Microelectrochemical and Corrosion Behaviour of Metal Alloy Waste Forms

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Abstract

Within the USDOE Fuel Cycle Research and Development Program steel-based alloys have shown promise as potential waste forms for Tc-based waste streams produced from spent fuel processing. Waste stream components are alloyed with steel to create an alloy with a complex microstructure. Surface analytical techniques (SEM, EDS) coupled with long-term corrosion studies and electrochemical techniques have been used to analyze the corrosion behaviour of this material. Due to the complex alloy structure it is difficult to determine which phases are active or passive to corrosion. A microelectrochemical cell system has been employed to isolate and study individual phases and regions to separate their corrosion behaviours. Such analyses lead to a much clearer picture of alloy corrosion processes when coupled with bulk studies.

1. Introduction

To deal with the increasing worldwide stockpile of spent nuclear fuel, much work is being done to develop technologies to safely manage these nuclear materials[1]. One approach is the development of nuclear metal alloy waste forms, primarily utilizing Fe-based alloys and a major initiative, the Fuel Cycle Research and Development program organized through Argonne National Labs (IL, USA), is now underway[2].

These particular waste forms are being developed primarily with one radionuclide in mind: ^{99}Tc, a long-lived β-emitter, produced in high yield by in-reactor fission. ^{99}Tc has a high environmental mobility in the anionic form as TcO_4^{2-}. Unlike cations, the anion TcO_4^{2-} will not be trapped through ion exchange processes with geological materials if fuel containers fail and the nuclear fuel is exposed to groundwater[3]. The proposed Uranium Extraction process (UREX) separates Tc along with U from other radionuclides in the waste stream[4]. Tc can then be further separated and incorporated into Fe-based alloy waste forms and immobilized in its metallic form. Whether or not it will be released then depends on the corrosion behaviour of the waste form.

Initial forms of this alloy used carbon steel as the matrix but displayed poor corrosion resistance and consequently stainless steel has subsequently been selected as the matrix. This introduces Cr and the improved corrosion resistance that goes with it. In future versions of the alloy the Cr content can then be adjusted to further improve corrosion properties. Stainless steel also allows the solubilization of metallic elements (Mo, Ru, Pd, Zr, Tc) present in the waste streams at processing temperatures upwards of 1600 ^{o}C. Zr is introduced from fuel cladding (as Zircaloy) and Ru and Pd are present from the epsilon particles produced by in-reactor fission.

The alloy is made up of a complex microstructure containing up to seven separate phases, Figure 1, and in order to develop a stable alloy knowledge of the behaviour and interactions of these phases is required. Given the non-homogeneous structure of the alloy, the different phases are expected to have differing corrosion behaviours. While studies on bulk specimens can yield valuable information on the corrosion properties, information on localized corrosion processes, such as pitting, can be difficult to obtain from the data. Consequently, there is a need to study such processes on the micrometer scale.

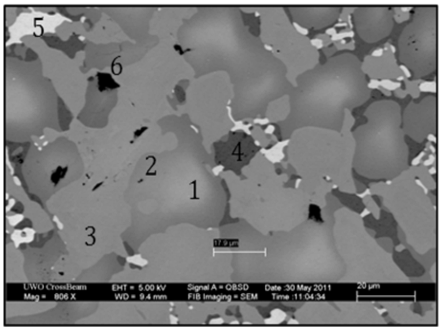

Figure 1 – Backscatter SEM image of the waste form alloy displaying the multi-phase microstructure

One technique that can be applied on the appropriate scale is the microelectrochemical technique first developed by Bohni and Suter[5]. In their design, Figure 2, the cell is comprised of a capillary pulled to a small opening diameter, and ground smooth with a silicone gasket placed on the end to prevent solution leakage. This cell is substituted for an objective lens on a standard optical microscope. An area of interest on the sample surface is then located with the microscope. The cell objective is then placed directly onto the sample surface, so that only the selected area is exposed to solution allowing electrochemical information from that local area to be gathered.

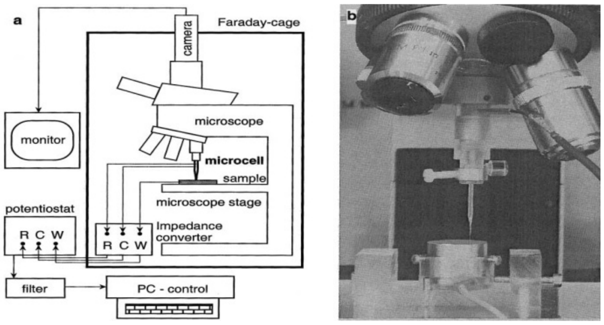

Figure 2 – The microelectrochemical setup [5]

2. Experimental

2.1 Electrochemical cell and equipment

A standard three electrode glass cell, placed in a Faradiac cage, is being used in bulk corrosion studies. A Pt-mesh welded to a Pt wire serves as the counter electrode, while a saturated calomel electrode (SCE) (242 mV vs standard hydrogen electrode (SHE)) is used as the reference electrode. Long-term corrosion experiments are carried out using a Solartron 1287 potentiostat with a Solartron 1255B frequency response analyzer (FRA) connected when electrochemical impedance spectroscopy (EIS) measurements are also made. Polarization experiments are made using either a Solartronmultistat workstation or a 1287 potentiostat.

2.2 Microelectrochemical Studies

The cell was made by heating a capillary and pulling it to reduce its original diameter. A Pt-wire counter electrode and a 3 M Ag/AgCl (227 mV vs SHE) reference electrode serves were used. Thermcoat^{TM} silicone lacquer was applied create a seal between the capillary electrode surface and the solution. Electrochemical control is achieved with a Keithley 6430 subammeterusing in-house software.

2.3 Electrochemical Experiments

Studies have been conducted in six different solutions covering a wide pH range with and without added chloride: 0.1 mMNaOH; 0.1 mMNaOH + 10 mMNaCl; 10 mMNaCl; 200 mM $Na_2B_4O_7$; 0.1 mM H_2SO_4; and 0.1 mM H_2SO_4 + 10 mMNaCl. Solutions were prepared using deionized Millipore water (18.2 MΩ·cm), and analytical-grade reagents. The samples were received from Savannah River National Laboratory and contained Re as a surrogate for radioactive Tc. Prior to experiments, the samples are polished with 600, 800, 1000, 1200 grit SiC paper followed by micropolishing suspensions of 1 μm, 0.3 μm and 0.05 μm Al_2SiO_5 powder. The samples are rinsed with Millipore^{TM} (18 mΩ-cm) water between each polishing step and after the final polishing step and finally dried with $Ar_{(g)}$.

2.4 Surface Analysis

Surface imaging was performed with a Texas Instruments Optical microscope, while electron microscopy with either a LEO (Zeiss) 1540 SEM/FIB equipped with an Oxford Instruments x-ray system for EDS, or a LEO 440 SEM equipped with a Gresham light element detector and a Quartz XOne EDX system.

3. Results

3.1 Electrochemical and Corrosion Study

The polarization behaviour of the alloy in the six solutions is shown in Figure 3. In each solution the alloy shows a low current from E_{CORR} up to ~600 mV due to the presence of a passive film. At more positive potentials the current increases, likely due to oxidation of Cr to CrO_4^{2-} and the onset of transpassivity.

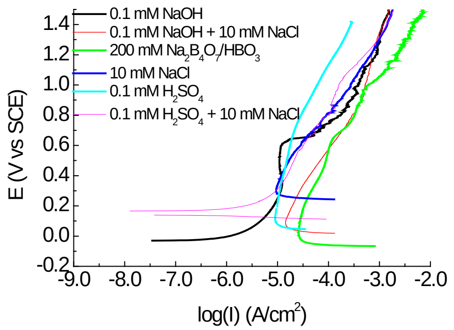

Figure 3 Polarization scans on the alloy performed in the six test solutions

The polarization scans in Figure 3 provide a quick snapshot of the anodic behaviour but yield little information about the long term corrosion performance of the alloy. To overcome this limitation the alloys were exposed to the various solutions for up to 180 hr while monitoring E_{CORR} and its evolution over time. Periodically, EIS measurements were collected to gather information on the surface reactivity. A summary of the E_{CORR} values is given in Table 1.

Solution	E_{CORR}	
	90 hr	180 hr
0.1 mMNaOH	-210 mV	-140 mV
0.1 mMNaOH + 10 mMNaCl	-130 mV	-135 mV
200 mM $Na_2B_4O_7/HBO_3$	-65 mV	-65 mV
10 mMNaCl	-75 mV	-65 mV
0.1 mM H_2SO_4	170 mV	130 mV
0.1 mM H_2SO_4 + 10 mMNaCl	200 mV	190 mV

Table 1 Corrosion potentials observed on the waste form alloy in the various solutions

During the monitoring of E_{CORR}, the alloy displays increased local attack in the presence of chloride. However in all of these cases the alloy is able to regain passivity. The cause of the local attack and loss of passivity needs to be understood and the MEC technique is being utilized to investigate individual phases.

3.2 Microelectrochemical Studies

Using the MEC, polarization scans were performed on four areas in 0.1 mMNaOH solution, Figure 4. For the Mo-Fe-Cr-Re matrix phase (Area 1), very little activity is observed, and the phase remains passive throughout the polarization scan. This observation is a positive sign for the alloy since it is this Mo-rich phase which contains Re, the element whose release is to be controlled. As expected the Mo-Fe-Cr-Re(low) phase (area 2) behaves in a similar fashion with the alloy maintaining a passive region to a high potential. The Fe-Zr phase, area 3, has a higher current in the scan, and this is expected as Zr is expected to be reactive in alkaline conditions. The highest activity is seen in the nearly pure Fe phase, area 4, which gives the highest current during the scan. In the plot of the Fe phase, a very sharp and reproducible increase in current is observed at ~400 mV, whose origin is not yet understood.

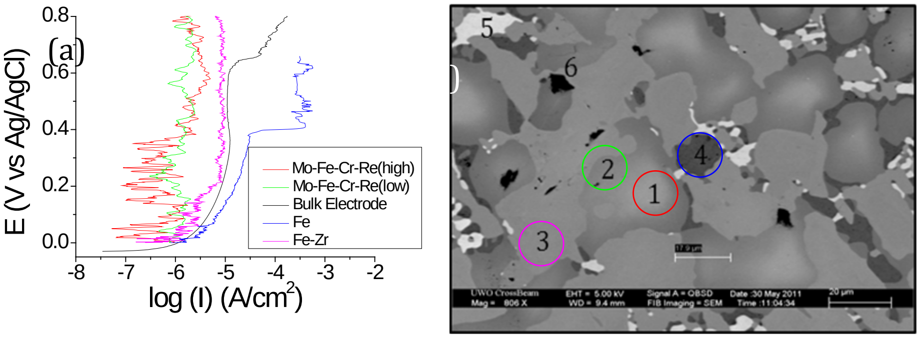

Figure 4 (a) Polarization scans recorded on the different phases in Raw-Re1 using the MEC technique. Current densities are corrected for the exposed area under the MEC cell. The colour co-coordinated areas are displayed in (b)

4. Summary

i) The alloy has a multi-phased dendritic structure with an uneven distribution of alloying elements. Polarization curves recorded in six different solutions indicate higher corrosivity in the presence of Cl^-. Altering pH also alters the polarization characteristics of the alloy.

ii) In long term corrosion experiments Cl^- was shown to increase localized attack of the alloy, however these local events were not sustained and the alloy was able to regain passivity in alkaline, acidic and neutral solutions both with and without Cl^-.

iii) MEC analyses of the different phases in alkaline solution show the Fe phase to have the highest activity with the Fe-Zr phase also being active. A possible reason is that the Fe-rich phase is galvanically coupled to other phases.

5. Acknowledgement

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