X-ray absorption spectroscopy study of the effects of Si addition on the properties of hard nitride coatings

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Nanostructured ceramic coatings are being intensively investigated because they open a wide field of new materials with improved mechanical and tribological properties. The final behaviour of such coatings depends on their composition and microstructure. Si addition in nitride compounds has shown to improve significantly their hardness. For instance, in the Ti-Si-N coating system, coating hardness ranging from 40 to 80 GPa has been reported in the composition range of 2-20 at.% Si. To explain this improvement, a detailed investigation on composition, structure, and atomic short-range order surrounding Ti and Si atoms is needed. X-ray absortion spectroscopy (XAS) is a very appropriate tool for this kind of studies since it is very sensitive to the local environment around a specific atomic element, giving information on the composition, structure, and short range symmetry

In this work, several TiSiN and AlCrSiN coating compounds with different Si content have been studied by XAS in order to investigate the effects of Si addition on the composition, structure and phase development of these coatings. AlCrSiN thin films have been obtained by cathodic arc evaporation, whereas TiSiN coatings have been grown by magnetron sputtering. Changes in the structure and chemistry of the Si-containing coatings as compared with those without Si can influence the mechanical properties, grain size and morphology, defect content, film porosity or phase content of this films. To get some insight on these changes, X-ray absorption spectra have been measured at the Si, Cr, and Ti K-edges in fluorescence yield mode. XAS measurements were carried out at the BESSY KMC1 line, using a standard chamber equiped with a solid state fluorescence detector.

Figure 1(a) shows XAS spectra at the Ti K-edge of TiSiN samples with different Si content. In this case, all spectra keep a similar lineshape to that of titanium nitride, independently of Si content. The pre-edge region, which is associated to transitions from Ti-1s states to Ti-3d states hybridized with Si-2p states, does not show significant changes with Si-addition. This suggests a weak interaction between Ti and Si. Fig. 1(b) shows XAS spectra at the Si K-edge of the same TiSiN samples, as well as a SiO_2 single crystal, as a reference sample for comparison. In all cases the spectral lineshape is typical of amorphous Si_3N_4 [1], with a main peak at 1845 eV, and a weaker structure at 1861 eV. The main peak of SiO_2 is located at 1847, so we can not exclude the presence of SiO_2 for very low Si content. Except for this small oxygen presence no significant changes in the lineshape is observed with silicon content. Hence, both Ti-K and Si-K XAS results suggest that the interaction between Ti and Si is weak and that amorphous Si_3N_4 aggregates are formed inside a TiN matrix.

Fig. 2(a) shows XAS spectra at the Cr K-edge of AlCrSiN with different Si content. Similarly to the TiSiN samples, the pre-edge region, at 5960 eV, is associated with transitions from Cr-1s states to Cr-3d states hybridized with 2p empty states of the ligand atoms. This hybridization allows 1s-3d transitions, which are otherwise dipole forbidden. The spectrum for the AlCrN sample shows only a tiny pre-edge peak at this position, very similar to that reported in previous works for Cr_2O_3 [2-4], suggesting that Cr in this compound is in the form of Cr^{3+}. The intensity of this peak slightly increases for sample with a Si content of 5%. For samples with even higher Si content, the intensity increase is still more predominant. The increase of this feature could be explained in the case of oxide compounds in terms of a valence increase from +3 to +4, +5 or +6, or in terms of a reduction of crystalline domains down to the nanoscale [12]. The presence of high valence Cr would involve a shift to higher energies of the main absorption edge, which is not observed in our samples, so the presence of

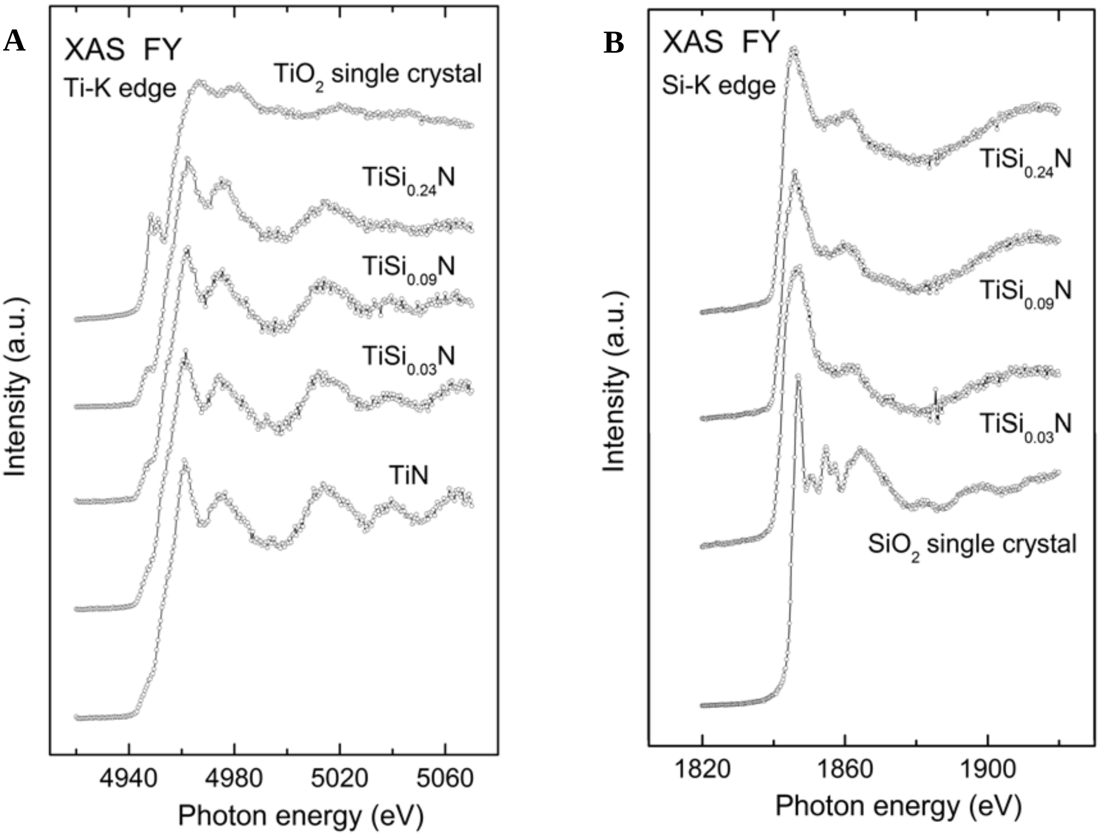

Figure 1: X-ray absorption spectra at the Ti-K edge (a), and at the Si-K edge (b) of several TiSiN samples with different Si content.

this kind of Cr compounds can be excluded. The only explanation for the observed intensity increase in samples must take into account a chemical interaction between Si and Cr, which would give rise to Cr-3d Si-2p hybridization. Consequently, the peak at 5960 eV can be assigned to transitions from Cr-1s states to Cr-3d states hybridized with Si-2p empty states. Additionally to this pre-edge intensity increase, the addition of Si produces a smoothening of the overall spectral lineshape, which is consistent with the amorphization of the microstructure, as observed by XRD [1]. Fig 2 (b) shows XAS spectra at the Si K-edge of AlCrSiN samples with different Si content, as well as a pure SiO_2 single crystal as a reference sample. We can exclude that Si incorporates to the lattice as an atomic solid solution, because the spectra do not resemble that of pure Si [1]. The spectrum for sample with 5 at. % Si (bottom), has a peak at 1847 eV, which is aligned with the main peak of the spectrum for SiO_2 single crystal. This indicates that at low Si content there is some oxygen contamination in the form of SiO_2. Additionally, the edge positions at 1842 eV, as well as the peak observed at 1850 eV, are evidences for the presence of crystalline Si-N compounds in this sample. The feature assigned to SiO_2 disappears for samples with higher Si content. The spectra for samples with 9 and 14 at. % of Si are very similar, with a main peak at 1844 eV. This energy position corresponds to the main peak observed for Si_3N_4, suggesting that Si is in the form of some nitride compound. However, the more complex spectral lineshape as compared to that of Si_3N_4, could be an evidence of the formation of some ternary Si-N-X compound.

In summary, the present comparative work reports evidence of both reduced and increased silicon solubility for samples prepared at a high deposition temperature. In the TiSiN system, we have observed features corresponding to a-Si3N4 in all of the deposited samples and there was not any significant change with silicon content. Both Ti-K and Si-K spectra suggests that there was a weak interaction between Ti and Si. On the other hand, for

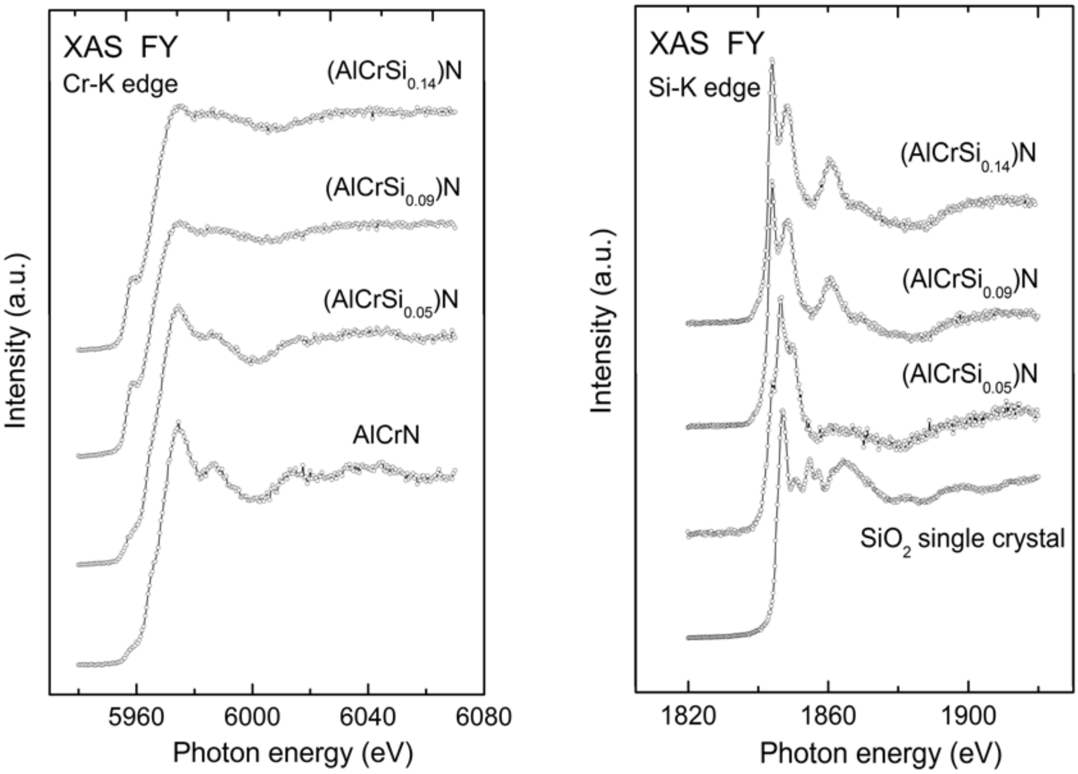

Figure 2 X-ray absorption spectra at the Cr-K edge (a), and at the Si-K edge (b) of several CrAlSiN samples with different Si content.

the quaternary AlCrSiN system, there was strong evidence of the formation of Si-N-X complex compounds, where X could account for Cr, Al, or both. Samples also showed the amorphization of the Cr-based crystal structure with increasing Si content.

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