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Study of the Chemical State and Local Structure of Zirconium in Polycrystalline α -Alumina by X-Ray Absorption Spectroscopy and STEM Analysis of Thin Foils

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Abstract: The chemical state and local structure around zirconium in doped α -polycrystalline alumina (300 wt. ppm % ZrO_2) was studied by Extended X-Ray Absorption Fine Structure (EXAFS) measurements at zirconium K-edge energy and by STEM analysis on thin foils. It appeared that most of the zirconium is located in grain boundaries as nanocrystalline tetragonal zirconia particles. This allotropic tetragonal zirconia form is stabilised at room temperature because of the important contribution of the surface free energy.

1. Material and Experiment

The experimental XAS measurements were performed on two zirconium-doped α -polycrystalline alumina; the samples were obtained by hot pressing at at 1400°C for Zr1-sample whose grain size $\overline{G1} \approx 1 \mu\text{m}$, (Fig. 1a), and at 1550°C for Zr2-sample with a mean grain size $\overline{G2} \approx 3.5 \mu\text{m}$ was obtained by hot pressing at 1550°C (Fig. 1b). A tetragonal single crystal of yttrium-doped zirconia was used as standard. The experimental measurements were performed at room temperature at LURE-DCI (Orsay), using the EXAFS II spectrometer. In the fluorescence mode the EXAFS signal was obtained by measuring $I_0(E)$ and $I_f(E)$ with an ionization chamber and a 7-elements germanium crystals. This XAS study was completed by EDXS analysis on thin foil (STEM).

2. Microstructure results and chemical analysis on thin foils

The EDXS analysis of zirconium-doped α -alumina shows that the zirconium is detected only in grain boundaries and triple junctions of the Zr2-sample. The true concentrations of zirconia located in grain boundaries (as C_{gbR}) and in the bulk C_{bR} were calculated from the apparent grain boundary concentration C_{gbap} , measurements and from the zirconium mass conservation equation [1] which can be written as: $(1 - f) C_{bR} + f C_{gbR} = 300 \text{ ppm ZrO}_2$, where f represents the volumic

fraction of grain boundaries in the material, and δ is about 0.5 nm with the grain boundary width of $\frac{C_{gbR}}{C_{bR}} \approx 2 \cdot 10^3$.

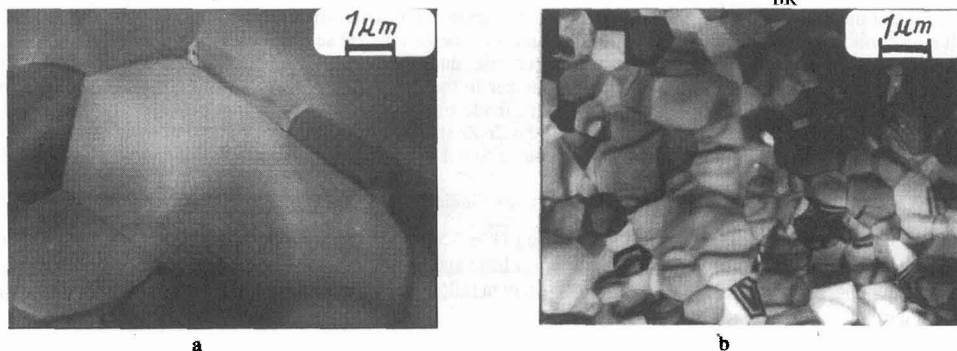


Fig 1: Microstructure of the two zirconium doped-alumina samples, a- Zr1 ($\overline{G1} \approx 1 \mu\text{m}$), b- Zr2 ($\overline{G2} \approx 3.5 \mu\text{m}$)

3. X.A.S results

Figs. 2a-b shows for the zirconium doped-alumina and for the standard sample the Fourier transform spectrum, $F(r)$. The true distances R_j and the number of neighbours N_j , reported in Table 1, in each shell have been accurately determined by fitting the experimental and calculated functions ($\chi(k)_{\text{exp}}$ and $\chi(k)_{\text{ca}}$) taking into account the phase shift. It must be noted that the uncertainty on the determination of the neighbouring atom number is about 20%.

2 and Table-1, the coordination number of the Zr-O and Zr-Zr shells for Zr2 sample is more important than for Zr1 sample. The shell distributions of O, Zr atoms around the Zr-absorber atom in this sample are similar to those of the metastable tetragonal zirconia-ZrO₂ (Table-1).

- in case of Zr1-sample, Fig. 2b, the F(r) curve shows three peaks which correspond to the neighbouring j shells. The first peak is the most important corresponding to the oxygen shell, which includes the first neighbour of the zirconium absorber atoms. The other peaks with a small amplitude correspond to Zr-Zr and Zr-O shells; there is a drastic reduction of the coordination number of the Zr-Zr shell, so that the second peak is made of about less than one atom of zirconium.

Table 1: Fit of the distances R_j(Å) and neighbour numbers N_j, determined for the doped alumina and tetragonal zirconia(Fig. 2).

Sample-Zr1 ($\bar{G}1 \approx 1 \mu\text{m}$)			Sample-Zr2 ($\bar{G}2 \approx 3.5 \mu\text{m}$)			Tetragonal zirconia single crystal in transmission mode		
Shells	R _j (Å)	N _j ± 0.5	Shells	R _j (Å)	N _j ± 0.5	Shells	R _j (Å)	N _j ± 0.5
	± 0.05			± 0.05			± 0.05	
<Zr - O>1	2.04	3.2	<Zr - O>1	2.06	3.5	<Zr - O>1	2.09	4
<Zr - O>2	2.16	3.4	<Zr - O>2	2.19	3.5	<Zr - O>2	2.23	4
<Zr - Zr>	3.42	0.5	<Zr - Zr>	3.66	5.4	<Zr - Zr>	3.62	12
<Zr - O>	3.80	4	<Zr - O>	4	5	<Zr - O>	4.1	8

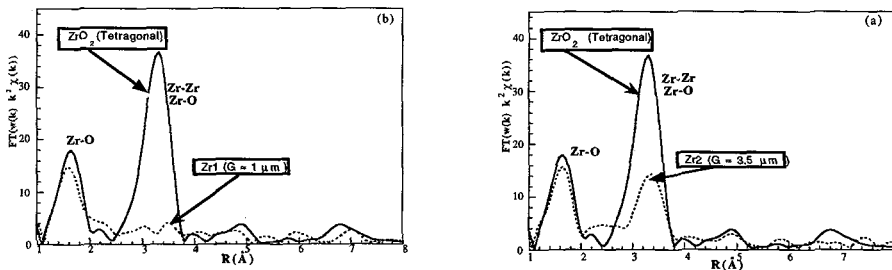


Fig 2: Fourier-transform magnitude spectrum (uncorrected for the phase shift) of standard (tetragonal-ZrO₂) and polycrystalline doped- α -alumina samples: Zr2 (a) and Zr1 (b).

4. Discussion and conclusion

In the case of the Zr2-sample, the EDXS analysis shows that most of the zirconium atoms are located in grain boundaries, where they form nanometric crystalline particles which present a local environment of tetragonal zirconia. This metastable allotropic form of zirconia is stabilized in doped alumina probably because of the important contribution of free surface energy. This interpretation is proposed by several authors [2-5] to explain the tetragonal zirconia structure observed for nanometric zirconia particles.

In the case of the Zr1-sample, the breakdown of the long-range order in the structure observed with less than one atom by Zr-Zr shell may come from two facts: the first one is that most of the Zr-ions are segregated along grain boundaries, and the second is that all the Zr-ions forms oxide nanoparticles; in that case, due to the great grain boundary density, the size of the particles is smaller than in Zr2-sample and the coordination number in the Zr-Zr shell decreases when the ratio of surface over volume increase. These results agree the K-edge XAS work made on nanocrystalline zirconia powders by Yurent [2]: the author observed a decrease of the coordination number of the Zr-Zr shell when the average particle size decreases to ≈ 5 nm, and an increase of this number when the particle size increases to ≈ 11 nm, so that the local environment becomes similar to that in tetragonal zirconia.

These XAS study at the Zr- K-edge, of Zr-doped alumina indicates that Zr-ions have a strong tendency to localize in alumina grain boundaries with an enrichment ratio $\approx 10^3$ when $\bar{G} \approx 3.5 \mu\text{m}$. In the grain boundaries, Zr-ions form nanometric oxide clusters whose structure depends on their size. For a little size of such clusters, the contribution of the free surface energy becomes preponderant and the tetragonal phase of zirconia (allotropic form stable at high temperature), becomes stable at room temperature.

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