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## Local structure of pre-alloyed Al/Y/SiCN nanopowders studied by XAS at the Al K-edge using fluorescence yield detection

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As the processing of Si<sub>3</sub>N<sub>4</sub> dense ceramics by sintering is promoted by using additives such as Al<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub>, the possibility to introduce these compounds in the starting SiCN powder is explored by adding appropriate precursors like Al and Y isopropoxydes. The fluorescence yield detection is used at the Al K-edge to describe the local structure around this element in these as-prepared pre-alloyed new phases as well as its evolution during annealing under nitrogen. Results are compared with that of reference amorphous and crystalline phases. With annealing Al local structure shows an evolution towards that of crystalline AlN, while the presence of other different disordered sites like AlO<sub>4</sub> and AlN<sub>3</sub>O cannot be excluded.

**Keywords:** pre-alloyed nanometric powders, Al K edge, fluorescence yield detection

### 1. Introduction

Laser pyrolysis of gaseous or liquid precursors is a promising technique to synthesize nanoscale SiCN powders (Cauchetier, 1991 and 1994). Such powders have been sintered to obtain dense materials with improved mechanical properties or with high temperature plasticity. In most cases, the sintering of SiCN powders is carried out in presence of sintering aids such as Y<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> which form a YSiAlON liquid phase during thermal treatment. In order to obtain a uniform dispersion of the sintering aid elements in the SiCN matrix, the metallic elements (Y, Al) are incorporated into the silicon carbonitride matrix from chemical processing routes using organometallic precursors (Iawamoto, 1998).

The laser synthesis process is an alternative route to prepare SiAl(Y)CNO nanopowders and it has already been described (Mayne, 1998). Aerosol droplets of an organometallic precursor mixture obtained by dissolution of solid aluminum and yttrium isopropoxides ( $[(CH_3)_2CHO]_3Al$  and  $[(CH_3)_2CHO]_3Y$ ) into liquid hexamethyldisilazane ( $[(CH_3)_3Si]_2NH$ , HMDS) are carried out into the laser beam through a gas flow of argon or argon + ammonia. As-prepared powders are amorphous and contain "in situ" the sintering aid elements (Y and Al) dispersed in an homogeneous matrix. They are then annealed at 1400 and 1600°C under N<sub>2</sub> atmosphere.

The aim of the present study is to determine the atomic environment of Al both in as-formed and annealed powders, in order to get informations on a possible formation of the (Y)SiAlON liquid phase during sintering, necessary for producing dense ceramics and leading to an intergranular phase

after cooling. We compare it with the structure found in crystalline Al(O)N, with YSiAlO(N) amorphous phases, and with a sintered sample where the intergranular phase is present.

### 2. Experimental

Al K edge (1559 eV) XANES and EXAFS spectra were recorded at room temperature at beamline SA32 of the 800MeV positron storage ring SuperACO at LURE, by collecting at RT the total electron yield for the references compounds and the fluorescence yield for the dilute samples. We used a mono-element Ge detector (Eurisy-Mesures), with an energy resolution of 140eV. The monochromator was a scanning two-crystal set-up with quartz (10 $\bar{1}0$ ) crystals. As a consequence, the EXAFS data were recorded only up to 1830eV. For the XANES part of the absorption spectra a constant background has been subtracted in the pre-edge region, and except for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, the spectra were normalized to the atomic absorption above the threshold. All Al XANES spectra were calibrated with an Al metallic foil at the inflexion point (1559eV). The extraction of the EXAFS oscillations was performed in a classical way: modellization of the atomic background by a 5th order polynomial, and normalization using the Heitler approximation. Fourier transforms of the k<sup>2</sup> weighted oscillations were calculated over the same energy range for all the compounds and the references. The chemical compositions of the samples as well as those of the amorphous references are presented in table 1.

**Table 1.**

Elemental analysis (at%) of the amorphous reference phases, and of the pre-alloyed samples (AP = as-prepared, AN = annealed at 1600°C).

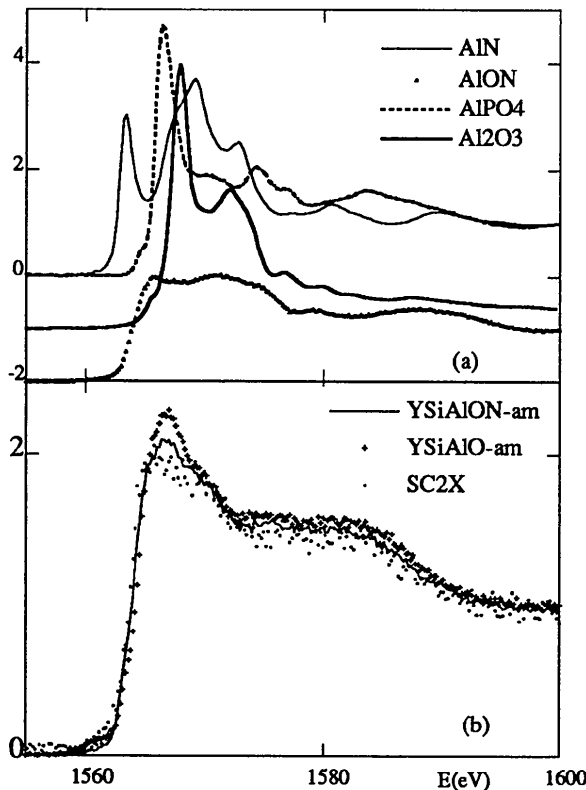
|           | Si   | C  | N    | O    | Al   | Y    |
|-----------|------|----|------|------|------|------|
| HSA117-AP | 33.5 | 26 | 33.5 | 6.2  | .6   | .2   |
| HSA117-AN | 44   | 24 | 29.9 | 1.6  | .4   | .1   |
| YSiAlON   | 12.3 | -  | 7.5  | 54.7 | 18.5 | 12.3 |
| YSiAlO    | 6.8  | -  | -    | 63.6 | 17.7 | 11.9 |

### 3. Results

As we are dealing with amorphous compounds where XANES multiple scattering calculations in the "muffin-tin approximation" are difficult to perform, our approach was to measure aluminum oxides and nitrides as well as amorphous YSiAlO(N), pure or embedded in the sintered material. From direct comparison with that in model compounds, the Al environment of unknown compounds can be "fingerprinted" in term of differences in XANES (Idefonse, 1994 and 1998 and references therein). Experimental Al spectra of references compounds are plotted on figure 1-a. The differences observed between berlinite (AlPO<sub>4</sub>, with Al<sup>IV</sup>-O) and corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, with Al<sup>VI</sup>-O) have been fully investigated and simulated previously (Cabaret 1996). In AlN, Al is coordinated to four nitrogen atoms. Its XANES spectrum presents a large resonance located 3eV below the characteristic white line of Al<sup>IV</sup>-O in AlPO<sub>4</sub>. The oxynitride phase AlON is usually described as a solid solution in the Al<sub>2</sub>O<sub>3</sub>-AlN structure, isostructural to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, where it is expected that Al have a range of local tetrahedral and octahedral environments

including mixed anion (i.e. nitrogen and oxygen) coordinations (Dupree 1988). The XANES spectrum of this last system is characteristic of a mixture of sites, but we have to point out that the threshold position is more than 3eV below that one found in corundum, in line with the presence of Al four-fold coordinated, and that the spectrum presents some structures characteristic of an ordered structure also evidenced by X-ray diffraction.

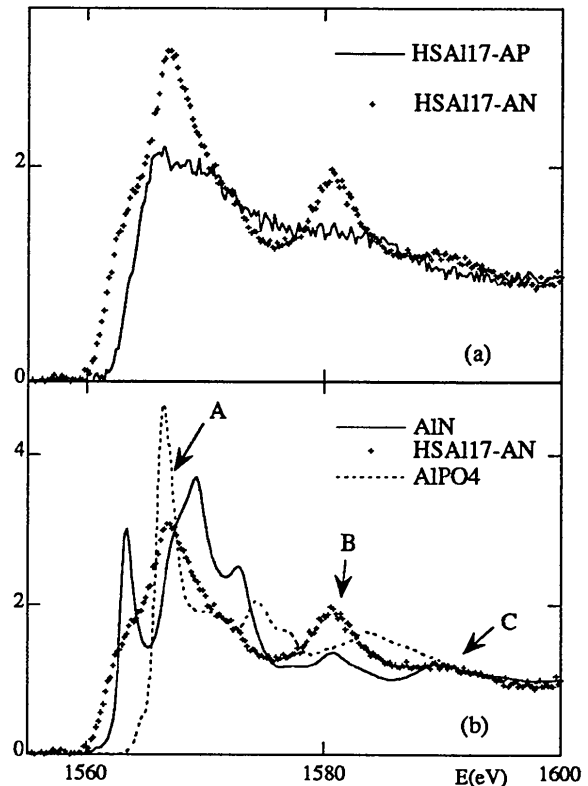
On figure 1-b XANES spectra of the amorphous phases YSiAlO(N) are compared to SC2X. SC2X refers to the Al spectrum of the sintered compound where Al is supposed to be both in the intergranular phase YSiAlON and in the  $\beta$ -SiAlON obtained after annealing treatment. Except a very small shift towards high energy values of the threshold of the sample without nitrogen (YSiAlO), all the spectra are identical, reflecting a structural similarity between these different phases. From previous observations (Ildefonse 1998), the edges shapes (a small white line located at 1566.6eV followed by a wide resonance), lead us to the assumption that the dominant site for Al atoms in these phases is four-fold with some amount of penta and hexa coordinated aluminum. But it is difficult to conclude about the existence of mixed environment. Actually the edge position in four-fold coordinated Al compounds depends on the nature of the second neighbour of Al atoms (Ildefonse 1998).



**Figure 1**  
a- Al K edge XANES spectra for references where Al is four-fold coordinated ( $\text{AlPO}_4$  and  $\text{AlN}$ ), six-fold coordinated ( $\text{Al}_2\text{O}_3$ ), and in a mixture of sites ( $\text{AlON}$ )  
b- Al K edge XANES spectra for amorphous references

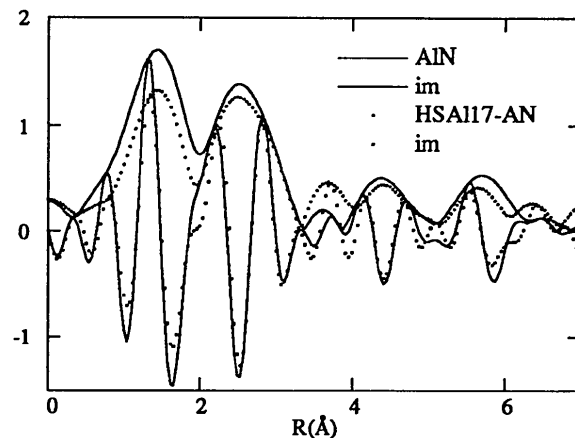
As well, qualitative conclusions can be drawn about the coordination number and the nature of the neighbours of aluminum in prealloyed Al/Y/SiCN powders. The XANES of the as-prepared powder presents a double structure (figure 2). The threshold position is located at the same position than for the

amorphous references phases, i.e. between  $\text{AlPO}_4$  and  $\text{AlN}$ . We cannot then conclude to a single aluminum environment.



**Figure 2**  
Al K edge XANES spectra for prealloyed Al/Y/SiCN nanopowders :  
(a) evolution with annealing  
(b) comparison with references

After annealing at 1600°C, the Al K edge is much more structured (figure 2) : a resonance A appears at the same position than that of Al four-fold coordinated to O atoms indicating the presence of  $\text{AlO}_4$  sites, the edge position is shifted to lower energy when compared to the as-prepared spectrum indicating the presence of  $\text{AlN}_4$  sites, and finally the resonances B and C also observed for the  $\text{AlN}$  crystalline structure prove the formation of  $\text{AlN}$  crystallites.



**Figure 3**  
Comparison of the FT ( $k^2$  weighted oscillations over 2-7  $\text{\AA}^{-1}$  EXAFS  $k$  range) for  $\text{AlN}$  and HSA117 annealed at 1600°C.

An EXAFS analysis of these compounds has been undertaken at the Al K edge. The pseudo radial distribution function of the AlN phase presents 4 peaks. The first one comes from the first shell of 4 N atoms at  $R=1.88\text{\AA}$ . The three following peaks are a mixture of the different contributions of the next shells. AlON's FT exhibits 3 main peaks. The amorphous phases give both one significant peak at a smaller distance than the first peak of AlN, but a similar amplitude. The FT of the sample HSA1-17 annealed at  $1600^{\circ}\text{C}$  (figure 3) confirms the hypothesis drawn from the observation of the XANES: Al atoms are mainly present in a crystalline AlN type structure.

#### 4. Discussion

The unknown compounds have also been investigated by NMR (Espinose de la Caillerie, 1998) which reveals that Al can be found in 3 different sites in the as-prepared compound: tetra, penta and octa coordinated to oxygen atoms, while after annealing, 4 sites are still present: Al octa, Al tetra with AlO<sub>4</sub>, AlN<sub>3</sub>O, and AlN<sub>4</sub>. Because of the limited k range which does not allow a sufficient distinction between the AlN and the other phases, the EXAFS spectrum of the annealed sample seems dominated by the contribution of Al atoms in the

ordered phase AlN. But the shape of the XANES induces to claim the presence of other different disordered sites, consistent with NMR results.

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