(Y-Ti-O)-Cr core-shell structure and Ti oxidation states in ferritic ODS steels designed for sodium fast reactors by electron energy-loss spectroscopy

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Recent years have witnessed increasing research efforts concerning materials for the next-generation nuclear fission reactors, which will need to work at higher temperature and radiation levels. For these applications, oxide dispersion strengthened (ODS) steels are the most promising candidates.

We present a study by scanning transmission electron microscopy coupled with electron energy-loss spectroscopy (STEM-EELS) of an ODS steel with the nominal composition Fe-14Cr-1W-0.3TiH_2-0.3Y_2O_3 (wt.%). After denoising the spectrum-images via principal component analysis (PCA), the obtained elemental maps (Y-M_3, Ti-$L_{2,3}$, O-K, Cr-$L_{2,3}$ and Fe-$L_{2,3}$) show a (Y-Ti-O)-Cr core-shell structure (fig 1c) and Cr segregation at the matrix grain boundary. Alternately Ti-rich and Y-rich atomic planes with the interreticular distance of d~2.87Å can be seen in Y-M_3 and Ti-$L_{2,3}$ elemental maps (fig 1b), which correspond to the (222) family planes of cubic pyrochlore $Y_2Ti_2O_7$ (d_{222}=2.91Å). EELS quantification performed on these nanoparticles gives the result O/Ti~3.25, close to the value of 3.5 for stoichiometric $Y_2Ti_2O_7$. The smaller O/Ti ratio and the non homogeneity of the interreticular distance d_{222} through the particle (figs 1) was interpreted due to defects in the particles structure, already observed in other ODS sample by S. Yamashita et al. [1]. The Ti local environment was studied using the Ti-$L_{2,3}$ and O-K edges fine structure (ELNES) and novel multivariate statistical analysis such as independent component analysis (ICA) [2] was used to separate the individual spectral responses of the EELS signal. The Ti oxidation state is shown to vary from the center of the nanoparticles to their periphery from Ti^{4+} in distorted O_h symmetry to a valency often lower than 3+. After ICA, the obtained independent components allow us to generate bonding maps (fig 2): the particle center presents Ti^{4+}, O and Y signatures where its periphery presents a reduced-Ti signature without crystal field splitting (CFS), depleted in Y and O.

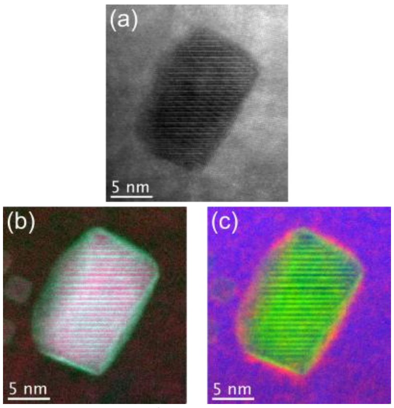

Fig 1: (a) HAADF image of a nanoparticle and its RGB elemental maps : (b) red=Y-M_3, green=Ti-$L_{2,3}$, blue=O-K and (c) red=Cr-$L_{2,3}$, green=Ti-$L_{2,3}$, blue=Fe-$L_{2,3}$.

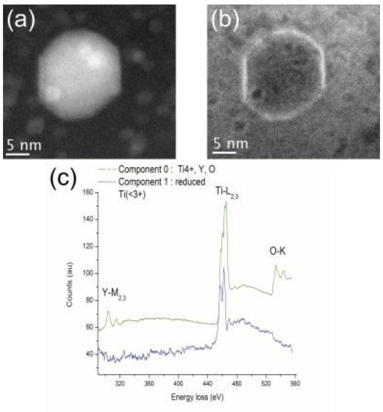

Fig 2: Results of the ICA with Y-$M_{2,3}$, Ti-$L_{2,3}$ and O-K edges - maps of 2 ICA components: (a) (Y, Ti^{4+}, O) and (b) reduced Ti (<3+). (c) Spectra of these 2 ICA components

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Références

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