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METASTABLE TETRAGONAL CeO$_2$-ZrO$_2$ SOLID SOLUTION

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Résumé : En refroidissant, en conditions hors équilibre, les solutions solides de structure fluorine zircone-oxyde de cé-rium, on a obtenu une nouvelle phase, riche en CeO$_2$, de structure tétragonale au lieu de la phase cubique, stable à haute température.

Abstract: When ceria-zirconia solid solutions with fluorite type of structure undergo a non-equilibrium cooling treatment, a new metastable, CeO$_2$ rich phase, of tetragonal symmetry is obtained instead of the high temperature cubic phase.

I - INTRODUCTION

Ceria - Zirconia solid solutions are known to display either a fluorite type of structure, based on the ceria crystal lattice, or another unit cell symmetry, based on the tetragonal (t) or monoclinic (m) zirconia polymorphs, depending on the temperature and relative amount of the two oxides /1-3/.

These solid solutions encounter a growing interest among the scientific and technological communities, because of their potential use as a high strength /4/ and electroconductive ceramics /5/.

Recently, a revised phase diagram of the system ZrO$_2$--CeO$_2$ below 1400°C was proposed, using hydrothermal techniques in order to accelerate reaction rates at low temperatures /6/.

With regard to the previously reported diagrams, this new investigation disclosed an eutectoid decomposition of the solid solution based on the tetragonal zirconia type of structure between 1000 and 1100°C. The two outcoming phases were the monoclinic and cubic solid solutions. In the discussion it has been pointed out that other authors has found and reported a tetragonal solid solution stable down to room temperature /1-3/ or slightly above it /4/. This was justified on the basis of the large excess energy necessary for the eutectoid reaction to take place. Where as the (t) - (m) transformation, diffusionless, needs only a much smaller amount of energy.

Sintering rate and diffusion coefficients of the Ce(+4) and Zr(+4) ions have been evaluated in the 16 mol % ceria-zirconia solid solution with tetragonal symmetry preserved throughout the whole experimental period, which lasted several hours, at elevated temperatures /7/.

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This work was undertaken to study the behaviour of the two oxides mixtures above 1400°C. Although this latter temperature was not exceeded, during the hydrothermal investigations of Tani et al., it is assumed that two phases are stable up to 1600°C: the cubic fluorite type solid solution, based on the ceria structure, and another based on the tetragonal zirconia.

The temperature of 1600°C was reached during the dry-firings performed to prepare the sintered samples. The ceria cubic type structure was found to extend from the 100 to the 40 mol % ceria concentration.

The results obtained in the present investigation indicate that a different phase could be obtained if a not-quenching cooling rate was applied to samples fired at 1450 - 1600°C and containing 60-20 mol % ceria.

II - EXPERIMENTAL METHODS

Samples were prepared by wet milling ZrO₂ - CeO₂ powders, of commercial origin, for two days in agate ball mills. The dried samples were pressed into disks which were fired in an electric furnace up to the soaking temperature, in air, at 10°C/min. The specimens were kept 24 h at 1450°C, 15 h at 1500°C, 12 h at 1550°C and 6 hours at 1600°C.

The cooling step, which was named "non-equilibrium", followed the natural cooling rate of the furnace: on average about 1°C/sec between the soaking temperatures and 900°C. At that moment the samples were quenched down to room temperature to be examined by X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM).

In order to reveal the microstructure, after diamond polishing, a thermal etching of about 1 hour at 1600°C was applied to the samples.

III - RESULTS AND DISCUSSION

The results are summarized in Fig. 1 (a-b-c-d) which reports the d(hkl) values of the cubic fluorite structure, labelled (422), (511 - 333).

The compositions ranged from the pure CeO₂ to the 30 mol % CeO₂ - 70 mol% ZrO₂ mixture. The recorded "d" values were observed to decrease with decreasing CeO₂ concentration. However, they became constant for CeO₂ content lower than 60 mol % value at 1450°C.

The constant values of the (hkl) spacings at 1450°C indicated that a two-phase region was encountered, as expected on the basis of the phase equilibrium diagram. The other equilibrium phase turned out to be the solution, based on the tetragonal zirconia (T²), containing about 18 - 20 mol % ceria. The (224) and (422-242) peaks appeared at 1.065 and at 1.055 Å, respectively, with minor differences at the other temperatures.
Fig. 1 - "d" spacings of (422) and (511-333) diffraction peaks as a function of cerium oxide concentration recorded for samples fired at 1600, 1550, 1500 and 1450 °C and cooled under a "not-quenching" rate. CeO₂ is reported as mole fractions (x).

What was unexpected was the splitting of the cubic fluorite diffraction peaks into two or three other lines, as reported in Fig. 1. The new lines became constant for CeO₂ content lower than 55 mol % at 1500°C, 45 mol% at 1550°C, 40 mol% at 1600°C. An uncertainty of ± 1 mol% is estimated.

At concentrations lower than 60 mol% ceria, the (hkl) lines of samples fired above 1450°C, became more and more splitted. The splitting increased with increasing firing temperature.

The reported "d" spacings are somewhat larger than the above mentioned TZO° values, in agreement with the higher ceria concentration. They indicate that the phase with the fluorite type structure has undergone a deformation, outcoming into a new, metastable phase which has been considered of tetragonal symmetry and named TΩ°.

Since a "not-quenching" cooling rate of about 1°C/sec was applied, the cubic fluorite structure could not be frozen in the sample at room temperature. On the other hand, this latter could not develop a true phase separation, able to deliver both the tetragonal(TΩ°) and the ceria-rich phase.
It is worth mentioning that a short treatment below 1450°C of the TZ' samples, restored the expected tetragonal TZ° and the CF cubic phases.

In order to reveal this new phase, SEM images were obtained on samples containing 60 and 40 mol % ceria, which exhibited the fluorite and the TZ' phase structure respectively. Their microstructures are reported in Fig. 2 and 3. The fine grooves are due to the thermal etching and are made evident by the tilting of the samples under the microscope.

The surface of the "fluorite" structure sample is homogeneous, as it is reported in Fig. 2, whereas a quite different surface texture was revealed by the TZ' sample, which is presented also in Fig. 4 under larger magnification.

The TZ' sample exhibits a microstructure made of "twinned" colonies /8/ that develop most probably according or a diffusionless type of transformation. This phenomenon is "cooling-rate" dependent and related to the cubic-tetragonal transformation which, on the other hand, is dependent on the overall composition of the sample.

It could be a matter of investigation to test for its further transformability according to stress-assisted mechanisms to the monoclinic symmetry. Taking into account a somewhat similar phenomenon, investigated within the zirconia-yttria system by Lantery et al /8/, further investigation will be undertaken to define the physical and mechanical properties of this new, metastable, TZ' phase.

A few words of comment about the unusual microstructure of the grain boundary presented in Fig. 2 which recalls a "zip" interface."
A wave-shaped morphology of the grain boundary has been observed in various metal alloy systems and was explained either in terms of diffusion induced grain boundary migration or discontinuous precipitation of two phases starting within the interface of a two component polycrystalline, single phase, solid.

In ceramic systems neither phenomenon has been, so far, unequivocally observed /9/.

In this case the striking resemblance of the "zip" interface of Fig. 2 with the expected shape of a grain boundary migration due to discontinuous precipitation, cannot be overlooked. The thermal history of these samples does not fit in the sequence proposed by other authors to let grain boundary phenomena occur; however, it looks like in this case a rather thick interface material became the locus of further growth of the main phase through nucleation and symmetrical expansion from adjacent grain surfaces. Further investigation is in progress to clarify it.

**Fig. 4 - SEM detail of the TZ' phase surface**

**IV - REFERENCES**

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**V - ACKNOWLEDGMENT**

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