ESRF	**Experiment title:** **Environmental friendly pre-treatments for aluminium alloys: a XAFS study in Ce-doped silane films**	**Experiment number**: MA-238
Beamline: BM-29	**Date of experiment**: from: 20 Sept. 2006 to: 22 Sept. 2006	**Date of report**: June 2007
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Report:

EXAFS experiments on *bis-silane films doped with cerium* were done to investigate the structure around cerium ions, in this environment-friendly pre-treatment for aluminum alloys.

Several spectra were also collected from prototypes selected to model cerium speciations (valence plus coordination environment): synthetic CeO_2 (a cubic oxide with fluorite-type crystal structure and regular cubic coordination of Ce^{4+}), monazite (La-rich natural $CePO_4$ with a less regular environment of Ce^{3+} ions), octa-hydrated Ce^{4+} sulphate $Ce(SO_4)_2 .8H_2O$, and hexa-hydrated Ce^{3+} nitrate $Ce(NO_3)_3 .6H_2O$.

The experiments were performed in transmission mode at the Ce K-edge (40443 eV) using a Si (311) monochromater, with the collaboration of the beamline scientist Dr. Sakura Pascarelli.

Data from synthetic ceria (CeO_2) fitted in *R*-space by taking into account only single scattering contributions due to the first four shells of atomic neighbours and using the FEFF code is presented in the Figure 1a. The inverse fast Fourier transforms of experimental and theoretical EXAFS (Figure1b) display a good agreement.

Further work is being carried out on data XAFS collected from Ce hydrated salts (sulphate and nitrate) and from monazite, an important natural Ce-carrier. Results of these experiment have already been presented [1].

[1] - M. O. Figueiredo, M. J. Carmezim, A. M. Cabral, M. G. S. Ferreira "A *XAFS* STUDY AT CERIUM *K*-EDGE IN COMPOUNDS FIGURING OUT VARIOUS *Ce* -SPECIATIONS AND COORDINATION ENVIRONMENTS", IV International Materials Symposium, MATERIAIS 2007 – A Materials Science Forum, April, 1-4, Faculdade de Engenharia da Universidade do Porto, Oporto/Portugal.

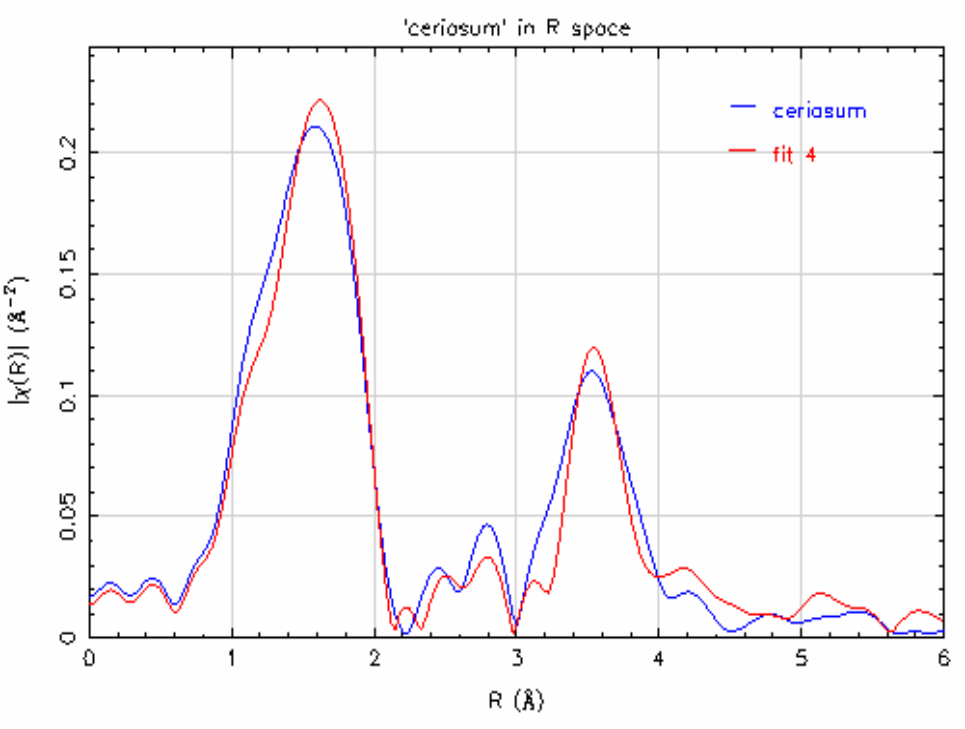

Figure 1(a)

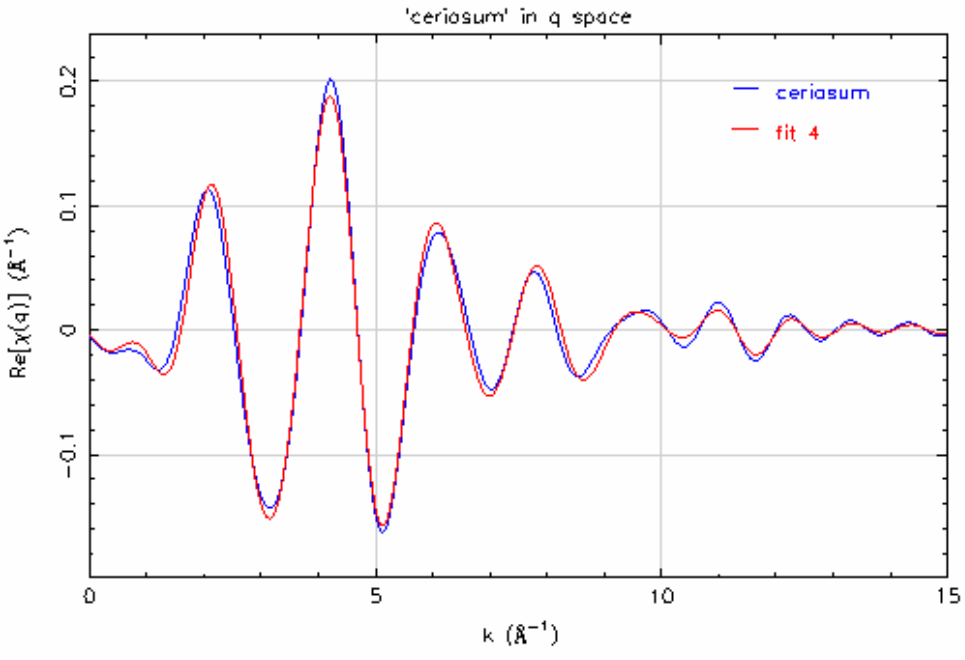

Figure 1(b)

A *XAFS* STUDY AT CERIUM *K*-EDGE IN COMPOUNDS FIGURING OUT VARIOUS *Ce*-SPECIATIONS AND COORDINATION ENVIRONMENTS

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Abstract

The application fields of cerium compounds have enlarged in the last years. Cerium oxide is emerging as a hydrocarbon catalyst in self cleaning ovens and is now extensively used as a promoter in three-way catalysts (TWCs) for automotive emission control [1]. This oxide allows for selective absorption of ultraviolet light in glass and, owing to its nonstoichiometric behaviour once the oxidation state of Ce can be 3+ or 4+, CeO_2 also proved to be a good promoter for oxygen storage [2]. The cerium oxide is also used in diesel fuels for a more complete combustion to abate soot formation [3]. Moreover the magneto-optical signals of Ce-compounds have an outstanding figure of merit amongst other classes of magnetic materials [4].

Synchrotron radiation is nowadays a powerful means of studying X-ray absorption fine-structure spectroscopy (XAFS), either close to the absorption edge (XANES) or up to a hundred electron volts above the edge (EXAFS). The latter has revealed itself as an outstanding technique for structural characterization of catalytic systems [5].

As a preparatory approach to the characterization of corrosion behavior of bis-silane Ce-treated films over aluminum alloys [6], a XAFS study at the Ce *K*-edge in compounds with well-known crystal structure and chemical composition was undertaken at the ESRF[#] using the instrumental set-up of beamline BM29. The following prototypes were selected to model cerium speciations (valence plus coordination environment): synthetic CeO_2 (a cubic oxide with fluorite-type crystal structure and regular cubic coordination of Ce^{4+}), monazite (La-rich natural $CePO_4$ with a less regular environment of Ce^{3+} ions),), octa-hydrated Ce^{4+} sulphate $Ce(SO_4)_2$ **.**$8H_2O$, and the hexa-hydrated Ce^{3+} nitrate $Ce(NO_3)_3$ **.**$6H_2O$. A discussion is presented on the local structure parameters extracted from collected EXAFS spectra, along with prospective comments concerning the role of cerium in the pre-treatment of bis-silane films deposited onto alloy substrates.

References

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