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The ZrO_2-rich region of the ZrO_2–MgO system

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The solubility limits of MgO in tetragonal zirconia were studied by combining the differential thermal analysis data and X-ray disappearing phase method. From these experiments a eutectoid reaction, tetragonal ZrO_2 solid solution → monoclinic ZrO_2 solid solution + MgO, at $1120 \pm 10\,^{\circ}C$ and 1.6 ± 0.2 mol% MgO was established. The solubility of MgO in tetragonal ZrO_2 diminished as the temperature increased, and at 1700 °C the solubility was less than 0.5 mol% MgO. The extent of the cubic zirconia solid solution single field was determined by using precise lattice parameter measurements and SEM observations. In this way an invariant eutectoid point, cubic ZrO_2 solid solution → tetragonal ZrO_2 solid solution + MgO, was located at $1420 \pm 10\,^{\circ}C$ and 14.8 ± 0.5 mol% MgO.

1. Introduction

Since the first major contribution of Duwez *et al.* [1] to the study of the ZrO_2–MgO system, many papers [2–4] have been devoted to clarify further aspects of the system. In general, there is close agreement that a eutectoidal point exists at which the cubic zirconia solid solution decomposes at approximately 1400 °C into tetragonal zirconia solid solution and MgO. The MgO concentration at which that reaction takes place is in permanent controversy, ranging from 28.8 mol % MgO and 1320 °C as reported by Duwez *et. al.* [1], 17.2 mol % MgO and 1390 °C by Dietzel and Tober [2] up to the more recent publication of Sim and Stubican [3] who placed the eutectoid at 13.2 ± 0.7 mol% MgO and $1406 \pm 7\,^{\circ}C$. Their results were in fair agreement to those of Grain [4]; 13 mol % MgO at 1400 °C.

Stronger discrepancies exist concerning the eutectoid decomposition of tetragonal zirconia solid solution at low temperature: whether MgO is soluble in tetragonal zirconia, as according to Sim and Stubican [3], or whether solubility is negligible, as assumed by Kauer *et al.* [5] and Grain [4]. The problem is then probably focused on the low MgO solubility in ZrO_2, therefore the data reported by Duwez *et al.* [1], and Viechnicki and Stubican [6] will not be considered.

The purpose of the present work was to reinvestigate those zones of the system in which some discrepancies still exist. To achieve this objective, differential thermal analysis (DTA) data, precision lattice parameter measurements, X-ray disappearing method, and SEM observations were used.

2. Experimental procedure

In all cases, zirconium dioxide (>99% pure) and magnesium carbonate were used as the starting materials to prepare samples of desired compositions. The samples, after a careful homogenization in a zirconia ball mill for 4 h, were calcined at 1200 °C for several hours, ground, and then isopressed at 200 MPa into pellets. After pelletizing, the samples were heat-treated at approximately 1700 °C for 2 h and rapidly air quenched. No MgO losses after this heating were detected. After quenching, the samples were isothermically heat treated at 1395, 1420, 1500, 1550, 1600 and 1650 °C. The samples were quenched by air blasting after heating. Because of the non-quenchability of tetragonal zirconia solid solution the phase disappearance method for establishing its existence domain was used. Wherever possible, the lattice parameter measurements were used to determine the extent of the single and/or two-phase fields. To do that a Philips model 1040 diffractometer and CuK_{α} radiation were used. To calculate the lattice parameters with precision ($\pm 0.000\,05$ nm), only high-angle peaks ($2\theta > 60^{\circ}$) were used, obtained by using the $\frac{1}{2}(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$ Riley and Nelson function.

At low temperature the influence of MgO addition on the monoclinic–tetragonal transformation temperature of zirconia was studied using high-temperature quenched samples by means of DTA, with Al_2O_3 as a reference material. Samples containing 0 to 8 mol % MgO, in steps of 0.5 mol % MgO, after quenching and grinding, were heated in DTA equipment at 10 °C min^{-1} to 1250 °C. DTA peak temperatures of the heating and cooling cycles were taken as the tetragonal–monoclinic zirconia transformation temperatures. DTA data were compared with those obtained using the phase disappearance method.

Ordering phenomena in the ZrO_2–MgO system were studied on a coprecipitated powder sample containing 28.6 mol % MgO. Part of the coprecipitated powder was calcined, ball milled, pressed, and sintered at about 1700 °C for 2 h and quenched. After quenching, one sample was annealed for a long time (> 1000 h) below 1000 °C. Another sample was slowly calcined up to 1200 °C, cooled to 800 °C, and maintained at that temperature for a long period of time. In this way the ordering phenomenon could be studied

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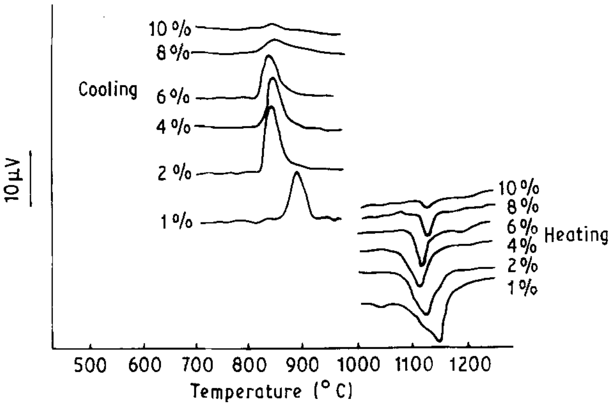

Figure 1 DTA study of the ZrO_2–MgO system as a function of MgO content (heating and cooling cycles).

by X-ray diffraction (XRD) from the high-temperature quenched sample, and from a room-temperature amorphous powder.

In order to achieve a better precision in the eutectoid temperature for the fluorite phase decomposition, specific high-temperature quenched and polished samples containing between 9 and 17 mol % MgO were heat-treated for different times at 1395 and 1420 °C and rapidly air quenched. After quenching the samples were observed by SEM.

3. Results and discussion

3.1. The low-temperature eutectoid

All the high-temperature quenched samples containing less than 0.5 mol % MgO consisted of monoclinic (m) zirconia. The 0.5 mol % MgO composition quenched from 1700 °C showed the incipient appearance of cubic ZrO_2. Below 1700 °C, the cubic phase was not detected up to MgO concentrations of 0.7 mol % at 1600 °C, 1 mol % at 1500 °C and 1.3 mol % at 1450 °C. Lower MgO concentrations showed that at those temperatures the samples were tetragonal (t) ZrO_2 solid solutions which, on cooling, invert to the monoclinic ZrO_2. As shown in Fig. 1 from DTA experiments, it can be seen that additions of MgO to zirconia had little influence on the monoclinic–tetragonal zirconia inversion temperature. Thus the inversion temperature on heating was diminished from 1190 °C (0 mol % MgO) to approximately 1120 °C (1.6 mol % MgO). For higher MgO concentrations, the inversion temperature remained constant (see Fig. 2). According to these experimental results it should be assumed that a eutectoid reaction exists for the low-temperature eutectoid of the system, of the type

$$\text{Monoclinic zirconia (ss)} + \text{MgO} \rightarrow \text{tetragonal zirconia (ss)}$$

at 1120 ± 10 °C. The same phenomenon was found on cooling in which the tetragonal-monoclinic inversion temperature diminished from 910 °C to approximately 845 °C as the MgO content increased. These results are in agreement with those reported by Sim and Stubican [3] although in our case both the temperature and the MgO content of the invariant point are somewhat higher. On the other hand, it seems clear that it is not possible to construct a correct phase equilibrium diagram for this system without admitting the existence of a eutectoid reaction involving the tetragonal–monoclinic transformation. Therefore, Kauer *et al.*'s [5] and Grain's [4] results claiming an MgO solubility in monoclinic ZrO_2 of less than 0.03 mol %, and less than 1 mol % in tetragonal ZrO_2, should be re-examined.

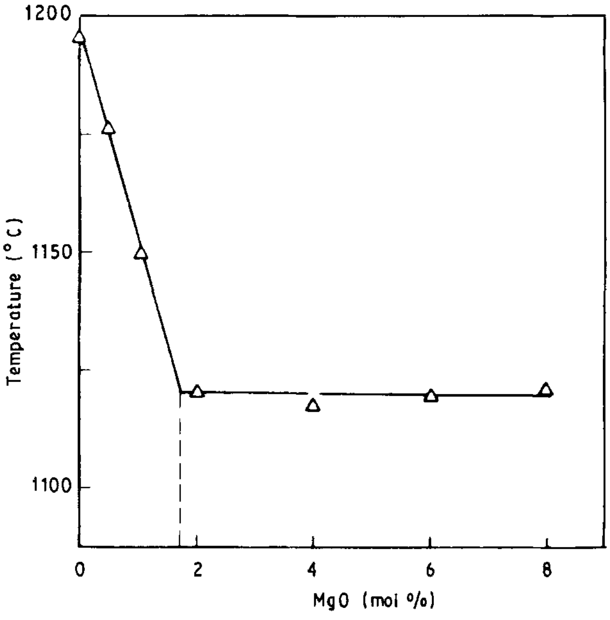

Figure 2 Effect of MgO on monoclinic to tetragonal inversion temperature of ZrO_2 on heating.

Above the eutectoid temperature the tetragonal ZrO_2 solid solution field extends from 0 to, at least, 1.6 ± 0.2 mol % MgO. Samples containing 1.5 mol % MgO were monoclinic ZrO_2 single phase after quenching from 1200 to 1300 °C. Furthermore, because a sample with 1.5 mol % MgO after annealing at 1400 °C for 24 h was monoclinic ZrO_2 single phase, this could indicate that the tetragonal ZrO_2 solid solution field was probably somewhat broader above 1120 °C. Taking this into account, the tetragonal ZrO_2 solid solution field was extended from 0 to approximately 1.7 ± 0.2 mol % MgO at 1400 °C. Above that temperature the cubic ZrO_2 phase appeared, and the solubility limit of MgO in tetragonal ZrO_2 diminished.

3.2. The cubic zirconia solid solution field

Fig. 3 shows the lattice parameters of cubic (c) zirconia solid solution as a function of composition for samples quenched from several temperatures. Above 1700 °C, compositions containing from 10 to 18 mol % MgO were single phase with the fluorite structure. The region of fluorite existence diminished as the temperature decreased and the lower limit of the fluorite solid solution was established quite accurately at 1700, 1650, 1600, 1550 and 1500 °C, by determining the lattice parameters of the cubic phase; it was found to be 10.1, 11.0, 11.8, 12.5 and 13.3 mol % MgO respectively. The solubility limits of MgO in zirconia to the

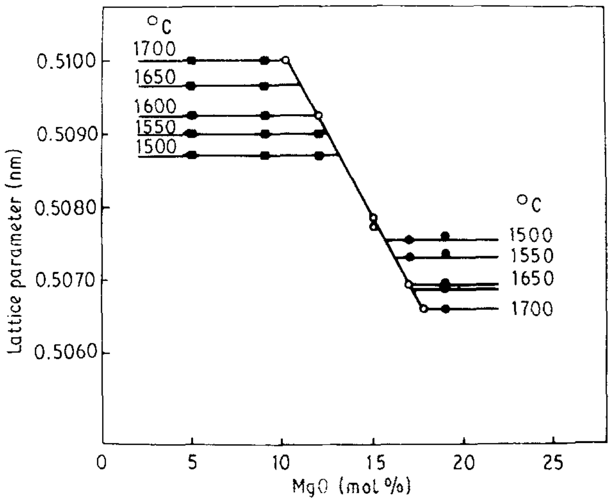

Figure 3 Variation of lattice parameters of cubic zirconia solid solution with MgO content at different temperatures.

right of the cubic solid solution domain were determined to be 17.8, 17.2, 16.8, 16.3, and 15.8 mol % MgO at the above temperatures.

Below 1500 °C the lower limit of the cubic zirconia solid solution was established by using the phase disappearance method, and it was found that compositions containing 14 and 15 mol % MgO were cubic single phase at 1450 °C, and when the temperature was lowered to 1420 °C only the composition containing 15 mol % MgO was cubic single phase. Taking these results into account, the eutectoid point for the decomposition of the cubic zirconia solid solutions was established from the intercepts of the lower and upper cubic solid solution limits. In this way the temperature and composition for the eutectoid reaction were located at 1420 ± 10 °C and 14.8 ± 0.5 mol % MgO, which are somewhat higher values than those given by Grain [4] and Sim and Stubican [3].

From this basis and in an attempt to establish the invariant eutectoid point more accurately, high-temperature specific-composition hypoeutectoid (9 mol % MgO), eutectoid (15 mol % MgO), and hypereutectoid (17 mol % MgO) were rapidly cooled to the two-phase t + c or t + MgO, annealed for 30 min at 1420 ± 10 °C and 1395 ± 10 °C respectively, air-blast quenched and observed by SEM.

Fig. 4a shows tetragonal precipitates of ~0.15 μm in their largest dimension which have been formed within the cubic grains (grain size ~40 μm) during controlled cooling at 1420 ± 10 °C from the solution treatment at 1700 °C. Therefore, this temperature can be considered to be above the eutectoid temperature. When the same sample was rapidly cooled at 1395 ± 10 °C and also annealed for 30 min, a rapid transformation of the tetragonal precipitates to the monoclinic structure on quenching took place, as shown in Fig. 4b. If the size of the tetragonal precipitates hardly changed, then it should be assumed that at such a temperature the tetragonal precipitates lose their coherence and rapidly transform on cooling to monoclinic symmetry. If this is so, then it should also be assumed that the stability requirements for tetragonal precipitate above and below the eutectoid temperature are quite different, and it could be related to a distinct tetragonal phase composition. Furthermore, it must also be taken into account that the tetragonal precipitate size is near the critical size [7] and, therefore, a partial spontaneous transformation could have been produced. However, a 9 mol % MgO sample annealed for 60 min at 1420 °C and rapidly air-quenched did not transform to the monoclinic symmetry.

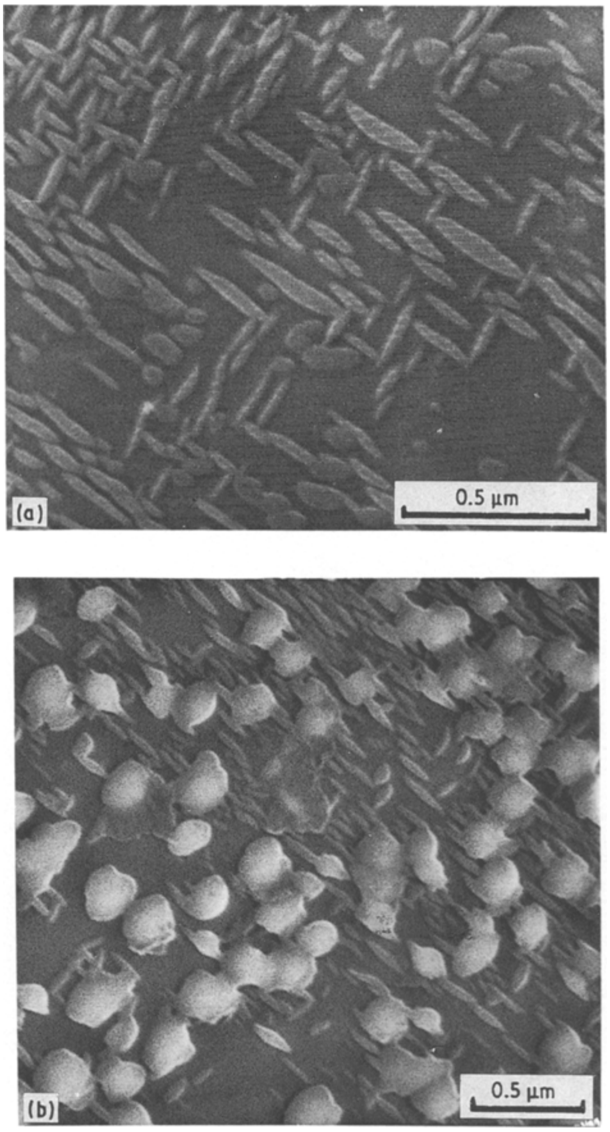

Figure 4 Microstructure of a 9 mol % MgO sample, (a) held for 30 min at 1420 °C showing coherent tetragonal particles, (b) annealed at 1395 °C for 30 min showing tetragonal particles transformed to monoclinic symmetry.

Fig. 5a shows the microstructure of a eutectoid 15 mol % MgO sample solution-annealed at 1700 °C for 5 min in which the cubic grains had an average size of 45 μm. Fig. 5b shows the microstructure of the same sample, cooled at 1420 °C, in which an incipient tetragonal precipitation took place. Some of those precipitates, with an average size of ~0.25 μm for their largest dimension, were transformed in the pore boundary or, perhaps clusters of tetragonal particles were formed. As shown in Fig. 5c, the transformation to monoclinic symmetry occurred in the sample annealed at 1395 °C. It appears that at this temperature the transformable tetragonal precipitates grew more rapidly than in the case of the 9 mol % MgO sample,

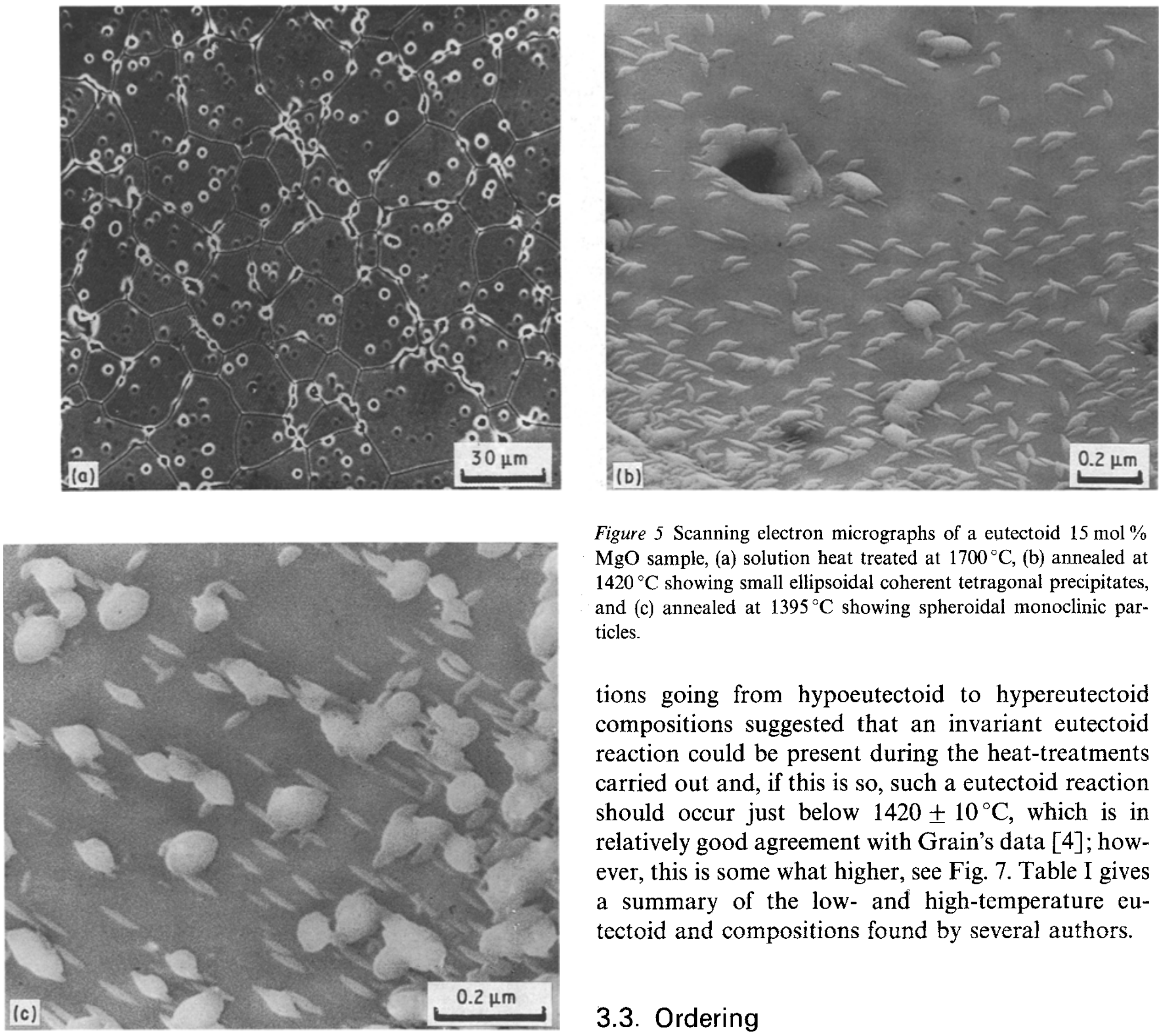

Figure 5 Scanning electron micrographs of a eutectoid 15 mol % MgO sample, (a) solution heat treated at 1700 °C, (b) annealed at 1420 °C showing small ellipsoidal coherent tetragonal precipitates, and (c) annealed at 1395 °C showing spheroidal monoclinic particles.

which could be related to the behaviour of a composition lying in or near the eutectoid composition.

Finally, the microstructure of a hypereutectoid sample containing 17 mol % MgO is shown in Fig. 6a. The average grain size of the cubic grains was ~50 µm. The microstructure shown in Fig. 6b revealed the appearance of some tetragonal precipitates, approximately 0.25 µm in size, formed during cooling to 1420 °C, and some black spots corresponding to MgO. When the sample was cooled to 1395 °C a massive tetragonal to monoclinic transformation took place, as shown in Fig. 6c.

All the similar features found between 1420 ± 10 °C and 1395 ± 10 °C in samples with MgO concentrations going from hypoeutectoid to hypereutectoid compositions suggested that an invariant eutectoid reaction could be present during the heat-treatments carried out and, if this is so, such a eutectoid reaction should occur just below 1420 ± 10 °C, which is in relatively good agreement with Grain's data [4]; however, this is some what higher, see Fig. 7. Table I gives a summary of the low- and high-temperature eutectoid and compositions found by several authors.

3.3. Ordering

Although an ordered δ-phase was reported by many authors [8–10], it was found to occur on cooling from solution heat-treated compositions containing between 8.1 [8, 9] and 14 mol % MgO [10]. Generally, the ordered phase was obtained by ageing at different temperatures a solution heat-treated sample, and it was considered that such a phase occurred as fine precipitates within the cubic zirconia grains. According to Farmer *et al.* [9], the best conditions for the ordered phase formation were a nucleation anneal at 800 °C and growth at 1100 °C. In our case, taking into account the ordered phase reported by Delamarre [11] and Yovanovitch and Delamarre [12], the study of the ordering phenomenon was carried out on a sample containing 28.6 mol % MgO prepared by coprecipitation of the hydroxides. After calcining and

TABLE I Comparison of eutectoid composition and temperatures determined by different authors

Low-temperature eutectoid		High-temperature eutectoid		Reference
Composition (mol %)	Temperature (°C)	Composition (mol %)	Temperature (°C)	
8	900 (cooling)	28.8	1320	[1]
None	None	17.2	1390	[2]
None	None	25.0	1400	[6]
None	None	13.0	1400	[4]
1	1070 (heating)	13.2 ± 0.7	1406 ± 7	[3]
1.6 ± 0.2	1120 (heating)	14.8 ± 0.5	1420 ± 10	Present work

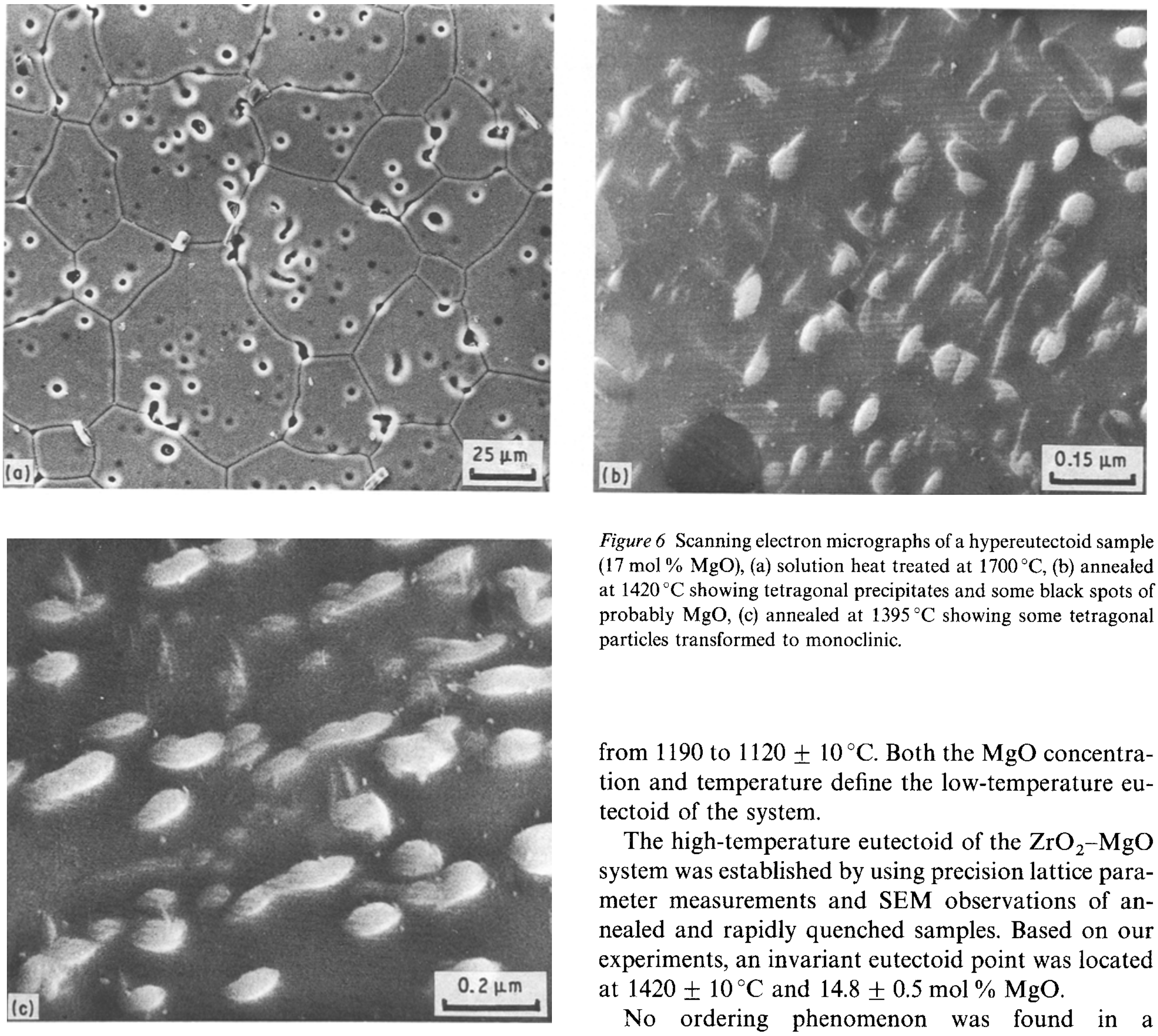

Figure 6 Scanning electron micrographs of a hypereutectoid sample (17 mol % MgO), (a) solution heat treated at 1700 °C, (b) annealed at 1420 °C showing tetragonal precipitates and some black spots of probably MgO, (c) annealed at 1395 °C showing some tetragonal particles transformed to monoclinic.

sintering, the sample was annealed for 3 to 4 mon at 800 °C. On the other hand, the amorphous hydroxide mixture was slowly heated up to 1200 °C for 72 h and then cooled at 800 °C and annealed for a long time. After annealing, the room-temperature X-ray diffraction pattern of neither sample showed evidence of any ordering. This could indicate that, (a) the ordered phase $Mg_2Zr_5O_{12}$ is not stable in the temperature range studied here, (b) the formation reaction is very sluggish, or (c) the ordered phase can only be formed by annealing from the cubic zirconia solid solution. Given that the ordered phase $Mg_2Zr_5O_{12}$ in the ZrO_2–MgO has also been more recently studied and well defined by Chaim and Brandon [13] and named the β-phase, this is also incorporated in our phase diagram, see Fig. 8.

4. Conclusion

Based on DTA experiments and XRD phase studies, the low MgO concentration part of the ZrO_2–MgO system has been reinvestigated. It was found that addition of up to 1.6 mol % MgO to ZrO_2 decreases the monoclinic to tetragonal inversion temperature from 1190 to 1120 ± 10 °C. Both the MgO concentration and temperature define the low-temperature eutectoid of the system.

The high-temperature eutectoid of the ZrO_2–MgO system was established by using precision lattice parameter measurements and SEM observations of annealed and rapidly quenched samples. Based on our experiments, an invariant eutectoid point was located at 1420 ± 10 °C and 14.8 ± 0.5 mol % MgO.

No ordering phenomenon was found in a 28.6 mol % MgO coprecipitated calcined or sintered sample annealed for a long period of time at 800 °C, and it was concluded that the known $Mg_2Zr_5O_{12}$ ordered phase could only be formed, in a metastable way, on cooling from the high-temperature cubic zirconia solid solution. Such an ordered phase (β-phase) was incorporated in our phase diagram which is quite similar to those previously established for the

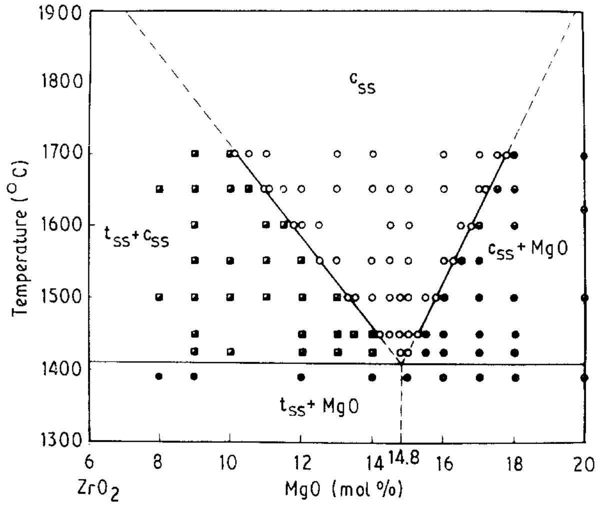

Figure 7 Zirconia-rich part of the ZrO_2–MgO system, showing the high-temperature eutectoid of cubic zirconia solid solution.

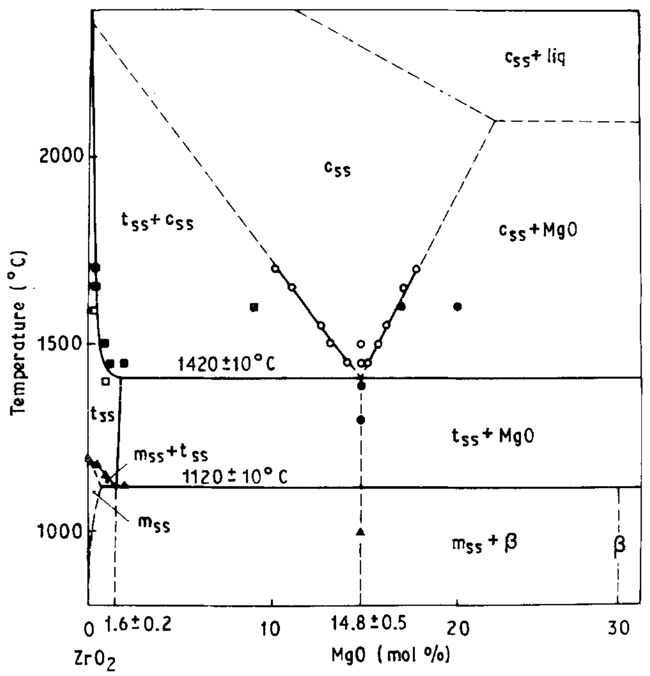

Figure 8 Tentative phase diagram of the ZrO_2–MgO system.

ZrO_2–MgO system. Nevertheless some discrepancies are still present.

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