ESRF	Time resolved in-situ powder diffraction of metal dusting corrosive attack on high alloyed steels (Inconel 601)	number: ME-252
Beamline: BM01B (SNBL-B)	**Date of experiment:** from: 21.11.01 to: 27.11.01	**Date of report:** 15.06.02
Shifts: 15	**Local contact(s):** Dr. Wouter Van Beek	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):
Ragnvald H. Mathiesen* & Emil Samuelsen*, Dept. of Physics, NTNU, Trondheim, Norway. Poul Norby*, Dept. of Inorg. Chemistry, Univ. Oslo, Norway.

Report:

The aim of the experiment was to study metal dusting (MD) corrosive attack in Inconel 601 at 923 K in a 75% H_2 - 25% CO (+ 2% humidity) atmosphere by means of powder diffraction. To accomodate to the ESRF safety regulations on working with toxic and flammable gases, we had designed a special setup for the experiment. Some of this setup was brought along for the experiment while others were parts supplied by the beamline. Prior to the experiment the setup was assembled at the ESRF chemistry laboratories where it was checked for leakage by the ESRF safety group, who degraded the experiment from red to yellow. The opportunity was also used to pre-expose a Inconel 601 sample while we had the equipment assembled. We could verify attack visually after 15 hrs. of exposure.

MD corrosion is an attack of carbon deposited from the syngas onto the metals surface under Boudouard ($2CO \rightarrow CO_2 + C$) or water-gas/syngas ($CO+H_2 \rightarrow H_2O + C$) reactions. Inconel 601 is a ternary based Ni (60%) Cr(22%) Fe (17%) alloy, balanced in other alloying (Al, Ti, Cu, Si, Mg, C) elements at the% - sub% level. Inconel 601 has a Ni based lattice with Cr and Fe as substitutionals, yielding a slightly elongated Ni lattice, and a strain induced broadening in the diffraction peaks from the unexposed material. The role of the Cr in this type of stainless materials is to build a protective Cr_2O_3 oxide at the surface. However, when the operating temperature for the material is less than 1300-1400 K, the Cr-diffusion rate in the austenitic microstructure is inadequate for building the protective scale. Consequentially, less favorable ferrites of the type $Fe_{1+x}Cr_{2-x}O_4$ are formed at the surface. These are known to be catalytically active with CO, and will lead to a C coating at the surface. The role played by the carbon layer to disintegrate the material is through inward C diffusion in to the metal with a subsequent formation of metastable carbides as the metal out toward the surface has become a supersaturated solid solution of C. The formation of carbides introduce local strains that aid to the inward C diffusion When C has diffused through the outermost grains, and into the grain boundaries it accumulates and forms graphite. Graphite deposits with a free end at the surface transports intermetallic particles from the grain boundaries to the surface by intercalation. Consequentially entire grains detach at the surface leaving visual pitting.

The MD reaction takes place in the 3-4 outermost μm of the material. Therefore to study MD *in-situ* by powder diffraction a flat-bed geometry furnace with a incident beam at a small angle is preferable, and intentionally the idea was to construct a dedicated furnace for this experiment.

However, the cramped space at the SNBL 01B, due to constraints imposed by stationary equipment and the lead pipe for the BM01A beam, did not allow for easy adaption of remotely constructed apparatus onto the sample stage. Therefore, when it was informed by the SNBL contact that they were about to build a furnace for experiments with reactions in gaseous environments, it was decided that the MD experiments were to be carried out using the beamline furnace. Since the furnace geometry was built for capillaries/cylindrical samples this was not a fully optimal solution, but the idea was to use a large diameter sample and displace its rotation axis with respect to the detector rotation axis so that the latter would be centered marginally into the sample from the top surface. By varying the incident beam energy, and thereby the sample attenuation, diffraction from the sample interior could be avoided, yielding a signal which was dominated by the regions where MD attack was expected to happen. However, the SNBL furnace was not equipped as intended. It was, due to its construction, virtually impossible to align the sample as intended. Furthermore, it was discovered that the beam entrance and exit windows were made from a 1 mm thick quartz glass tube.

Accordingly it was not possible to displace the sample rotation as accurately as needed with respect to the detector rotation axis. In addition penetration of the incident and diffracted beams through the 1mm of quartz required high energies $>$ (30 KeV) to be used. The attenuation length for Inconel 601 at such energies is $> 100\mu$m, and since the sample could not be properly aligned, considerable diffraction signals would arise from as deep as 50-60μm into the material. The monitoring of MD attack consists in detecting adequate diffraction signals from a sub-μm thick Chromite/ferrite scale and from local carbide particles of size 50-100 nm. Due to the improper sample alignment and the high penetration depth at the energy made necessary by the quartz tube, the interesting signals were indistinguishable from the background from the sample and the quartz.

It was tried to machine the samples down to smaller diameters in order to bypass the problems with sample alignment, but surface working is known to increase Cr diffusion to the surface, thus to prevent or slow down MD attack. Therefore this strategy did not lead to success. In conclusion the attempts on performing XRD *in-situ* on MD attack in Inconel 601 was abandoned. Final *ex-situ* investigations outside the furnace of the samples exposed both at the chemistry lab and during the experiments showed that MD attacks had started in all cases except for the surface worked Inconel 601 sample. In the diffractograms, Cr_2O_3, $Fe_{1+x}Cr_{2-x}O_4$ as well as M_7C_3 type carbides were found. Also the main peaks from the austenitic matrix show signs of MD. In the surface near region, the peaks show a Fe/Cr depletion as a continuous broad intensity from the original Inconel 601 lattice at $a \simeq 3.55$ toward a pure Ni at $a \simeq 3.53$ Å.