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Ceria-Doped Zirconia–Graphite as Possible Refractory for Tundish Nozzles in Steelmaking

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Abstract

In zirconia–graphite refractories, calcia-stabilized zirconia is sensitive to silica coming from oxidized additives (Si, SiC). Accordingly, ceria is considered here as an alternative cheap stabilizer.

Ceria-doped zirconia has been prepared and the monoclinic/tetragonal distribution has been analysed. At 1500°C in oxygen, the solution of ceria in zirconia is sluggish; to obtain a pure tetragonal phase, a 16 mol% ceria concentration (equal to the solubility limit) is necessary. Such samples are stable below 1050°C, in spite of previous claims to the contrary.

At 1300°C, silica does not destabilize these samples, even in reducing conditions. However, at low oxygen pressure, the pyrochlore $Ce_2Zr_2O_7$ *is formed, and the remaining zirconia transforms into the monoclinic modification. Nevertheless, below 1175°C, a metastable, purely tetragonal modification is obtained, because the activation energy needed for the formation of* $Ce_2Zr_2O_7$ *is too high.*

In any case, the reduction does not destroy the polycrystalline texture. This fact, combined with the resistance to silica, favours the use of these materials in steelmaking.

In feuerfesten Zirkoniumdioxid-Graphit Keramiken reagiert die Kalziumoxid-stabilisierte Zirkoniumdioxid-Phase sehr empfindlich gegenüber Siliziumdioxid, welches durch Oxidation von Additiven (Si, SiC) freigesetzt wird. Als alternativer wirtschaftlicher Stabilisator wird in dieser Arbeit daher Cerdioxid betrachtet.

Hierzu wurde mit Cerdioxid dotiertes Zirkoniumdioxid hergestellt und die Verteilung der monoklinen und der tetragonalen Phase untersucht. Unter Sauerstoffatmosphäre verläuft die Auflösung des Cerdioxids in Zirconiumdioxid sehr langsam. Um die reine tetragonale Phase herzustellen, ist ein Zusatz von 16 Mol-% Cerdioxid—dies entspricht der maximalen Löslichkeit—erforderlich. Proben dieser Zusammensetzung sind unterhalb 1050°C stabil. Dies steht im Widerspruch zu früheren Untersuchungen.

Bei 1300°C führt Siliziumdioxid nicht zu einer Destabilisierung der Proben, auch nicht bei reduzierender Umgebung. Bei geringen Sauerstoffdrucken wird allerdings Cerzirkonat $Ce_2Zr_2O_7$ *gebildet und das restliche Zirkoniumdioxid wandelt in die monokline Modifikation um. Unterhalb 1175°C bildet sich eine metastabile rein tetragonale Modifikation, da die Aktivierungsenergie für die Bildung von Cerzirkonat bei dieser Temperatur zu hoch ist.*

Die Desoxidation zerstört jedenfalls nicht die Textur des polykristallinen Materials. Diese Tatsache und die Stabilität gegenüber Siliziumdioxid sprechen für den Einsatz dieser Werkstoffe bei der Stahlerzeugung.

Dans les réfractaires zircone–graphite, la zircone stabilisée à la chaux est sensible à la silice venant de l'oxydation des additifs (Si, SiC). C'est pourquoi le dioxyde de cérium est considéré ici comme un autre stabilisant relativement bon marché de la zircone.

La zircone stabilisée au cérium est préparée et sa répartition en variétés monoclinique et quadratique est précisée. A 1500°C dans l'oxygène, la dissolution de CeO_2 *dans la zircone est lente; pour obtenir la variété quadratique pure, une concentration de* CeO_2 *de 16 mol%, égale à la solubilité limite, est nécessaire. Les échantillons obtenus sont stables en dessous de 1050°C, en dépit d'affirmations antérieures opposées.*

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A 1300°C, la silice ne déstabilise pas ces échantillons, même dans des conditions réductrices. Cependant à basse pression d'oxygène se forme le pyrochlore $Ce_2Zr_2O_7$, et la zircone restante se transforme en variété monoclinique. Cependant en dessous de 1175°C, la variété métastable quadratique se forme car l'énergie d'activation demandée pour $Ce_2Zr_2O_7$ est trop forte.

En tout cas la réduction ne détruit pas la texture polycristalline. Ce fait, plus la résistance à la silice, pourrait favoriser l'emploi de ces matériaux en aciérie.

1 Introduction

Stabilized zirconia is widely used for tundish nozzles in continuous casting of steel. Such submerged nozzles aim to prevent the molten steel from oxidizing, to facilitate the removal of inclusions, and to allow the molten steel to be poured under stable conditions. In order to achieve this, it is necessary for these nozzles to show excellent resistance to erosion, to thermal shock, and to corrosion at the powder line, where they may be corroded both by molten steel and by molten oxides of the slag.

In order to fulfill these requirements, zirconia–graphite refractories are supplied, in which the addition of carbon improves the thermal properties but also decreases the wettability by molten oxides and accordingly limits their corrosive action on stabilized zirconia. However, graphite is of course sensitive to oxidation by gaseous oxygen or CO_2 as well as by oxides present in the slag; therefore the refractory manufacturers incorporate anti-oxidation additives such as silicon or silicon carbide.[1-7]

However, when these additives are oxidized, they produce silica, which can then react with the calcium oxide dissolved in the zirconia, with obvious drawbacks, mainly the destabilization of the zirconia, which transforms into the tetragonal and then the monoclinic modification. This is a process that has been observed and analysed in detail in a previous publication.[8]

Accordingly it is desirable to find another dopant for zirconia, which would resist corrosion by silica. Clearly Y_2O_3, which is widely used as a zirconia stabilizer, would be suitable; but it is rather expensive, so that it seemed preferable to test cerium dioxide.

This oxide has already given rise to numerous investigations as a dopant in tetragonal zirconia, because it may be considered as a better dopant than Y_2O_3 in zirconia polycrystals from the viewpoint of toughness[9] and thermal stability.[10]

Nevertheless, the CeO_2–ZrO_2 phase diagram is still a matter for discussion, probably because the equilibria are difficult to reach, especially of course at low temperature; even the existence of $Ce_2Zr_3O_{10}$ has been questioned.[11]

In the present work, the authors prepare ceria-doped tetragonal zirconia, and first consider its thermal stability at low temperature, in view of the discrepancies in the literature data. The two features related to the working conditions are investigated: the behaviour in low oxygen pressure and the reactivity with silica. In each case, the formation of trivalent cerium is expected, with consequences for the zirconia stabilization.

2 Experimental

The zirconia samples were provided by Labosi, and contain less than 150 ppm Hf; the ceria, from Fluka, has 99% purity. These reagents were thoroughly mixed and ground together, before being annealed in an alumina crucible.

For the reduction by CO–CO_2, a thermal balance was used. The oxygen partial pressure in these mixtures was measured by a zirconia gauge.

The volume fraction of monoclinic zirconia, in the mixtures of monoclinic and tetragonal zirconia, was determined by quantitative X-ray diffraction, using the equation

$$V_m = \frac{P[I_m(111) + I_m(11\bar{1})]}{I_t(111) + P[I_m(111) + I_m(11\bar{1})]} \qquad V_t = 1 - V_m$$

$$\left[I = K \cdot \frac{1}{V^2} |F|^2 \cdot \rho \cdot LP \cdot \frac{e^{-2m}}{2\mu} = KR/2\mu \right.$$

where K: an independent constant of the diffracted product, but dependent on the radiation type and of the beam size, V: cell volume, F: structure factor, ρ: multiplicity, LP: Lorentz-polarisation factor, μ: linear adsorption coefficient of the product and e^{-2m}: temperature factor

$$\left. P = \frac{R_c(111)}{R_m(111) + R_m(11\bar{1})} \right]$$

where different values of P have been proposed,[12,13] and I_m and I_t are the intensities diffracted by the monoclinic and tetragonal modifications respectively. The authors have redetermined $P = 0{\cdot}55$ by careful calibration with eight mixtures of the two modifications over a large range of compositions.

3 Preparation and Stability

In order to refer to previous work on calcia-stabilized zirconia,[8,9] which contained 13 mol% CaO, the authors prepared ceria-doped zirconia with the same molar amount: 13 mol% CeO_2. The

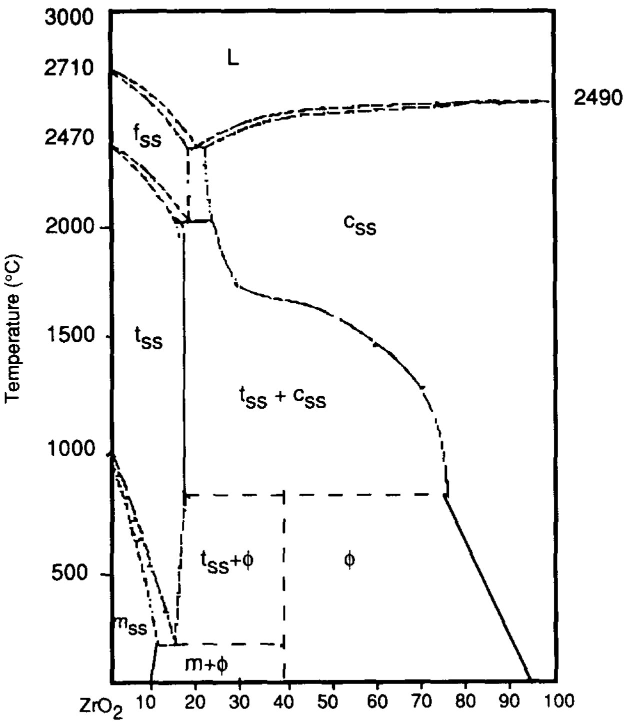


Fig. 1. The ZrO_2–CeO_2 phase diagram, after Duran *et al.*[14] t_{ss}: tetragonal solid solution; c: cubic; m: monoclinic; f: fluorine; L: liquid.

ZrO_2–CeO_2 mixture was heated, in an alumina crucible, at 1500°C for 65 h, in oxygen. The volume fraction V_t of tetragonal zirconia thus obtained is in the range 0·65–0·70, and does not increase with additional annealing. On the other hand, an increase of the CeO_2 to 16 mol% results in a 100% tetragonal zirconia, as shown by the X-ray pattern, which also detects a tiny amount of $Ce_2Zr_3O_{10}$.

If the ZrO_2–CeO_2 phase diagram established by Duran *et al.*[14] recently (Fig. 1) is considered, 13 mol% CeO_2 should have been quite sufficient to obtain pure tetragonal zirconia at 1500°C. However, the dissolution of ceria into zirconia is too slow at 1500°C to obtain homogeneously doped zirconia; then the cerium content depends on the zirconia grain size: only the small grains are sufficiently doped in these conditions. Secondly, during the quenching to room temperature, the low-doped grains may undergo the tetragonal → monoclinic transformation at a sufficiently high temperature, according to the phase diagram, to profit from favourable kinetic conditions.

Always, the dissolution of ceria into zirconia is not a simple process, as noted by previous authors,[14–18] because there is a competition with sintering, arising from the fact that the stability of the ceria-doped zirconia depends inversely on the grain size; this is why a longer annealing does not necessarily improve the tetragonal content.

Another question, related to the stability of the ceria-doped zirconia, is the disproportionation of the tetragonal modification under 1050°C into a monoclinic–cubic mixture, as claimed by Tani *et al.*[11] As such a behaviour would be detrimental for the refractories, it was desirable to check this point.

Accordingly two samples with $V_t = 73$ and 76% respectively were annealed at 1000°C for several hours (Table 1) without any significant structural evolution being found. Such a stability is observed both in air or oxygen, with or without quenching.

4 Check for Possible Reaction with Silica

4.1 In air

Mixtures of ceria–zirconia ($V_t = 65$ or 70%) with silica (10 wt%) were annealed at 1300°C (Table 2), without any change being found. This is consistent with the lack of compound or solid solution in the CeO_2–SiO_2 system. On the other hand, there is a disilicate $Ce_2Si_2O_7$, with Ce^{3+}, which might be produced in reducing conditions.

4.2 In low oxygen pressure

Similar mixtures of ceria-doped zirconia (V_t = 100%) with silica (10 wt%) were annealed at 1300°C for 2 days in N_2/6% H_2. The X-ray pattern

Table 1. Annealing of ceria-doped zirconia at 1000°C (other $ZSCeO_2$)[a]

	Time (h)										
	0	*1*	*2*	*4*	*5*	*19*	*24*	*0*[a]	*26*	*44*	*47*
V_t (%)	76	76	78	79	73	76	78	73	75	74	73

[a] $ZSCeO_2$: ceria-doped (or stabilized) zirconia.

Table 2. Mixtures of $ZSCeO_2$[a] (13 mol%) with silica (10 wt%) annealed at 1300°C

	Time (h)											
	0	*1*	*4*	*6*	*7·5*	*0*	*21*	*24*	*27*	*63·5*	*33·5*	*112·5*
V_t (%)	70	70	72	71	71	65	62	63	63	63	62·5	65

[a] $ZSCeO_2$: ceria-doped (or stabilized) zirconia.

shows the presence of partly destabilized zirconia, $Ce_2Zr_2O_7$ and a small quantity of $Ce_2Si_2O_7$.

It seems therefore that, in reducing conditions, the formation of $Ce_2Zr_2O_7$ is preponderant, whereas SiO_2 plays a minor role. Therefore the behaviour of ceria-doped zirconia in reducing conditions without any silica has also been considered.

5 Behaviour at Low Oxygen Pressure

For the sake of clarity, pure CeO_2, then ceria-doped zirconia are considered successively.

5.1 CeO_2

Compacted samples (4 × 6 × 20 mm) are heated, in an alumina crucible, inside a thermal balance, at 3 K/min, up to 1300°C. After a given annealing at 1300°C, they are cooled at 2 K/min. The reducing gases are 20% CO/80% CO_2, 80% CO/20% CO_2, 94% N_2/6% H_2, flowing at 5 l/h.

As shown, for instance by Fig. 2, a loss of water occurs at $T < 300°C$, then a continuous loss of oxygen is observed, which does not increase when the temperature is maintained at 1300°C, suggesting that the equilibrium has been reached during the heating period.

Cerium dioxide is known to be non-stoichiometric with formation of oxygen vacancies: CeO_{2-x}. Blumenthal and Panlener[19] have determined $x = f(T, p_{O_2})$. With the two CO/CO_2 mixtures, which correspond to $p_{O_2} = 10^{-8 \cdot 5}$ and 10^{-11} atm at 1300°C, $x = 0 \cdot 087$ and 0·17 respectively, in good agreement with these authors (0·085 and 0·17). With the first mixture ($p_{O_2} = 10^{-8 \cdot 5}$ atm) $x = f(T)$ was also measured (Table 3). The oxygen vacancy formation is written:

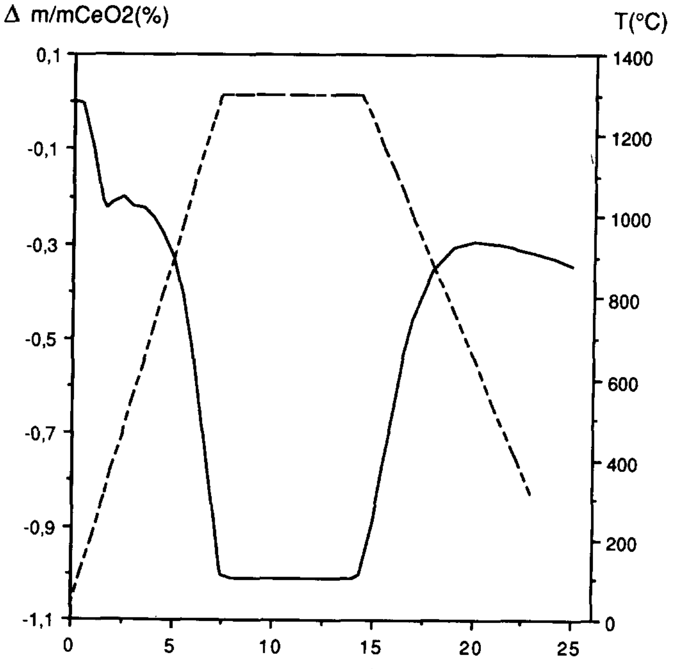


Fig. 2. Reduction of CeO_2 by 20% CO/80% CO_2; mass and temperature variation versus time. ——: m/mCeO_2; – – – –: T (°C). Δ m/mCeO_2: mass variation compared with the CeO_2 mass in the sample.

Table 3. Values of x and n in the compounds CeO_{2-x} at different temperatures

Temperature (°C)	*Experiment* (x)	*Ref. 19* (x)	*n*
900	0·016	0·011	2·9
950	—	0·021	3·0
1 000	—	0·027	3·1
1 024	0·030	0·027	3·1
1 050	—	0·035	3·3
1 100	0·043	0·045	3·4
1 150	—	0·056	4·3
1 200	0·066	0·063	4·7
1 250	—	0·072	5·2
1 300	0·087	0·087	5·5

$$CeO_2 = \tfrac{1}{2}O_2 + V_0^{\alpha} + \alpha e' + Ce_{Ce}^{x} + O_0^{x}$$

(α: ionization degree) with $[Ce_{Ce}^{x}]$ and $[O_0^{x}] = 1$

$$K = p_{O_2}^{1/2}[V_0^{\alpha}][e']^{\alpha} = \exp\left(-\frac{\Delta H}{RT} + \frac{\Delta S}{R}\right)$$

$$\frac{n}{2}\ln x + \alpha \ln \alpha + \frac{1}{2}\ln p_{O_2} = -\frac{\Delta G}{RT}$$

$$n = 2(\alpha + 1)$$

The values of n for each experimental condition are deduced from Ref. 19, and given by Table 3. The corresponding ΔG values are obtained by the preceding equation, and are represented in Fig. 3. It is note-worthy that n and ΔG strongly depend on temperature; moreover, there are two ranges for ΔH:

$900 \leqslant T \leqslant 1100°C$	$\Delta H = 149$ kcal/mol
$1100 \leqslant T \leqslant 1300°C$	$\Delta H = 95$ kcal/mol

5.2 Ceria-doped zirconia

5.2.1 Reduction at 1300°C

The same kind of reduction is depicted in Fig. 4 for a 13 mol% doped zirconia. It appears that the oxygen loss is greater than with pure ceria (3·3% instead of 0·81%, corresponding to $CeO_{1 \cdot 29}$ instead of $CeO_{1 \cdot 83}$) and is not completely reversible.

According to the X-ray diffraction patterns, the pyrochlore $Ce_2Zr_2O_7$ has been formed in this reduction; its cell parameter is slightly greater (+1·3%) than the expected value, but it is known[20,21] that this corresponds to reoxidation into $Ce_2Zr_2O_{7+x}$ at low temperature. As a consequence of the pyrochlore formation, the zirconia is depleted in ceria and transforms into the monoclinic modification during cooling.

The micrographs (Fig. 5) show the grain size

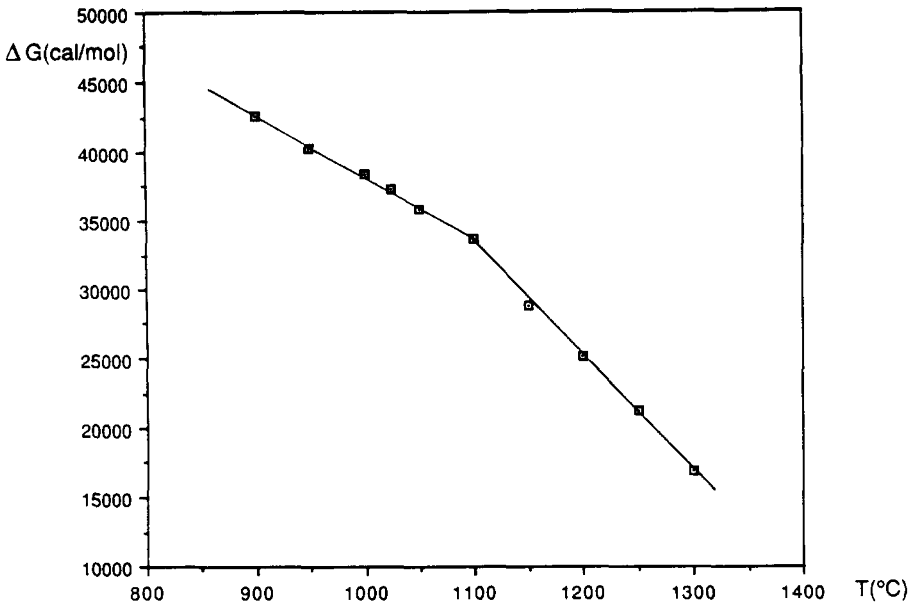


Fig. 3. Free enthalpy for the oxygen vacancies formation versus temperature.

distribution in the reduced samples. They have been analysed with the electron microprobe (Table 4); the smaller they are the more ceria they contain (this is consistent with the slow dissolution of ceria in zirconia invoked in Section 3), but the X-ray map also shows that, in spite of the reduction, there is a fairly homogeneous distribution of cerium inside the grains; this is quite different from the calcium distribution in calcia-doped zirconia after reaction with silica.

One question is: in the reduction of Ce-doped zirconia into $Ce_2Zr_2O_7$, what is the cerium concentration in equilibrium with $Ce_2Zr_2O_7$ (under this concentration the reduction does not take place).

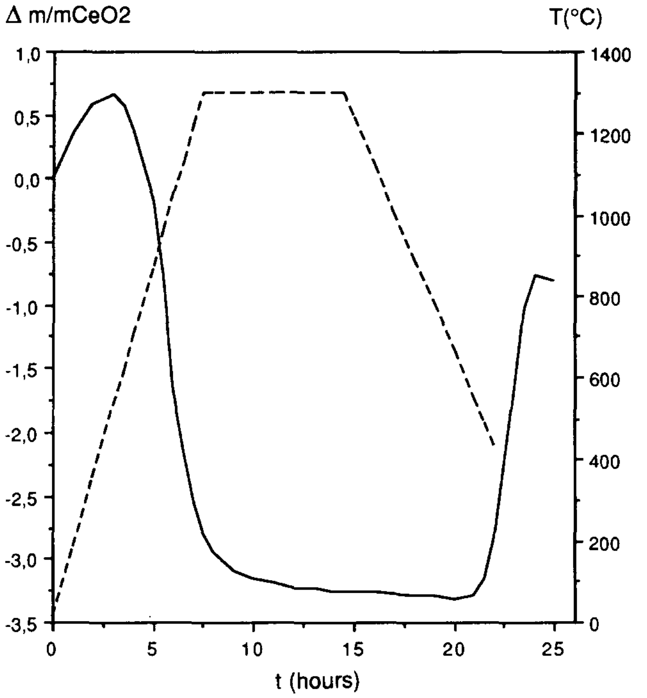


Fig. 4. Reduction of ceria-doped zirconia by 20% CO/80% CO_2; mass and temperature variations versus time. ——— : Δ m/mCeO_2; - - - : T (°C). Δ m/mCeO_2: mass variation compared with the CeO_2 mass in the sample.

Due to the lack of thermodynamic data on $Ce_2Zr_2O_7$, the data of Paputskii *et al.*[22] on $Nd_2Zr_2O_7$, and those of Kubaschewski & Alcock[23] for the other components of the reactions:

$$2CeO_2 = Ce_2O_3 + \tfrac{1}{2}O_2 \qquad \Delta G_{1^\circ} = 85\,600 - 30{\cdot}7T\ \text{(cal)}$$

$$Ce_2O_3 + 2ZrO_2 = Ce_2Zr_2O_7 \qquad \Delta G_{2^\circ} = -25\,600 - 1{\cdot}8\,T\ \text{(cal)}$$

$$2CeO_2 + 2ZrO_2 = Ce_2Zr_2O_7 + \tfrac{1}{2}O_2 \qquad \Delta G_{T^\circ} = 59\,100 - 32{\cdot}5\,T\ \text{(cal)}$$

$$RT\ln\left[p_{O_2}^{1/2}/c^2(1-c)^2\right] = -59\,100 + 32{\cdot}5T$$

c(molar fraction of ceria in zirconia)

$$\approx p_{O_2}^{1/4}\exp\left(\frac{14\,800}{T} - 8{\cdot}1\right)$$

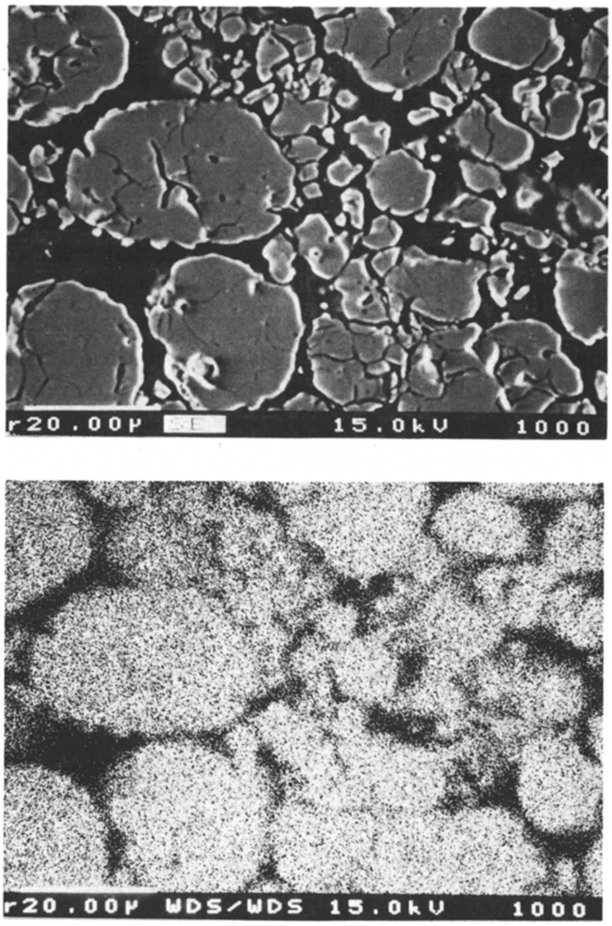
At 1300°C, with the two CO/CO_2 mixtures, $c = 0{\cdot}028$ and $6{\cdot}6 \times 10^{-3}$ respectively. In other words, when starting from $c = 0{\cdot}13$, the zirconia should be depleted in ceria to an extent of 78 and 95% respectively, if equilibrium is reached.

5.2.2 Reduction in the 900–1300°C range

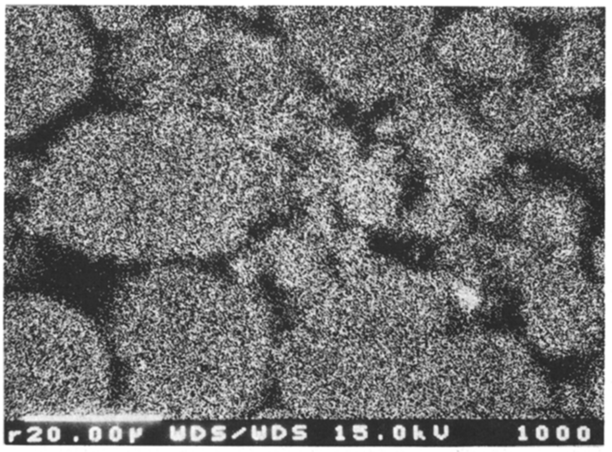
It is interesting to note two different behaviours:

(i) For $T \leqslant 1150$°C, the partially stabilized zirconia (13 mol% CeO_2, $V_t = 76\%$) is progressively transformed into completely stabilized zirconia ($V_t \neq 100\%$), with only traces of $Ce_2Zr_2O_7$ and of $(Zr,Ce)O_2$ (95% ZrO_2) cited by the Joint Committee for Powder Diffraction Standard, Entry No. 2-1334.

(ii) For $T > 1150$°C, the behaviour is the same as described previously for $T = 1300$°C.



Element Zr



Element Ce

Fig. 5. (a) Cross-section and (b) X-ray image of the cerium distribution in the reduced ceria-doped zirconia.

Table 4. Analyses with the electron microprobe in Ce-doped zirconia samples after reduction

	ZrO_2 (wt%)	CeO_2 (wt%)	HfO_2 (wt%)
TGA[a] $ZSCeO_2$ (20% CO/80% CO_2)			
Small grain of zirconia	83·51	15·13	0·032
Small grain of zirconia	83·14	15·67	—
Very small grain of zirconia	81·74	16·35	—
Very small grain of zirconia	82·00	18·15	—
Large grain of zirconia	89·33	9·50	0·08
Split large grain	88·80	8·72	—
Large grain	90·57	8·94	—
Split large grain	89·93	9·43	—
Large grain	81·37	18·85	—
	82·88	15·67	0·08
TGA[a] (80% CO/20% CO_2)			
Split grain	87·10	13·16	—
Split grain	83·47	15·28	0·03
Small grain	80·84	15·83	—
Small grain	78·32	18·65	—
Large grain	84·20	13·59	—
	86·45	13·23	

[a] TGA: thermal gravimetric analysis.

At first sight these results are surprising, as the transformation m-$ZrO_2 \rightarrow$ t-ZrO_2 is reversed at 1175°C, but in the opposite direction to that observed at 1000°C with pure zirconia. However, there are two differences from pure zirconia: the cerium content and the oxygen vacancies due to the low oxygen pressure. It has been reported[24] that the oxygen deficiency, which results from the low oxygen pressure, stabilizes the more symmetrical zirconia modifications. Accordingly, as long as the pyrochlore $Ce_2Zr_2O_7$ does not form, the loss of oxygen favours the dissolution of cerium into zirconia, as Ce^{3+} ion, which, moreover, is more mobile than Ce^{4+} thanks to its lower charge. In other words, the low oxygen pressure has a double effect:

(i) Thermodynamic: it stabilizes Ce^{3+} in zirconia.
(ii) Kinetic: it increases the cerium mobility in zirconia.

These two facts work for a higher concentration of the tetragonal modification, as observed below 1175°C, but when the temperature is sufficient, the pyrochlore $Ce_2Zr_2O_7$ forms, because the thermal energy is high enough to overcome the activation energy for pyrochlore formation; this means that the situation observed below 1175°C is out of equilibrium in terms of the Ce_2O_3–ZrO_2 phase diagram.[25]

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