A new tentative phase equilibrium diagram for the ZrO_2–CeO_2 system in air

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The phase relationships over a wide range of temperature and compositions in the ZrO_2–CeO_2 system have been reinvestigated. From DTA results, thermal expansion measurements and K_{IC} determinations it was established that additions of CeO_2 to ZrO_2 decreases the monoclinic to tetragonal ZrO_2 transition temperature, from 990° C to 150 $\mp$ 50° C, and an invariant eutectoid point at approximately 15 mol % CeO_2 exists. The extent of the different single- and two-phase fields were determined with precise lattice parameter measurements on quenched samples. Evidence for the existence of a binary compound $Ce_2Zr_3O_{10}$ (ϕ-phase) was obtained by X-ray diffraction. The ϕ-phase was stable below approximately 800° C, above which it decomposes into tetragonal zirconia + fluorite ceria solid solutions. Taking into account the polymorphic tetragonal–cubic transition and the narrowness of the two-phase tetragonal zirconia + fluorite ceria field above 2000° C, the existence of a new invariant eutectoid point was assumed, in which the metastable fluorite zirconia solid solution decomposes into tetragonal zirconia + fluorite ceria solid solutions. From the results obtained, the phase diagram also incorporates a eutectic point located at approximately 2300° C and 24 mol % CeO_2.

1. Introduction

Several recent publications [1–5] have reported the importance of ceramic materials based on solid solutions of the ZrO_2–CeO_2 system, mainly those formulated in the ZrO_2-rich region. There are many potential applications of these materials, such as in magnetohydrodynamic electrodes or in fuel-cell systems due to their particular electrical behaviour or, on the other hand, as a toughened ceramic material in view of the existence of a relatively wide field of the tetragonal zirconia solid solution in the system ZrO_2–CeO_2. However, it is necessary to establish, through further study, the particular characteristics of the solid solution existing in that system in order to establish a definite phase equilibrium diagram.

1.1. Crystal chemistry

Polymorphism in pure zirconia is well known [6, 7] and a bibliographical revision is unnecessary.

Cerium is the second element of the rare earth series with an electronic configuration which can be described, taking into account that of Xenon, as (Xe) $6s^2 5d^1 4f^1$. In such a configuration, the volume of 6s and 5d orbitals are greater than that of the 4f orbital and, therefore, the three $6s^2$ and $5d^1$ electrons are the only ones participating for chemical bonds. For this reason the valence of the lanthanide elements in their configurations is habitually 3+. In the particular case of Ce^{3+}, of which the electronic configuration is (Xe) $4f^1$, the f electron is easily released, acquiring the more stable structure of the tetravalent ion Ce^{4+}. Effectively, cerium dioxide (CeO_2) is its state in nature. Its crystal structure is cubic of the fluoride type containing four formula units per unit cell. Each cation is coordinated to eight oxygen atoms and each anion is coordinated to four cerium atoms. The cerium atoms are located in the corner of a regular tetrahedron. The lattice parameter (8) of CeO_2 is approximately 0.5411 nm, and its melting point is not well known because of its volatility at high temperature. Nevertheless, Rouanet [7] reported a tentative value of 2480° C.

Under low oxygen partial pressure conditions, CeO_2 gives rise to an oxide series with complex stoichiometry in which the term more reduced is Ce_2O_3. The study of any system in which Ce_2O_3 participates becomes very intricate because it is necessary to take into account the pressure–temperature–composition diagram.

1.2. Previous studies on the Ceria–zirconia system

Due to the peculiar behaviour of CeO_2 in different environments, the system ZrO_2–CeO_2 is not well known, and the controversy in the literature data is quite significant. The first contribution to this system was that of Passerini [9], who found a complete solubility between the two oxides from 0 to 100 mol % ceria and the structure of the solid solution was cubic of the fluorite type over the whole composition range.

Several years later, Duwez and Odell [10] constructed a phase diagram from the study of eleven samples which had been heated at 2000° C and further annealed at 1375° C and 1100° C for several periods of time. They proposed the existence of a eutectic point above 2000° C at approximately 20 mol % CeO_2. However, it

was not very consistent because they did not take into account the tetragonal–cubic zirconia transition at $\sim 2370°C$ [11].

The ZrO_2-rich region was studied by thermal expansion measurements and it was found that up to 13 mol % CeO_2 additions diminished the tetragonal–monoclinic transition temperature, in which the zirconia was stabilized as a solid solution with tetragonal structure. Using X-ray diffraction (XRD), the different single- or two-phase fields were established. It was found that a single phase of fluorite type between 24 and 100 mol % CeO_2 at 2000°C existed. A two-phase field between 20 and 65 mol % CeO_2 was present at 1375°C and this was somewhat broader, between 20 and 85 mol % CeO_2, at 1100°C.

Guillon et al. [12] found three regions at low temperature. The first was monoclinic solid solution between 5 and 10 mol % CeO_2. Between 10 and 18 mol % CeO_2 a two-phase field, monoclinic + tetragonal, was present and beyond 25 mol % CeO_2, was a region in which three phases, tetragonal + cubic A + cubic B, coexisted. A content higher than 60 mol % CeO_2 showed the presence of the cubic B phase. Guillon et al. suggested that the presence of the cubic A phase was related to the reduction process $CeO_2 \rightarrow Ce_2O_3$ and, therefore, the cubic A phase was of the pyrochlore type.

Most authors agree about the non-existence of an ordered phase in ZrO_2–CeO_2, and only Palguev and Volchenkova [4] and Longo and Minichelli [13] reported the presence of an ordered phase for 15 to 20 mol % CeO_2 and 40 mol % CeO_2 concentrations, respectively.

The last major contribution to this system was made by Yoshimura and co-workers [14–16]. Their results, based on a study under hydrothermal conditions at different temperatures, widely agree with those of Duwez and Odell [10] although according to these authors the invariant point for tetragonal solid solution decomposition took place at 1000°C and 10 mol % CeO_2. The two-phase field, tetragonal + cubic solid solutions, was also somewhat broader.

The present work was mainly undertaken to clarify some discrepancies which still exist concerning the existence of a eutectoid point in the ZrO_2-rich region of the system and also to study a possible ordering phenomenon at low temperature.

2. Experimental procedure
The materials used were 99.8% zirconium dioxide and 99.9% cerium dioxide. Weighed amounts of the starting materials were thoroughly mixed and finely ground, pressed into small pellets and fired at 1200°C for several hours before further treatment. The samples were subsequently sintered at 1720°C or melted in a solar furnace and annealed at various temperatures below 1720°C.

Heat treatments were carried out in air using a furnace heated to 1720°C. Temperature was controlled within about 5°C by conventional electronic controllers. Up to 1720°C the pellets were enclosed in platinum foil and bonded with platinum wire to the junction of the 6 Rh–Pt 30 Rh thermocouple used. The samples were held at the required temperature for long enough to establish equilibrium and then air-quenched by rapid withdrawal from the furnace and allowing to cool to room temperature before being examined by XRD. The heating times were 1 min at the melting temperature, 5 h at 1720°C, 50 h at 1550°C, 264 h at 1450°C, 750 h at 1265°C, 1440 h at 1080°C, and more than 4 mon at 720°C.

To establish the reactions and the exact location of the boundaries in the region involving the monoclinic–tetragonal zirconia transformation, melted and sintered samples ranging from 0 to 20 mol % CeO_2 in steps of 1 mol % CeO_2, were studied using the following experimental methods: (a) differential thermal analysis and alumina as a reference material, (b) thermal expansion measurements between room temperature and 1200°C on sintered bars with a high-temperature dilatometer, using alumina as the reference material, and (c) microindentation technique in which the induced transformation phase could help to elucidate the existence of a eutectoid reaction in this region of the ZrO_2–CeO_2 system.

In order to establish with precision the composition and extent of the possible ordered phases in this system, sintered and melted samples in the concentration range 18 to 40 mol % CeO_2 were annealed for several months below 1000°C with grinding and pelletizing at monthly intervals.

The phases present in the quenched samples were identified by XRD, and the phase boundaries of the single- and two-phase fields were determined from precision lattice parameters, as described previously [17].

3. Results and discussion
3.1. The tetragonal–monoclinic transformation region
DTA data, see Fig. 1a, obtained during cooling (8°C min^{-1}) in compositions containing less than 15 mol % CeO_2 show that small additions of CeO_2 to zirconia strongly decreases the tetragonal–monoclinic transformation temperature from 990°C to approximately 400°C at 9 mol % CeO_2. Beyond that CeO_2 content the transformation temperature remains constant up to 13 mol % CeO_2 in which no tetragonal–monoclinic transformation peak was detected. These data, along with those obtained by X-ray diffraction, allow it to be established that a monoclinic solid solution exists between 0 and approximately 9 mol % CeO_2 and a two-phase field, monoclinic + tetragonal solid solutions, between 9 and 13 mol % CeO_2. The XRD study showed the co-existence of these two phases in that CeO_2 concentration range.

Fig. 1b shows the variation of the tetragonal–monoclinic transformation temperature as registered by thermal expansion measurements. It can be seen that the transformation temperature steadily decreases as the CeO_2 concentration increases up to 12 mol % CeO_2 and approximately 200°C. Beyond that CeO_2 concentration, no transformation was detected. This may indicate that above 12 mol % CeO_2 the amount of transformation, which depends on the amount of the present tetragonal phase, is so small
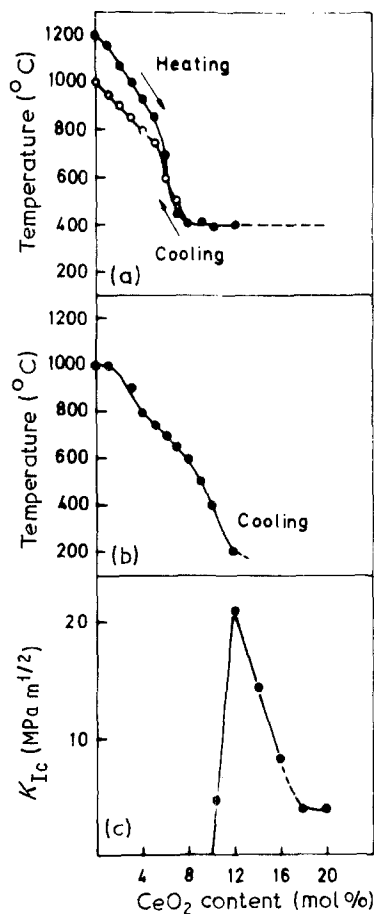
Figure 1 Influence of CeO_2 content on (a) DTA peak temperatures for tetragonal–monoclinic transformation, (b) thermal expansion tetragonal–monoclinic transformation temperatures, and (c) fracture toughness (K_{IC}).

that it was not possible to detect it with our dilatometer. Thus it can be suggested that, (a) more than 12 mol % CeO_2 is necessary to prevent tetragonal to monoclinic inversion, or (b) below approximately 200° C a eutectoid point, tetragonal zirconia to monoclinic + cubic zirconia solid solutions, may be present at that CeO_2 content. If these last assumptions were correct, then all those compositions lying in the composition range involving the eutectoidal tetragonal zirconia decomposition, could undergo an induced phase-transformation phenomenon.

In order to elucidate such an assumption, co-precipitated and sintered samples ranging from 10 to 20 mol % CeO_2 were studied by a microindentation technique with a Vickers indentor. As can be seen from Fig. 1c, a stress-induced phase-transformation toughening phenomenon was present in all the samples, and K_{IC} decreased from $\simeq 21\,MPa\,m^{1/2}$ for 12 mol % CeO_2 to $\simeq 4.5\,MPa\,m^{1/2}$ for 17 and 20 mol % CeO_2. Compositions containing less than 12 mol % CeO_2 showed a considerable amount of monoclinic zirconia solid solution and its K_{IC} values were low ($\leqslant 2\,MPa\,m^{1/2}$). All these features may indicate that, (a) the transformability of metastable tetragonal zirconia and, therefore, the toughening phenomenon was lower as the CeO_2 content increased beyond 12 mol % CeO_2, and (b) the presence of a toughening phenomenon in all the samples may be an indicative of the existence of a eutectoid point in this region of the system at approximately $150 \pm 50°\,C$ and $\simeq 15\,mol\,\%$

CeO_2. It must be mentioned that Lange [18] from fracture-mechanics data estimated a eutectoid temperature near 270° C at $\simeq 20\,mol\,\%\ CeO_2$ which is in good agreement with our experimental data. Tani *et al.* [16], using hydrothermal experiments, located such a eutectoid point at approximately 1000° C and $\simeq 10\,mol\,\%\ CeO_2$. This last result is in strong disagreement with those of the present work which could be related to the non-equilibrium achievement in their experiments. Nevertheless, there is a general coincidence concerning the existence of a eutectoid reaction for tetragonal zirconia solid solution decomposition at low temperature.

3.2. Low-temperature ordering

Fig. 2 shows the phase evolution in the concentration range 18 to 40 mol % CeO_2 for melted and/or co-precipitated sintered samples annealed at 720° C for 2 to 4 months in air. New extra lines are seen as the CeO_2 content increases, and a redistribution of the intensities took place. In such a way the lines corresponding to tetragonal zirconia solid solution slowly vanished, and at 40 mol % CeO_2 the coexistence of tetragonal zirconia solid solution with another non-identified phase was present. That situation could correspond to an incomplete ordering process.

The existence of intermediate phases was not previously mentioned for this system except by Longo and Minichelli [13] who reported a binary compound
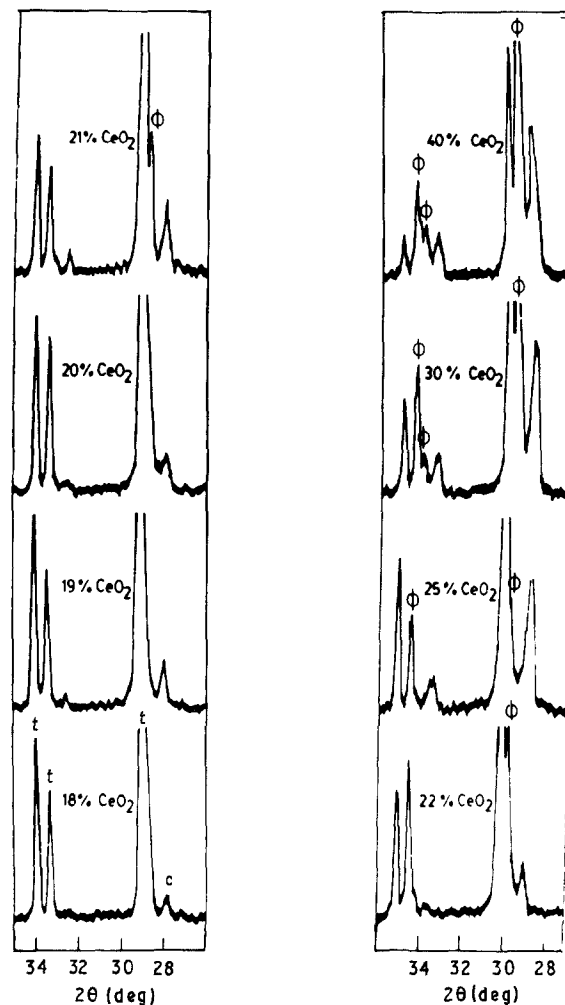

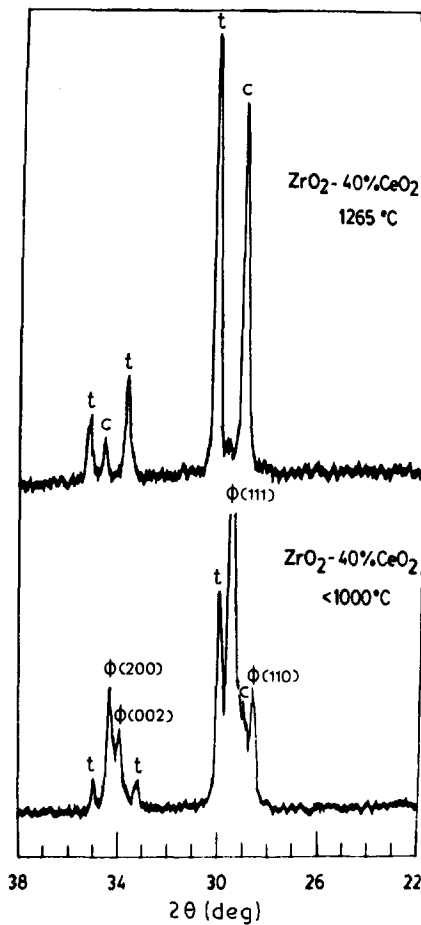*Figure 2* XRD phase evolution with CeO_2 content in high-temperature quenched samples annealed at 720° C for 4 mon.

Figure 3 XRD patterns of high-temperature two-phase tetragonal zirconia + fluorite ceria solid solutions, and low-temperature ordered ϕ-phase.

for a concentration of 40 mol % CeO_2. Such a compound (ϕ-phase) with the formula $Ce_2Zr_3O_{10}$, or $2CeO_2 \cdot 3ZrO_2$, was found to be stable below 870° C, and its structure was of the tetragonal type. The few reflections observed did not allow determination of its space group. Tani *et al.* [16] attempted to synthesize this compound by hydrothermal experiments; nevertheless it was unsuccessful after several hydrothermal treatments at low temperature.

In our case, both melted and co-precipitated sintered samples containing 40 mol % CeO_2 were quenched and annealed for long periods of time ($\geqslant 4$ mon) from 1265 to 720° C. As shown in Fig. 3, new reflections appear in addition to traces corresponding to the two-phase tetragonal zirconia + fluorite solid solutions, which have not yet been consumed in the formation reaction of the new ϕ-phase. By comparison, such new reflections do not correspond either to monoclinic zirconia solid solution or to fluorite ceria solid solution. Meriani [19] also found a probable new tetragonal phase for compositions containing less than 60 mol % CeO_2, and that phase coexisted with the known tetragonal zirconia containing less than 40 mol % CeO_2. From the experimental conditions given in the Meriani's paper it could be assumed that, (a) a high impurity level in his sample could result from the use of agate ball mills, and (b) the experimental firing temperature was probably not sufficiently high for to achieve complete reaction and, if this is so, then a nonequilibrium phase mixture could be present.

On the other hand, their X-ray diffraction patterns for angles $2\theta > 90°$ do not help to clarify the presence of the two tetragonal phases in samples with very different compositions.

Even though the phase structure reported by Longo and Minichelli [13] was not well defined, it could be assumed from our long-term annealing experiments that evidence exists for the existence of a binary compound (ϕ-phase) at 40 mol % CeO_2 in this system, which is formed by a sluggish reaction below 1000° C. Because no anionic vacancies are formed during that reaction it must be assumed that certain defects or cationic ordering phenomenon exist. Nevertheless, such an assumption at the present time is not sufficiently sustained, and the necessary additional experiments are now in progress.

3.3. The high-temperature fluorite solid solutions

All samples containing > 15 mol % CeO_2, and which had been melted in a solar furnace and rapidly cooled, were of cubic fluorite structure over the entire composition range. This apparently continuous transition from the zirconia fluorite type solid solution to ceria fluorite type solid solution was less certain when samples containing 20 to 40 mol % CeO_2 were melted and slowly solidified or annealed below 2000° C. A two-phase field (tetragonal + fluorite solid solutions) which narrowed with increasing temperature was present. As can be seen from Fig. 4, the limits of such a two-phase field were 30 mol % CeO_2 at 1720° C, 53 mol % CeO_2 at 1550° C, 65 mol % CeO_2 at 1450° C and 70 mol % CeO_2 at 1265° C. At 2000° C or above, the two-phase field was so narrow that it was very difficult to measure a clear difference in the lattice parameters for the two phase present. Duwez and Odell [10] found that such a two-phase field extended between 20 and 24 mol % CeO_2 at 2000° C, and was constituted by the tetragonal zirconia solid solution + ceria fluorite solid solution. These data are in close agreement with our experimental results, although we found 18 mol % CeO_2 as the concentration limit for
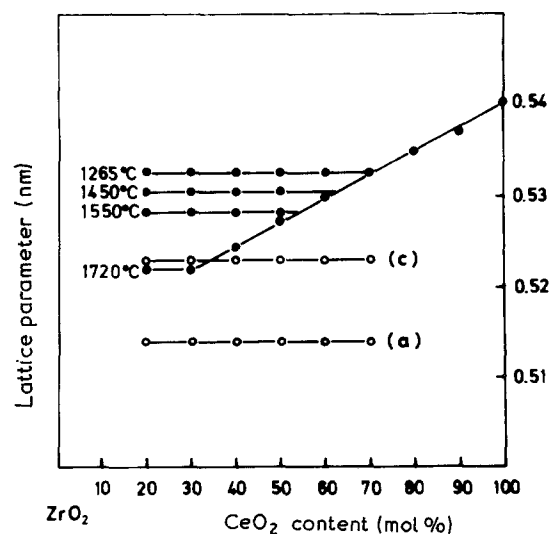

Figure 4 Variation of lattice parameters of tetragonal zirconia and fluorite ceria solid solutions with CeO_2 content. (●) Cubic phase, (○) tetragonal phase.
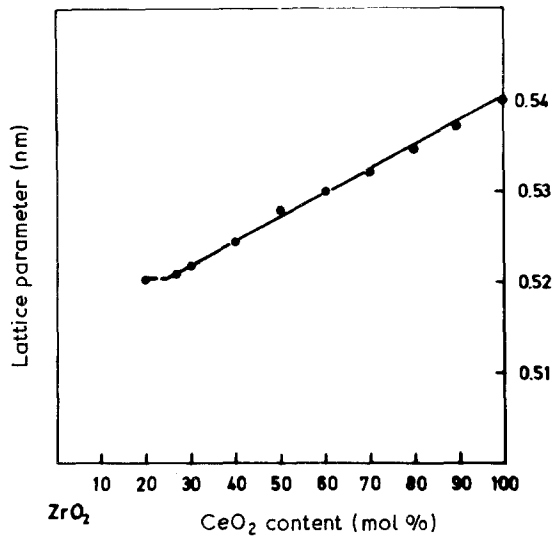
Figure 5 Variation of lattice parameters of fluorite zirconia and fluorite ceria solid solutions with CeO_2 content above 2000°C.

the tetragonal zirconia solid solution single phase. At the present time it should be considered that such a two-phase field could be constituted by the two high-temperature end members of the system, i.e. fluorite zirconia + fluorite ceria solid solutions, although it was not possible to establish a clear difference between the lattice parameters of the two phases, see Fig. 5.

Melted samples containing < 15 mol % CeO_2 showed the presence of monoclinic zirconia solid solution or a mixture of both monoclinic + tetragonal zirconia solid solutions. If the polymorphic tetragonal–cubic zirconia transition at approximately 2370°C is taken into account [11], it should be assumed that the probable fluorite zirconia solid solution, formed by dissolving CeO_2 in pure cubic zirconia at high temperature, is not retained at room temperature, despite the extremely fast quenching of the samples from the melting point, and it could be related to the particular crystal chemistry of such a fluorite solid solution.

It is well known [20] that the theoretical requirement for the fluorite structure formation in oxides is that the cationic to anionic radii ratio is equal to 0.732. The addition of 15 mol % CeO_2 to ZrO_2 increases the average cationic radius from 0.073 nm, which is the cationic radius of Zr^{4+} in pure ZrO_2, to 0.076 nm in the $(ZrO_2)_{0.85}-(CeO_2)_{0.15}$ solid solution. With such an average cationic radius the cationic to anionic radii ratio increases from 0.57 for pure ZrO_2 up to 0.60 for the fluorite solid solution. Such a cationic to anionic radii ratio is not sufficiently high to retain the fluorite structure of the $(ZrO_2)_{0.85}-(CeO_2)_{0.15}$ solid solution at room temperature, and to rapidly transform it into the low-temperature stable phases.

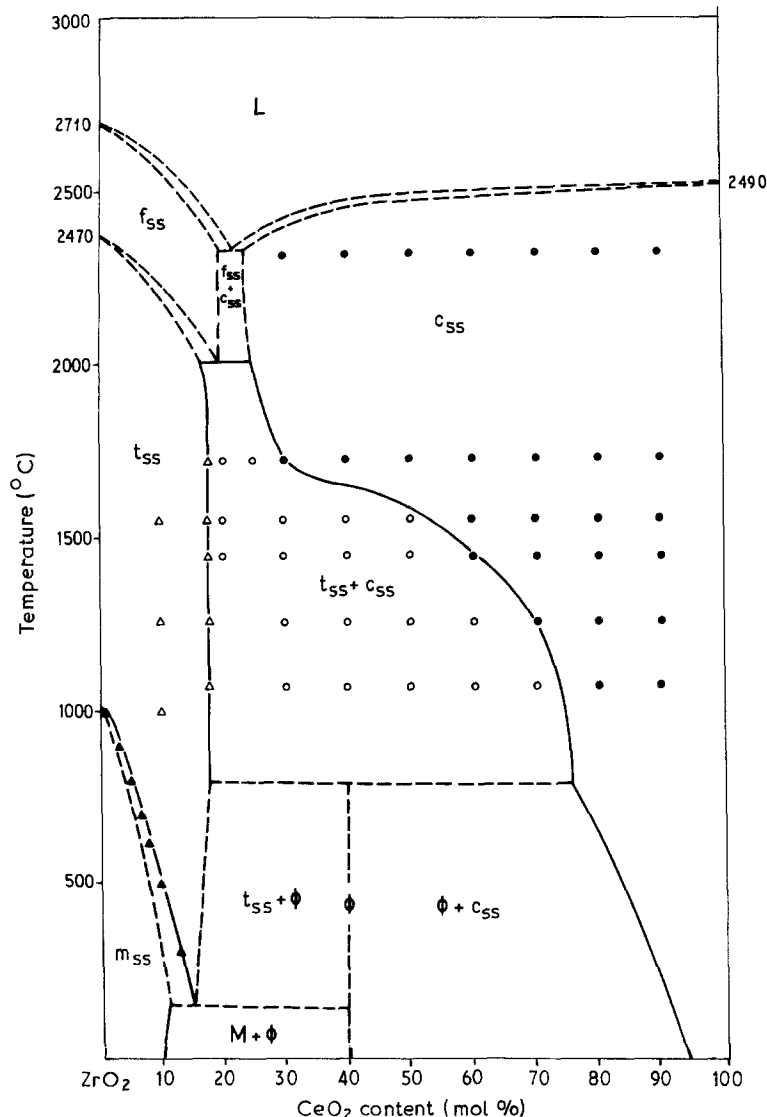Furthermore, Rouanet [7] reported that the liquidus

Figure 6 Tentative phase diagram for the ZrO_2-CeO_2 system.

temperature for this system diminished from the melting point of ZrO_2 (2710°C) and CeO_2 (2445°C) to a minimum which could be located at 2310°C and 40 mol% CeO_2, although the precision of such measurements was not very good. Therefore, taking into account Rouanet's assumption, the polymorphic tetragonal–cubic transformation of zirconia, and the narrow two-phase field at high temperature, it was assumed that the fluorite zirconia solid solution eutectoidally decomposes at approximately 2000°C into tetragonal zirconia solid solution and fluorite ceria solid solution. With this approach, a new phase diagram for the ZrO_2–CeO_2 system at high temperature was drawn, as can be seen in Fig. 6 which, on the other hand, is in agreement with the phase rules.

4. Construction of the phase diagram

Based on the results described above, a tentative phase diagram in the 0 to 100 mol% CeO_2 composition range has been constructed (see Fig. 6). Although some further experiments will be necessary to establish it definitely, the present phase diagram incorporates the following data.

1. The solubility of CeO_2 in ZrO_2 is 10 mol% at room temperature and beyond that CeO_2 concentration a mixture of monoclinic and binary compound is present. This feature indicates the probable existence of an invariant point in this zone of the system. Above the monoclinic–tetragonal transformation temperature a tetragonal ZrO_2 solid solution field extends from 0 to 18 mol% CeO_2. Nevertheless, taking into account the invariant transformation temperatures for 12, 14, 16 and 18 mol% CeO_2 from the DTA data, and the constancy of the K_{IC} value for the same compositions, see Fig. 1, the boundary of the tetragonal solid solution field is shown at approximately 15 mol% CeO_2 at 150 ± 50°C. Furthermore, the varying amounts of the coexisting phases with temperature allows it to be supposed that a eutectoid reaction takes place in this vicinity. According to our results, the lower limit tetragonal ZrO_2 solid solution was found to be 17 mol% CeO_2 at 500°C and 18 mol% above 1000°C. The phase boundary is extended to 2370°C, based on the known tetragonal to cubic polymorphic transformation for pure zirconia.

2. A single-phase zirconia solid solution of fluorite type extends from pure zirconia to approximately 20 mol% CeO_2 above 2370°C. This fluorite solid solution is strongly metastable and decomposes at ~2000°C into tetragonal zirconia and fluorite ceria solid solutions by a eutectoidal reaction. Beyond that CeO_2 concentration, a small miscibility gap between fluorite zirconia and fluorite ceria solid solutions is present. Such a miscibility gap is very narrow, between 20 and 24 mol% CeO_2, and difficult to define with precision, in view of the close similarity of the lattice parameters of the two fluorite solid solutions. Thermodynamically, this situation could be more consistent than that assuming a continuous fluorite ceria single phase over the entire composition range. This zone of the phase diagram incorporates a eutectic point at 2300°C and ~22 mol% CeO_2 supported by the two-phase field, and a eutectoid point at 2000°C and
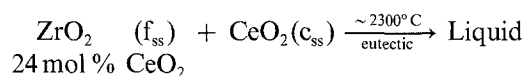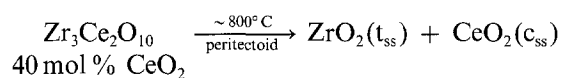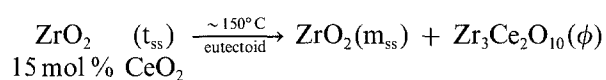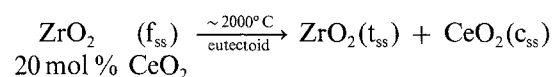
~20 mol% CeO_2. In this manner, the rules governing phase relationship for the binary system are satisfied.

3. An extensive cubic solid solution region of zirconia in cubic ceria, extends from 24 to 100 mol% CeO_2 above 2000°C, and from 75 to 100 mol% CeO_2 at 800°C. The width of this single-phase field was determined at 1080, 1265, 1450, 1550, 1720 and above 2000°C using the lattice parameter method (see Fig. 3).

4. Below 2000°C there is also a two-phase field of tetragonal zirconia and fluorite ceria solid solutions from 18 to ~25 mol% CeO_2, widening to 75 mol% CeO_2 at 800°C.

5. Below 800°C a binary compound, ϕ, with tetragonal symmetry at 40 mol% CeO_2 was found. Such a compound decomposes above that temperature into tetragonal zirconia and fluorite ceria solid solutions.

6. Based on the above data, four invariant points can be established for the ZrO_2–CeO_2 system

$$\underset{20\,\text{mol}\,\%\ CeO_2}{ZrO_2 \quad (f_{ss})} \xrightarrow[\text{eutectoid}]{\sim 2000°C} ZrO_2(t_{ss}) + CeO_2(c_{ss})$$

$$\underset{15\,\text{mol}\,\%\ CeO_2}{ZrO_2 \quad (t_{ss})} \xrightarrow[\text{eutectoid}]{\sim 150°C} ZrO_2(m_{ss}) + Zr_3Ce_2O_{10}(\phi)$$

$$\underset{40\,\text{mol}\,\%\ CeO_2}{Zr_3Ce_2O_{10}} \xrightarrow[\text{peritectoid}]{\sim 800°C} ZrO_2(t_{ss}) + CeO_2(c_{ss})$$

$$\underset{24\,\text{mol}\,\%\ CeO_2}{ZrO_2 \quad (f_{ss}) \ + \ CeO_2(c_{ss})} \xrightarrow[\text{eutectic}]{\sim 2300°C} Liquid$$

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