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STUDY BY EXAFS OF ZIRCONIUM ENVIRONMENT IN Al_2O_3 - ZrO_2 MATERIAL PREPARED FROM METAL - ALKOXIDES

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Résumé - La structure d'échantillons de composition 70 Al_2O_3-30 ZrO_2 préparés à partir d'alcoxydes métalliques dépend des conditions d'hydrolyse. L'étude de l'environnement du zirconium a été effectuée par EXAFS sur des matériaux élaborés de façon différente ; les expériences ont été conduites d'une part sur des échantillons bruts d'élaboration, d'autre part sur des échantillons correspondant à différentes étapes de cristallisation de l'oxyde ZrO_2.

Abstract - The structure of 70 Al_2O_3-30 ZrO_2 material prepared from metal alkoxides depends on hydrolysis conditions. EXAFS measurements were performed in order to determine the zirconium environment in the as prepared material and in annealed samples corresponding to various stages of crystallization of ZrO_2.

I - INTRODUCTION

The fracture toughness of Al_2O_3 can be increased by the incorporation of fine ZrO_2 particles /1/. The preparation of such materials by hydrolysis of metal alkoxides allows the mixing of the constituents at the atomic level. Appropriate thermal treatments make possible the control of the growth of zirconia grains. The first steps of the growth process can be studied by examining by EXAFS the evolution of zirconium environment.

II - EXPERIMENTAL

The structure of the aluminas prepared from aluminium alkoxide depends on hydrolysis conditions /2,3/. Cold water hydrolysis (T < 80°C) results in the formation of amorphous monohydrate AlO(OH) ; on the other hand, by hot water hydrolysis (T > 80°C) the monohydrate is obtained as crystalline boehmite. This compound can be peptized by addition of acid and the resulting sol can be gelled. Pyrolysis up to 500°C of the dried products leads to a pulverulent amorphous alumina in the case of the material prepared via the cold water hydrolysis route and to a bulky microcrystalline material in the case of the gel.
Both fabrication methods were applied to the hydrolysis of mixed aluminium and zirconium alkoxides in view of the preparation of Al_2O_3-ZrO_2 material containing 30 % of zirconia.
Pyrolized samples originating from both fabrication methods were submitted to subsequent one hour annealing at temperatures ranging from 600 to 1200°C, the resulting structure being checked by X-ray diffraction. The patterns of the pyrolized samples (500°C) were similar to those of pure alumina prepared by the two above mentioned methods : in the case of the gel route material (samples A) they exhibited broad reflections, the positions of which were close to those of δ-alumina, whereas for the samples prepared by cold water hydrolysis (samples B) no line was observed.
The onset of zirconia crystallization is detected by the appearence in the diffraction patterns of broad lines corresponding to the (101) and (112) lines of its tetragonal form. These lines are observed upon annealing above 800°C for samples A and above

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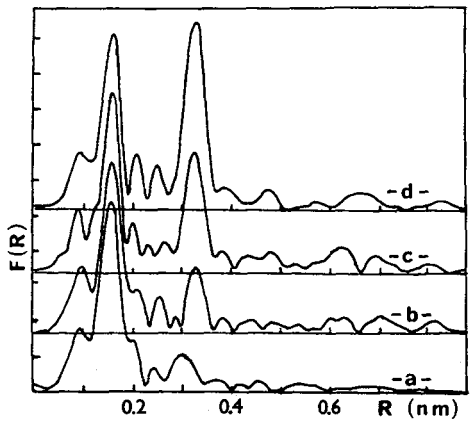

Fig. 1 - Radial distribution functions of samples prepared by hot water hydrolysis, pyrolyzed up to 500°C (a), annealed for one hour at 700°C (b), 800°C (c) and 950°C (d).

900°C for samples B. These lines remain broad at 1100°C where the (11$\bar{1}$) and (111) lines of monoclinic zirconia are also observed.
EXAFS spectra at the zirconium K edge were recorded using the synchrotron radiation of the DCI ring at LURE (Orsay). Experimental amplitude and phase of the Zr-O pair were extracted from the analysis of the spectrum of barium zirconate $BaZrO_3$, and those of the Zr-Zr pair from the spectrum of metallic zirconium. In $BaZrO_3$ which has a regular cubic perovskite structure, the zirconium atom is surrounded by six oxygen atoms at 0.2095 nm whereas in metallic zirconium the first shell of atoms is composed of two groups of six zirconium atoms at 0.317 and 0.323 nm respectively.
Radial distribution functions (RDF) relative to samples A are presented in figure 1. One can clearly note on the RDF of the pyrolized material (500°C) the absence of order beyond the oxygen shell (Fig. 1.a).
Fourier filtering of the peaks appearing on the RDF's makes possible the determination of the interatomic distances and of the nature of the backscattering atoms by fitting the experimental signal to a calculated model (Fig. 2). The parameters determined by this method are reported in Table I.

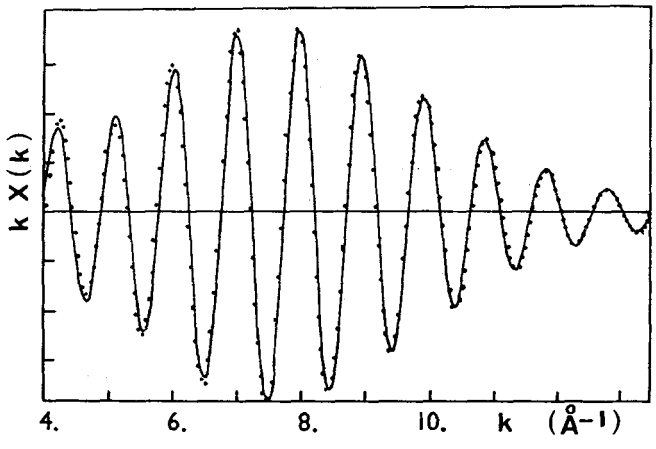

Fig. 2 - Fourier filtering (dotted curve) and theoretical fit (solid curve) of the zirconium shell of material A annealed at 800°C.

Samples		N (O)	d (Zr-O) nm	N (Zr)	d (Zr-Zr) nm
A	dried gel (100°C)	7.0	0.213	-	-
	pyrolyzed (500°C)	5.8	0.211	-	-
	700°C (1 h)	5.0	0.210	2.8	0.368
	750°C (1 h)	4.0	0.209	3.7	0.366
	800°C (1 h)	3.9	0.209	4.8	0.366
	900°C (1 h)	3.8	0.207	5.9	0.365
	950°C (1 h)	3.8	0.207	6.3	0.365
	1000°C (1 h)	3.9	0.207	7.2	0.366
B	pyrolyzed (500°C)	6.0	0.211	-	-
	755°C (1 h)	5.9	0.211	-	-
	833°C (1 h)	3.8	0.209	-	-
	950°C (1 h)	4.1	0.208	6.6	0.365
	1080°C (1 h)	3.7	0.207	7.1	0.366

Table I - Number of neighbours of a zirconium atom and interatomic distances determined in 70 Al_2O_3-30 ZrO_2 samples (A = hot water hydrolysis ; B = cold water hydrolysis).

III - INTERPRETATION AND DISCUSSION

From Table I it can be seen that zirconium atoms are in octahedral sites in pyrolyzed (500°C) material, as evidenced by the good fit between the number of oxygen neighbours (six) and the mean Zr-O distance (0.211 nm) which have been measured.
The oxygen shell relative to the dried gel (100°C) contains an additional atom : at this stage of the preparation the material still contains water ; the mean Zr-O distance (0.213 nm) is close to that found in monoclinic zirconia (0.216 nm) in which zirconium has also a sevenfold coordination /4/.
The oxygen shell is progressively modified upon heating and the number of atoms as well as the Zr-O distance decrease : at the highest temperature these values are the same as those found for the first oxygen shell in tetragonal zirconia /5/. It is interesting to note that the evolution of the number of atoms in the zirconium shell is correlated with the modification of the oxygen shell ; this number gives an indication of increasing amounts of crystalline zirconia in the material. One sees also that the mean Zr-Zr distance observed for all samples is close to that found in tetragonal zirconia.
A close examination of Table I also indicates that the evolution of the zirconium environment upon heating takes place in a larger temperature range for material A than for material B. Material A is microcrystalline and the broad lines observed on X-ray diffraction patterns are the same as those of pure alumina ; one can think then that this material exhibits a phase separation into microcrystalline alumina and amorphous zirconia. On the other hand, material B is completely amorphous and might be considered as homogeneous. The above mentioned phase separation of material A would then explain the onset of the crystallization of ZrO_2 at a lower temperature, since in this case the atomic displacements related to crystallization are smaller than in the case of an homogeneous material in which diffusion of zirconium atoms must take place.
The structural parameters determined on the samples annealed at 1000 and 1080°C agree only partially with those relative to tetragonal zirconia. In this ZrO_2 modification the zirconium atom is surrounded by 8 oxygens (4 at 0.207 nm and 4 at 0.246 nm) and by 12 zirconium atoms (4 at 0.364 nm and 8 at 0.368 nm). In the samples under study, only the first 4 oxygens were observed, the number of zirconium atoms being 7. It is

worth noting that there is no second oxygen shell peak in the RDF of tetragonal zirconia presented by Dumas et al /6/ and Catlow et al /7/ : this absence might be due to an interference with the first shell. The Zr-O distance which we have measured (0.207 nm) is however smaller than that found by these authors (0.216 nm and 0.211 nm respectively), who, besides, did not determine the number of zirconium neighbours. The rather small value of the number of Zr neighbours which we have observed might be due to the model compound that we have used in which the zirconium first shell is made of two closely placed groups of atoms. It is however also possible that the zirconium shell is not totally filled, a phenomenon which might result from the fact that zirconia is not totally crystallized or else that solid solution of alumina in zirconia takes place. The good quality of the fit obtained for the zirconium shell would rather lead us to discard this last hypothesis in spite of the fact that the substitution of aluminium atoms to zirconium atoms might have a stabilizing effect on the tetragonal modification. The X-ray diffraction patterns of samples annealed at temperatures higher than 1000 and 1080°C indicate that zirconia is partially in the monoclinic form ; this is why the EXAFS spectra of these samples cannot help us in choosing among the above mentioned hypotheses.

IV - CONCLUSION

Our study shows that EXAFS spectroscopy is an interesting tool for the study of the evolution of the structure of a material upon crystallization. One must nevertheless recognize that in the particular case of the system under study the analysis is complicated by the phase transformation of zirconia and also by the possibility of phase separation. Low angle X-ray scattering and TEM should improve the understanding of the evolution of the structure of our materials.

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