ESRF	**Experiment title:** In situ characterization of the corrosion of cermets by molten salts	**Experiment number**: MA581
Beamline: ID11	**Date of experiment**: from: 02/12/2009 to: 02/15/2009	**Date of report**: 02/27/2009
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Report:

These experimentations aimed to study the **corrosion of a cermet** (composite materials of ceramics and metals) **by molten salts** (fluoride bath) using **X-Ray diffraction in transmission mode**. They were performed on the ***ID11 Materials Science* beamline**. It has consisted in observing ***in situ*** the evolution of the crystallized phases at the interface between the cermet and the molten salt at high temperature during several hours. The main difficulty of investigating such a physicochemical process is to prevent the experimental apparatus from the high reactivity of molten fluorides and its vapours. To achieve this study, **an experimental set-up has been specifically designed for the ID11 beamline** (*Figure 1*).

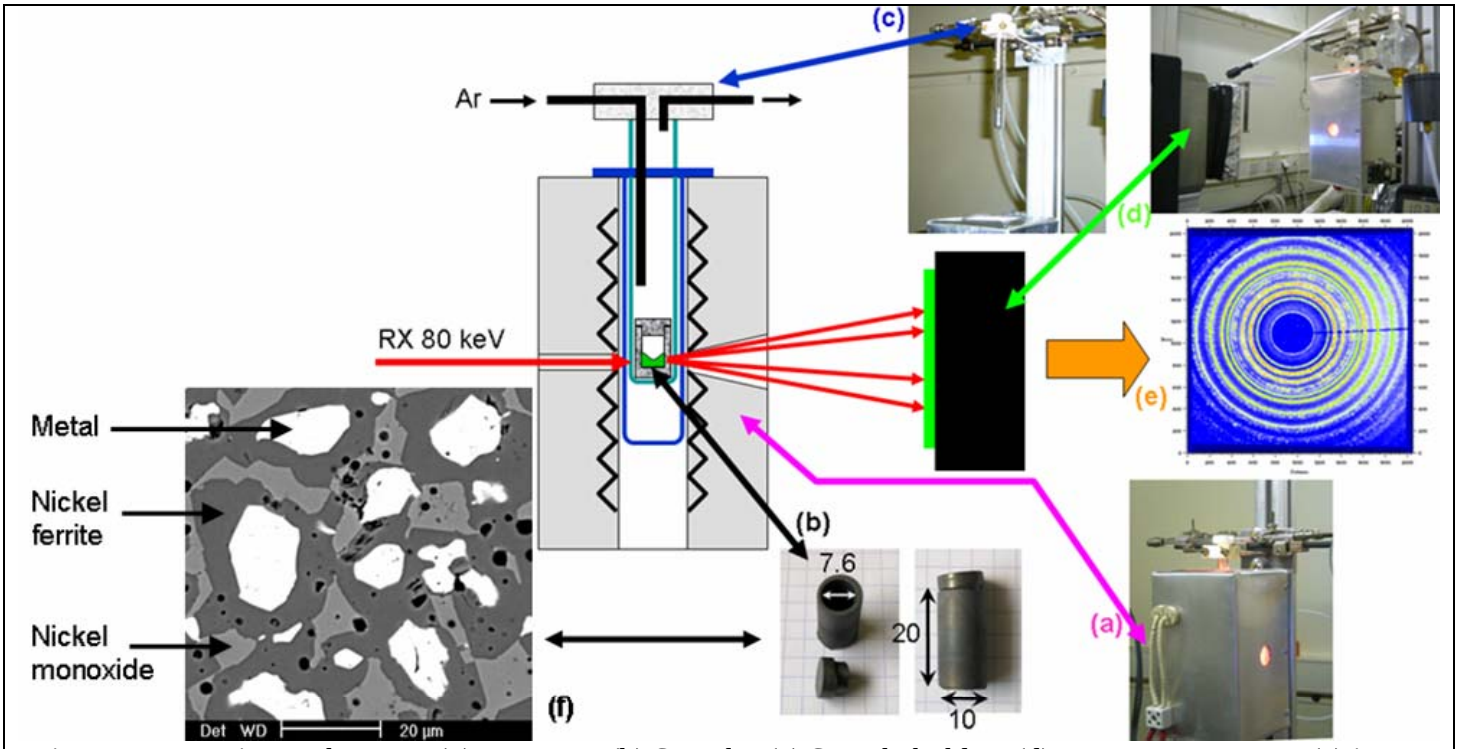

Figure 1: Experimental set-up. (a) Furnace; (b) Sample; (c) Sample holder; (d) 2D X-Ray camera; (e) image of the diffraction rings (FIT2D sofware); (f) SEM micrography of the cermet (BSE mode)..

A vertical compact furnace (a) was used with two accesses along the horizontal axis of the synchrotron beam. The sample (b) is a cermet crucible containing a compacted powder of salt (preliminary prepared in a glove box). It was placed in a glassy silica test tube under argon atmosphere to avoid oxidation. The sample holder (c) is introduced in the furnace at 1000°C and the sample reaches this temperature in about 20 minutes. After the experiments at 1000°C, samples were also characterized at room temperature in order to compare *in situ* and *ex situ* characterizations. The synchrotron beam was monochromatic with **E=80 keV** and a beam size of **50µm (V) x 100µm (H)**. Multiple scans (duration 10-120s/scan) were carried out at the interface between the cermet and the molten salt and just below (cermet only). Diffraction rings (e) were recorded with a 2D X-Ray camera (*ESRF Frelon2K*) (d) and their integrated intensities were calculated with *FIT2D*[1]. The cermet is a multiphase material (f) composed of a nickel ferrite (spinel), a nickel oxide (monoxide), and a copper nickel alloy (metal). Different molten salts have been tested: pure cryolite (Na_3AlF_6), and AlF_3-Na_3AlF_6 (CR=2.2), AlF_3-Na_3AlF_6-Al_2O_3 mixtures.

As shown on *Figure 2*, the diffraction pattern of the cermet obtained with the synchrotron radiation clearly exhibit Bragg's peaks. However, because of the sample thickness (10 mm), the spectral resolution is not completely optimized and it involves a significant overlapping of peaks of different phases.

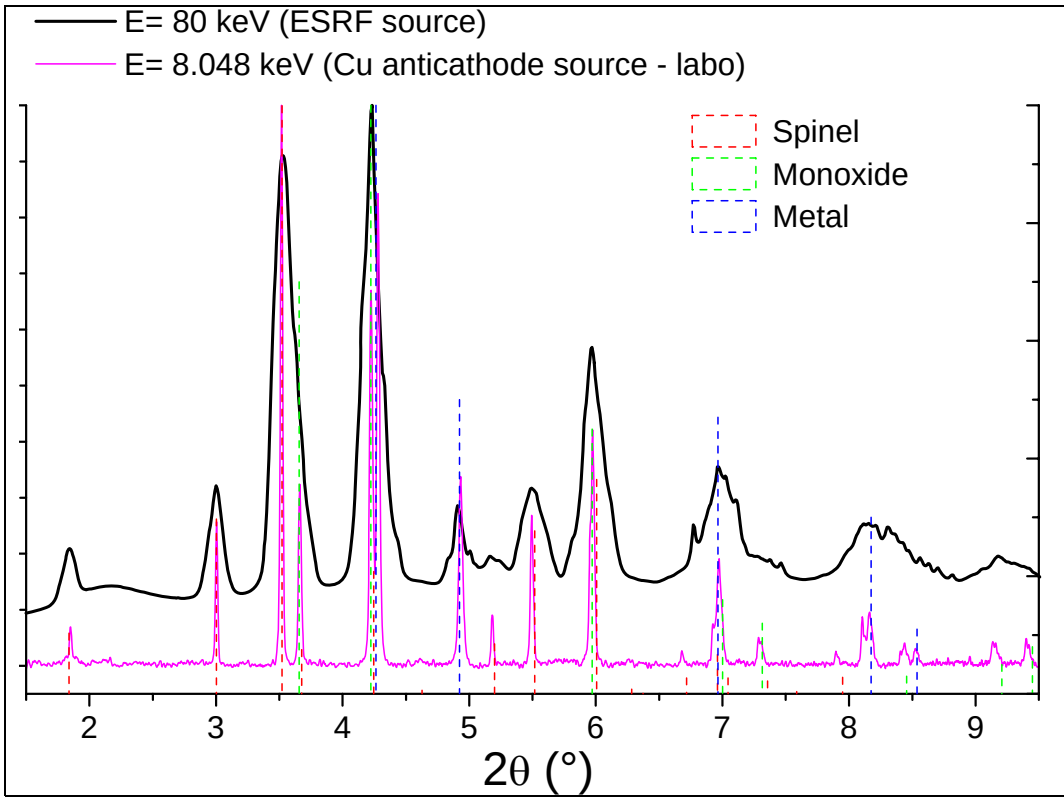

Figure 2: Diffraction patterns of the cermet. The black curve was obtained at ESRF from the integration of the diffraction rings. The magenta curve was obtained from a laboratory diffractometer (Bruker D8 Advance). Dashed lines correspond to the indexed positions of the cermet phases.

Figure 3a shows the evolution of the diffraction patterns of cermet/cryolite interface up to the melting of the salt. Between 500°C and 585°C, the phase transition of cryolite ($\alpha_{monocl} \rightarrow \beta_{cub}$) is not easily evidenced due to spectral resolution (peaks "α" in the figure). However, the melting of cryolite is clearly observed with the disappearance of the peak at $2\theta \approx 2.25°$.

All the experiments (effects of the bath composition and of the initial surface of the cermet → 6 expt.; 1700 diffraction patterns) performed during this beamtime allocation have been analyzed. *Figure 3b* illustrates an example of the diffraction patterns of the cermet/salt interface during 9 hours of corrosion. No significant evolution of the Bragg's peaks is observed during this period. Post-testing analyses of the interface after cooling by SEM-EDX (*Figure 4*) show that the oxide phases have been dissolved by the molten fluorides. Nevertheless, while the metallic phase is more abundant at the interface, the diffraction patterns do not exhibit higher intensities of its Bragg's peaks compared to the oxide phases ones. This point is mainly due to a too much higher vertical beam width (→ interface + cermet only).

[1] *FIT2D* software, A.P. Hammerley, ESRF, http://www.esrf.eu/computing/scientific/FIT2D/.

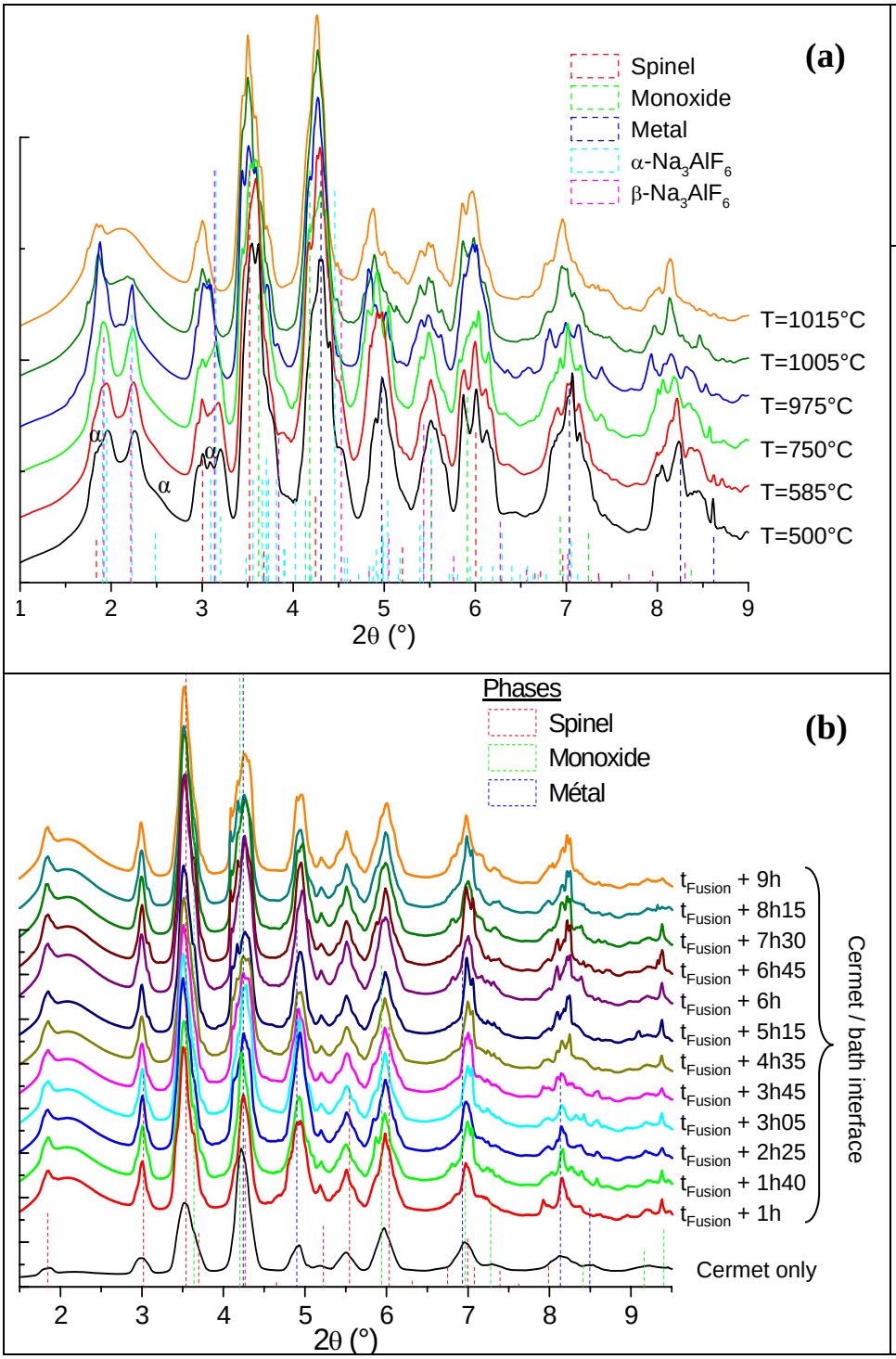

Figure 3: Left (a) Diffraction patterns of the interface between the cermet and the salt (Na_3AlF_6) during the heating phase. (b) Diffraction patterns of the interface between the cermet and the salt (AlF_3/Na_3AlF_6, CR=2.2) as a function of time.

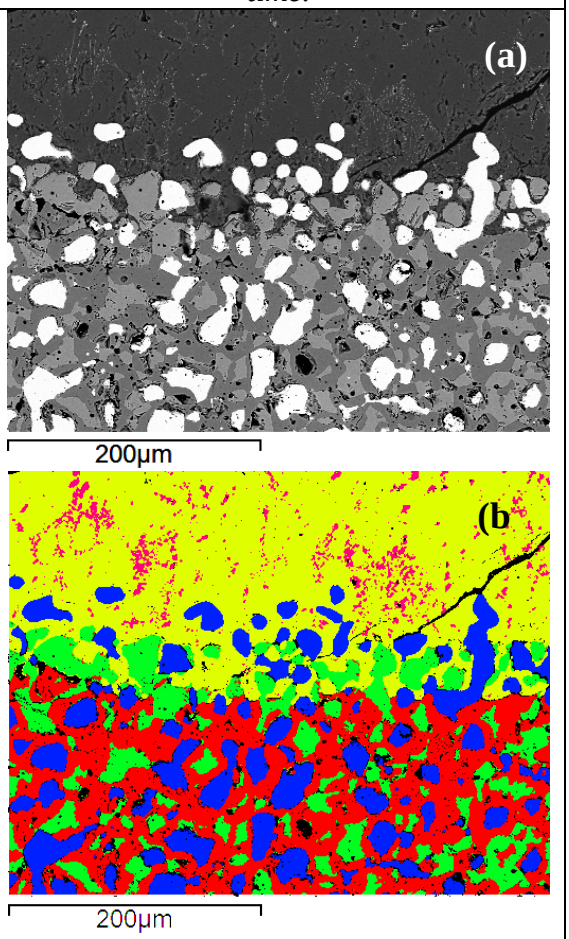

Figure 4: (Above) (a) SEM micrography of the cermet/salt interface after cooling. (b) EDX cartography; red=spinel, green=monoxide, blue=metal, yellow=salt, pink=dissolved cermet elements in the salt.

This beamtime allocation allows us to show that it was possible to study *in situ* the corrosion of cermets by molten fluorides up to 1000°C by developing an original set-up dedicated the characterization by X-Ray diffraction in transmission mode. We have succeeded in observing the melting of the salts, to keep them in the molten state; and to probe the cermet/salt interface during several hours with no significant vaporization and no damages for the apparatus. Obviously, some technical points such as the spectral and spatial resolutions have to be improved, but these results are still very encouraging because it is the first time that chemical interactions between a cermet and molten fluorides are investigated *in situ* at high temperature. Thanks to these preliminary experiments, we are confident for performing next experiments which would include electrochemical processes. Indeed, this cermet is proposed to be used as an anode for the production of aluminium.