskinetik mit Hilfe quantitativer Röntgenbeugungsexperimente

verfolgt. Die Meßwerte konnten durch die Jander-Gleichung beschrieben werden, so daß die Geschwindigkeitskonstante und die Aktivierungsenergie der Reaktion hiermit bestimmt werden konnten. Der Effekt von Silizium wurde mit der Wirkung verschiedener gebräuchlicher Oxide verglichen, woraus folgende Einteilung der untersuchten Oxide resultiert, beginnend mit dem meist reaktiven bis letztlich zu dem am wenigsten reaktiven Oxid:

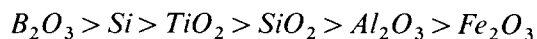


Die Auswertung der Daten erfolgte unter Zuhilfenahme der Polanyi-Beziehung, gemäß der die Kinetik und die Bildungsenthalpie ternärer Kalziumoxide, wie beispielsweise $CaSiO_3$, in Verbindung gesetzt werden. Der Aufbau der Reaktionsgrenzschicht ist komplex. Sie besteht aus drei Teilschichten: Die erste Teilschicht liegt ungeordnet in Verbindung mit kubischem Zirkoniumdioxid vor. Die zweite Schicht besteht aus monoklinen kalziumfreien Zirkoniumdioxid-Partikeln und die dritte aus Silikaten, wie $CaSiO_3$, $ZrSiO_4$ und $Ca_2ZrSi_4O_{12}$. Es werden Diffusion und Keimbildung diskutiert. Silizium scheint eine bedeutende Rolle bei diesen Prozessen einzunehmen.

La zircone stabilisée à la chaux peut réagir avec différents oxydes, susceptibles de se combiner à la chaux, et se transformer dans la variété monoclinique, avec des conséquences indésirables. La réaction avec la silice a été étudiée et la cinétique enregistrée par diffraction quantitative des rayons X; les données ont été ajustées par l'équation de Jander, d'où l'on déduit la constante de vitesse et l'énergie d'activation. Une comparaison a été faite avec l'action du silicium et de

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quelques oxydes courants, conduisant au classement suivant, du plus au moins actif:



Ces données ont été rationalisées par la relation de Polanyi, qui établit une corrélation entre la cinétique et l'enthalpie de formation des oxydes ternaires tels que $CaSiO_3$. L'interface réactionnel est complexe avec trois couches successives: l'une, mal organisée, au contact de la zircone cubique, une seconde faite de particules de zircone monoclinique, et une troisième avec les silicates $CaSiO_3$, $ZrSiO_4$ et $Ca_2ZrSi_4O_{12}$. Les processus de diffusion et de nucléation sont discutés; il semble que le silicium joue un rôle prépondérant.

1 Introduction

Calcium oxide is one of the most common of the oxides used to form a solid solution with ZrO_2 . It is well known that, according to the amount of calcium, substituted for zirconium, the doped zirconia may be tetragonal or even cubic, instead of monoclinic, above *c.* 1200°C.¹ Such a calcium-stabilized zirconia has found widespread applications in relation with its ability to withstand thermal shocks, for instance in some refractories for steelmaking, where it is combined with graphite in some industrial products, because graphite has a low wettability by liquid oxides.²

However, in many applications, this calcium-stabilized zirconia may react with other reagents, present within the refractory or the surroundings, and especially when the calcium oxide, dissolved in zirconia, is able to react with current acid oxides (SiO_2 , Al_2O_3 , TiO_2 ...), in spite of the fact that its activity is lowered by the solid solution. Then, when calcium oxide reacts with an external reagent, and is then extracted from the zirconia matrix, the more or less fully stabilized zirconia is progressively destabilized, and, according to the thermal treatment, may transform into the tetragonal or monoclinic modification, with the possibility of microcracking.

Previously, Ananthapadmanabhan *et al.*³ have considered the action of Al_2O_3 , SiO_2 and TiO_2 on calcia-stabilized zirconia, in the framework of obtaining a partially destabilized zirconia with better resistance to thermal shock. They studied the kinetics of the destabilization reaction, by the quantitative X-ray diffraction technique, from 1200 to 1400°C; they found that SiO_2 and TiO_2 are more active than Al_2O_3 , which accordingly is better suited for a controlled destabilization. According to them,

the destabilization process is ruled by the diffusion of the reactants through the product layer, because the reacted fraction obeys parabolic kinetics (with an activation energy of 190 kJ/mol in the reaction with Al_2O_3 ; however they do not mention the nature of this product layer, nor do they discuss the reaction mechanism). Accordingly the present authors have undertaken a more detailed investigation, in a greater range of experimental conditions, with many more reagents, but focusing mainly on SiO_2 because it is more frequent in refractories, where its action on zirconia materials had already been mentioned.⁴

2 Experimental

Stabilized zirconia, with 15 mol% CaO, was prepared by heating $CaCO_3$ with ZrO_2 at 1500°C for 48 h. Then a mixture of this stabilized zirconia and silicon dioxide or silicon was pressed into the form of small sticks and these mixtures were heated in a muffle oven in the open air at different temperatures and for various times. In this type of experiment with silicon, silicon dioxide or other oxides, the molar ratio of the reagents was unity and in the experiments where the destabilizing effect of silica was tested on differently stabilized zirconias, the quantity of silica in these samples was 10% in weight. All the as-received samples were characterized by X-ray diffraction and, using the polymorphic method,⁵ the fraction X_c of cubic zirconia in the cubic–monoclinic mixture was determined:

$$X_c = \frac{1 \cdot 13 I_c(111)}{1 \cdot 13 I_c(111) + I_m(111) + I_m(11\bar{1})}$$

where I_c and I_m are intensities of the given diffraction lines in the cubic and monoclinic modifications respectively.

The reacted samples were examined by X-ray diffraction, optical and scanning electron microscopy and by the electron microprobe.

3 Results and Discussion

3.1 Kinetics

3.1.1 Silicon dioxide

As shown by Fig. 1, the practical range of temperatures where the kinetics are measurable is 1150–1300°C; this limited range immediately suggests a rather high activation energy. First, however, kinetic law has to be considered; one of the simplest and most common, for solid–solid reactions, is the

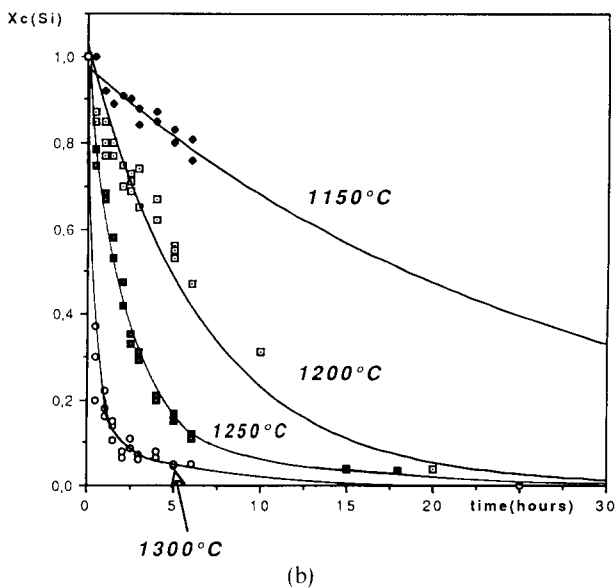
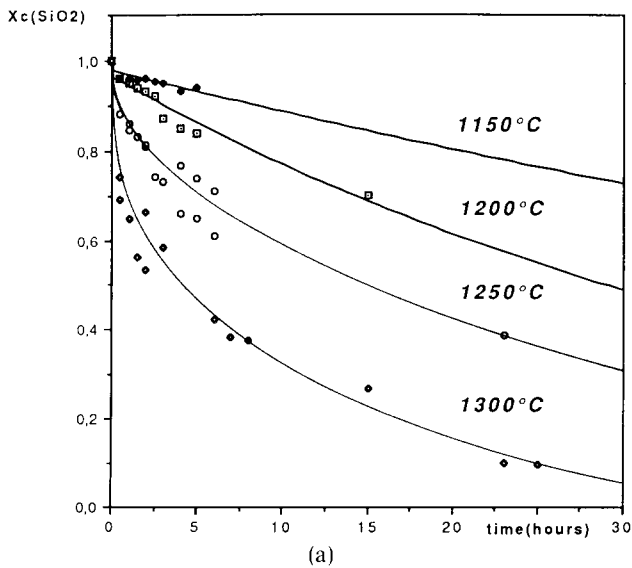


Fig. 1. Fraction of the ZrO₂ cubic modification versus time, at different temperatures, in the reaction with (a) silica and (b) silicon.

parabolic law already proposed by Ananthapadmanabhan *et al.*:³

$$x^2 = kt \quad (x: \text{reacted fraction}; t: \text{time})$$

However, as shown by Fig. 2, the fit is correct for a limited range of reacted fraction, suggesting that the product layer, through which diffusion has to take place, undergoes a breakaway with a subsequent acceleration of the reaction. From the acceptable part of this fit, a rate constant k may be derived:

$$k(\text{h}^{-1}) = 2.9 \times 10^{19} \exp(-620 \text{ kJ}/RT)$$

with a correlation coefficient of 0.989 (Fig. 3).

This is a rather high value for the activation energy, especially when compared to that of Ananthapadmanabhan *et al.*; however, such high values are not rare for diffusion in the solid state.^{6,7}

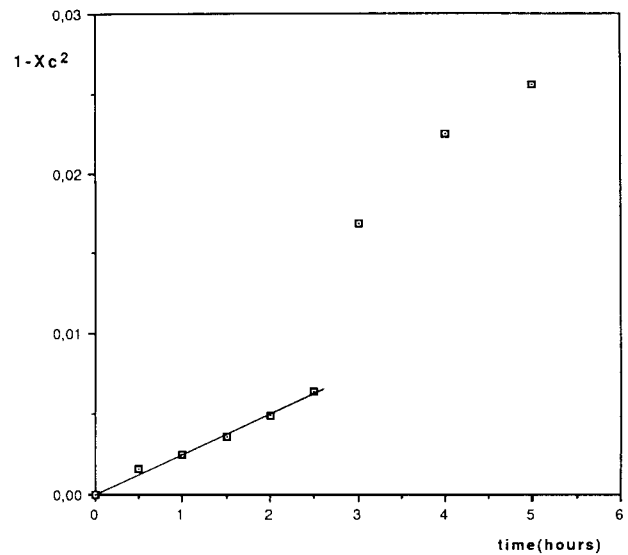


Fig. 2. Plot of the parabolic kinetic law, at 1200°C, for the reaction with silica.

On the other hand, as already stated, the rate of growth of the interfacial layer obeys the parabolic relationship for the initial part of the reaction only. It is indeed known that the geometry of powders reactions, where the particles of one reactant are spherical and embedded by much finer particles of the other reactant, obeys the Jander relationship:⁸

$$(1 - (1 - x)^{1/3})^2 = 2kt/r^2$$

where r is the initial radius of the coarser spherical particles. Actually the equation has been subsequently improved⁸ in order to take into account the volume change of the reacting particles, leading to:

$$(1 + (Z - 1)x)^{2/3} + (Z - 1)(1 - x)^{2/3} = Z + 2(1 - Z)kt/r^2$$

where Z is the volume of the particle formed per unit volume of the consumed particle. Here the value is

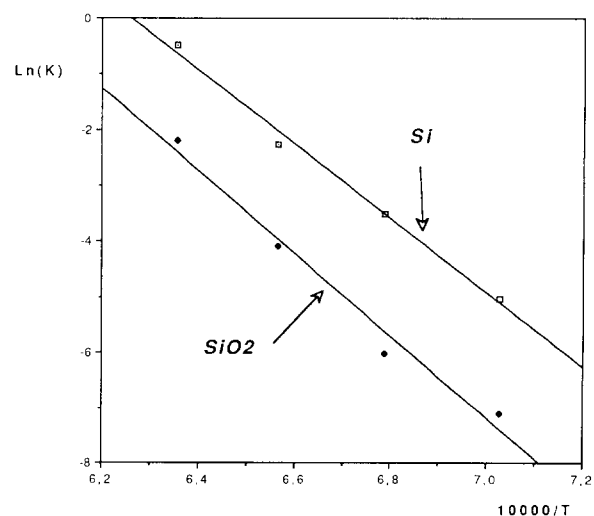
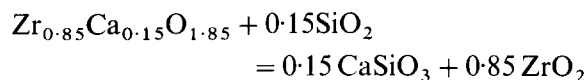


Fig. 3. Arrhenius plot of the parabolic rate constant in the reaction with silica and silicon.

taken as $Z=1$, as a first approximation, due to uncertainties regarding the exact nature of the interface layer (vide infra); indeed, if the reaction is



taking into account the densities of calcia-stabilized⁹ and monoclinic zirconia,¹⁰ then $Z=0.93$. This equation cannot be applied with $Z=1$ and Carter⁸ proposed in the case of no volume change the equation of Ginstling & Brounshtein:

$$X_c = \frac{2\alpha}{3} + (1-\alpha)^{2/3} = 1 - \frac{k}{r^2}t$$

but the development of this new equation gave the Jander equation. Then, when applying this equation to the previous data, an acceptable fit is obtained for a much higher range of reacted fraction (Fig. 4) than with the parabolic relationship, with:

$$\frac{k}{r^2}(\text{h}^{-1}) = 4.0 \times 10^{17} \exp(-595 \text{ kJ/RT})$$

correlation coefficient: 0.984

The fact that nearly the same activation energy is obtained is not surprising, as the Jander equation is equivalent, for small reacted fractions, to the parabolic equation. Knowing that r is in the range $15 < r < 20 \mu\text{m}$, then

$$k_0(\text{m}^2/\text{h}) \sim 1.31 \times 10^8 \exp(-595 \text{ kJ/RT})$$

where k_0 now includes r^2 with $r = 18 \mu\text{m}$.

3.1.2 Silicon

As the experiments have been carried out in air, the oxidation of silicon yields reactive silica which is

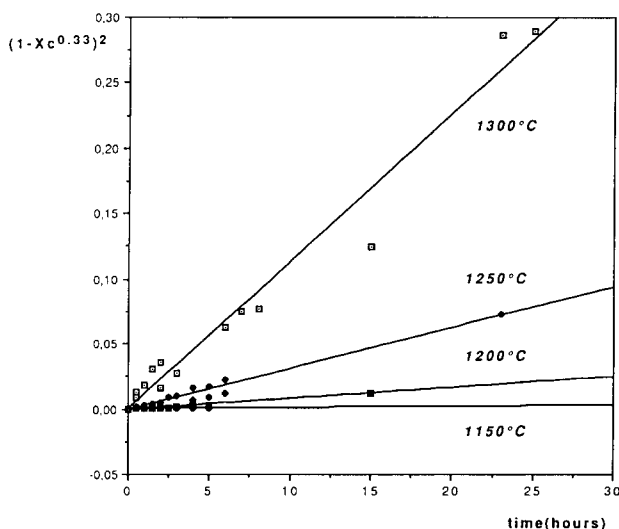


Fig. 4. Application of the Jander equation in the reaction with silica at different temperature.

prone to destabilize the calcia-doped zirconia, and accordingly it is indeed observed (Fig. 1) that the reaction is significantly faster with silicon than with silica.

The kinetic data have been treated along the same lines as previously, yielding:

$$k(\text{h}^{-1}) = 2.25 \times 10^{18} \exp(-565 \text{ kJ/RT})$$

correlation coefficient: 0.998

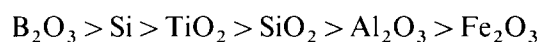
$$\frac{k}{r^2} = 2.1 \times 10^{18} \exp(-585 \text{ kJ/RT})$$

correlation coefficient: 0.97

The activation energy is quite comparable to that obtained with silica, which is consistent with the rate limitation by the same elementary step in the diffusion processes.

3.1.3 Other oxides

To obtain a better understanding of the zirconia destabilization, experiments were also carried out with some oxides which are currently present in zirconia refractories as additives or impurities: Na_2O , B_2O_3 , Al_2O_3 , Fe_2O_3 and TiO_2 . A comparison of the data obtained with these different oxides is given by Fig 5, with a classification:



B_2O_3 and Na_2O (introduced as Na_2CO_3) cannot be compared to these oxides, because they strongly volatilize during the experiment; it can just be stated that Na_2O has no effect on the destabilization, while

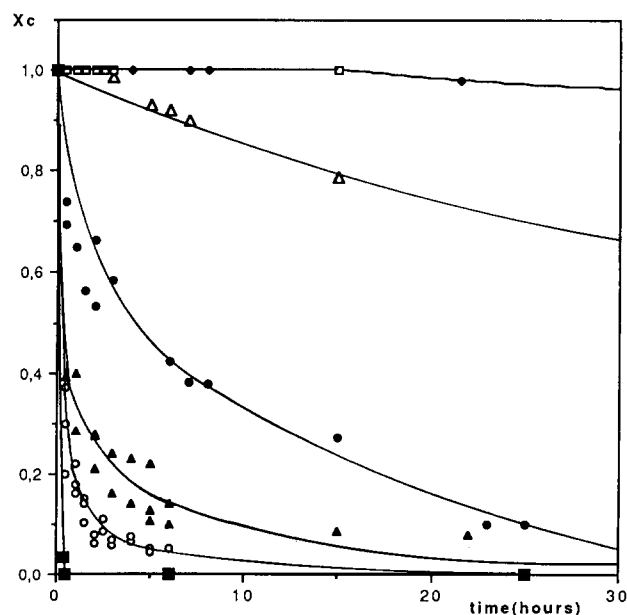


Fig. 5. Comparison of the reactivity with (○) Si, (●) SiO_2 , (■) B_2O_3 (5 mol%) Al_2O_3 (Δ , $\gamma\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$; \blacklozenge , $\alpha\text{-Al}_2\text{O}_3$), (□) Fe_2O_3 and (\blacktriangle) TiO_2 .

on the other hand B_2O_3 has a strong effect. The destabilization, on the other hand B_2O_3 has a strong effect and may be classed in the above series, because if it would not volatilize, it would have a still stronger effect.

In order to try to rationalize these results, the authors have looked for a correlation between these reaction rates and the thermodynamic quantities related to the formation of compounds such as $CaSiO_3$, CaB_2O_4 , etc. (Table 1), because according to the Polani relationship¹¹ in a family of exothermic reactions, when the reaction enthalpy increases, the activation energy barrier decreases:

$$E = E^0 + \alpha \Delta H \quad 0 < \alpha < 1$$

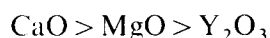
(where ΔH is negative and E^0 a constant)

and this may be extended, in the so-called Brönsted relationship, to a relation between the rate constant k and the equilibrium constant K

$$k = \text{const.} \times K^\alpha$$

if the entropy variation is approximately constant in the series (this is the case here, as in a solid state reaction there is little entropy change). Table 1 shows that the correlation is roughly obeyed. It may also be noted that these results are in agreement with Ananthapadmanabhan *et al.*³ as regards the oxides Al_2O_3 , SiO_2 , TiO_2 , and with Kyoden *et al.*⁴ who give $SiO_2 > \text{zircon} > \text{mullite} > Al_2O_3$ in air at $T < 1500^\circ C$

It is also worth mentioning that, as expected with these above considerations, in the comparison between three different zirconias stabilized by CaO , MgO and Y_2O_3 , the destabilization by silica at 1300 C may be classified as follows:



the last one being highly resistant to this treatment.

3.2 Morphology

The interface layer, as observed at 1300°C, for instance (Fig. 6), is rather complex; between calcia-

stabilized zirconia and the silica powder, there are:

- a highly disorganized zone, a few μm wide;
- fairly regular particles of monoclinic (calcium-free) zirconia; they are dense, round, with a size of a few μm ; and
- a complex zone with different silicates; according to electron microprobe analysis, $CaSiO_3$ is an important component in this region, but there are also ternary calcium-zirconium silicates and also patches of zircon.

According to the published ZrO_2 - SiO_2 - CaO phase diagrams,^{12,13} there are two ternary compounds: $Ca_2ZrSi_4O_{12}$ and $Ca_3ZrSi_2O_9$; the first one is of interest here, and may be formulated C_2ZS_4 (C for CaO , Z for ZrO_2 and S for SiO_2); it melts incongruently at 1430°C.

Actually the composition and texture of the silicate zone depends on temperature, duration, thermal treatments, etc. As a rule, when the samples are slowly cooled, the observed phases are in agreement with the phase diagram; on the other hand, when they are quenched from temperatures between 1300°C and 1500°C, besides C_2ZS_4 , another composition is observed with the electron microprobe: $C_2Z_{-0.5}S_4$ or C_4ZS_8 . Such a composition is found in rather wide area of the cross-sections, together with C_2ZS_4 ; however the X-ray diffraction patterns do not detect any new phase, and accordingly it must be admitted that this is nothing else than an intimate mixture of C_2ZS_4 , CS and S, at least at room temperature, because this is an indication of such another phase at high temperature; additional experiments will probably explain this point.

3.3 Mechanism

According to the description of the reaction front, the first zone to consider, in contact with unreacted zirconia, is badly organized and contains Zr, Ca and Si, in ill-defined proportions. Nevertheless, diffusion has to take place across this intermediate zone, and

Table 1. Reaction with different oxides

Reaction	ΔG^0 (J)	ΔH^0 (J)	k (1300 C)	
			Parabolic law	Jander law
$CaO + Al_2O_3 = CaAl_2O_4$	-52 250	-15 000	≈ 0	≈ 0
$CaO + Fe_2O_3 = CaFe_2O_4$	-49 700	-21 000	≈ 0	≈ 0
$CaO + SiO_2 = CaSiO_3$	-90 300	-88 000	0.11	0.011
$CaO + TiO_2 = CaTiO_3$	-86 500	-80 500	0.10	0.036
$CaO + B_2O_3 = CaB_2O_4$	-141 000	-123 000	≈ 1	≈ 1

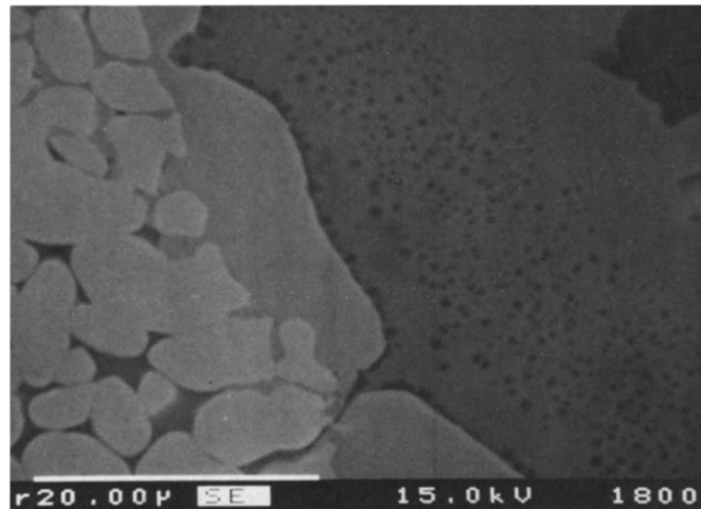
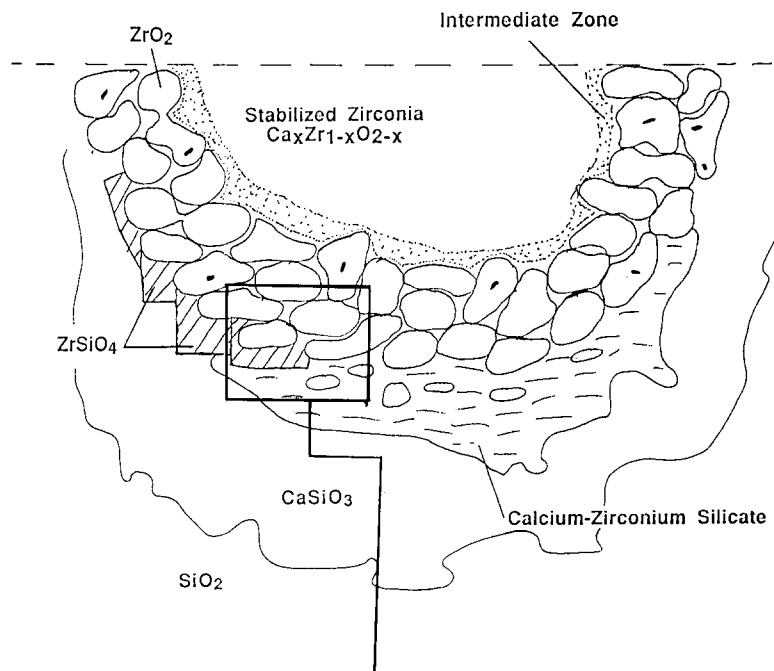


Fig. 6. Interface layer in the reaction with silica at 1300°C.

one question is, what is the rate-determining diffusive species?

In the formation of AB_2O_4 spinels, it is known that, among the three ions considered, the slowest ion plays no part in the reaction rate, while the movement of the fastest is coupled to the movement of the ion of intermediate velocity in order that electroneutrality be preserved; therefore it is the ion of intermediate velocity which determines the rate of reaction.

Here it is reasonable to consider that the main part of the driving force is provided by the formation of $CaSiO_3$, because firstly there is little zircon, and secondly the C_2ZS_4 has a low stability.¹² Then among Ca^{2+} , Si^{4+} and O^{2-} , the first is likely the fastest; but Si^{4+} and O^{2-} mobilities are known to have the same order of magnitude in silicates,

although these ions are in no way comparable, because their motions are correlated.⁶ Therefore here the transport is probably limited by the couple Si^{4+} , O^{2-} , and the formation of ternary oxides, like C_2ZS_4 , is a post-reaction.

Another question is about the initial step at the zirconia surface, because silica may react with calcia and with zirconia as well; however, as already stated, formation of $CaSiO_3$ is probably the driving step. Then, if the diffusion coefficient of Ca^{2+} , D_{Ca} , in zirconia is considered:¹⁴

$$D_{Ca} \text{ (m}^2\text{/s)} = 0.45 \times 10^{-4} \exp(-421 \text{ kJ/RT})$$

then it is found that the distance it may travel in zirconia is $0.15 \mu\text{m}$ at 1400°C . On the other hand, there are no data about diffusion of silicon in zirconia; however, careful electron microprobe analysis

of calcia-stabilized industrial zirconia crystals, after partial reaction at 1000°C with silica, show near the surface concentration gradients for Ca^{2+} and Si^{4+} :

- Ca^{2+} decreases from 3.5 at.% in the bulk to ~1 at.% at the surface.
- Si^{4+} increases from 0.2 at.% in the bulk to ~1 at.% at the surface.

This strongly suggests counter-diffusion of these ions; the next step is nucleation of CaSiO_3 in the zirconia matrix, with the conditions (neglecting the strain energy):

$$a_{\text{CaO}} \times a_{\text{SiO}_2} > \exp(-\Delta G^\circ/\text{RT})$$

$$\Delta G^\circ = -90\,700 \text{ J for } \text{CaSiO}_3$$

$$T = 1000^\circ \text{C} \rightarrow a_{\text{SiO}_2} > 2.1 \times 10^{-4}$$

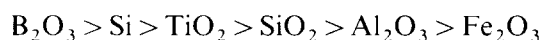
in reasonable agreement with the surface concentrations of Ca^{2+} and Si^{4+} .

Additional experiments, with low reaction durations, aimed to observe the CaSiO_3 nucleation, have not been successful as yet.

4 Conclusions

The kinetics of the silica decalcifying upon calcia-stabilized zirconia may be represented by the Jander equation in the range 1150–1300°C, yielding a rate constant with a rather high activation energy (620 kJ).

Comparison with silicon (in oxidizing atmosphere) and with some other oxides leads to the following sequence, from the most to the least active:



This may be correlated with the reaction enthalpies according to the Polanyi relationship.

The reaction interface morphology is quite complex, with three intermediate layers: the nearest to zirconia is not well defined and probably ill-crystallized, the second contains small decalcified

zirconia crystals, and the third is made of several calcium and/or zirconium silicates. Taking into account the higher mobility of calcium ions, it seems that silicon diffuses inside the calcia-stabilized zirconia crystals, and this process may be rate-determining.

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