The role of fission products (noble metal particles) in spent fuel corrosion process in a failed container

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Summary

The corrosion/dissolution of simulated spent fuel has been studied electrochemically. Fission products within the UO_2 matrix are found to have significant effect on the anodic dissolution behaviour of the fuel. It is observed that H_2O_2 oxidation is accelerated on the surfaces of doped noble metal (ε) particles existing in the fuel matrix. It is concluded that H_2O_2 decomposition rather than UO_2 corrosion should be the dominant reaction under high H_2O_2 concentrations.

1. Introduction

The recommended approach for the long term disposal of used nuclear fuel in Canada is adaptive phased management including the isolation of the used fuel in centralized containment in a deep geological repository [1]. Although it is not expected, in the event of container failure, fuel corrosion and release of radionuclides would occur within the groundwater flooded container. One of the alpha water radiolysis products, hydrogen peroxide, has been demonstrated to be the primary driving force for fuel corrosion [2]. Oxidation of fuel ($U^{IV}O_2$) will produce the oxidized form (U^{VI}) with a considerably higher solubility leading to fuel dissolution and the release of radionuclides. In addition to causing UO_2 dissolution, H_2O_2 reduction can couple with its own oxidation resulting in its overall decomposition to H_2O and O_2. Thus, competition between these two anodic reactions can occur and the rate of fuel corrosion will depend on their relative kinetics. The corrosion rate of spent fuel is also highly influenced by the presence of fission products from in-reactor burnup [3]. Previous investigations on high burnup UO_2 fuels indicate two major categories of fission products within the fuel, segregated noble metal particles and lattice-incorporated rare earth elements. The kinetics and mechanism of the cathodic reduction of H_2O_2 has been investigated intensively using a series of SIMFUEL specimens containing different amounts of simulated fission products [4-7]. However, there is little information on the anodic oxidation of H_2O_2 and the effect of ε-particles on this process.

In this paper, the kinetics for the H_2O_2 oxidation on SIMFUEL containing different doping elements has been studied. Since the two anodic processes (UO_2 dissolution and H_2O_2 oxidation) are occurring at the same time, they cannot be separated by electrochemical methods. Therefore, a series of solution and surface analysis have been performed to study the quantitative importance of the two competitive reactions.

2. Experimental

The working electrodes used in all experiments were SIMFUEL pellets fabricated by Atomic Energy of Canada Limited (Chalk River, Ontario). The electrodes are doped with either, or both, noble metal (ε-particles) and rare earth elements (RE) to simulate the irradiation effect [8]. The SIMFUEL used in this study mimics the in-reactor burn-up to an extend of 3.0 atomic %, and the procedure of electrode preparation has been described previously [5].

A conventional three electrode, three compartment electrochemical cell was used for all experiments. The reference electrode was a saturated calomel electrode (all potentials quoted are referred to this scale) and the counter electrode was a platinum sheet with a surface area of 6 cm^2. All experiments were conducted under Ar atmosphere at room temperature. The electrolyte solutions were prepared using distilled deionized water purified by Millipore milli-Q-plus units with a resistance of 18.2 MΩ.cm. The solutions contained 0.1 $mol.L^{-1}$ NaCl as the base electrolyte, and carbonate concentrations ranging from 10^{-4} to 2×10^{-1} $mol.L^{-1}$. The pH was adjusted to 9.7. Hydrogen peroxide (3% w/v) was added immediately prior to experiments to obtain a concentration of 0.02 $mol.L^{-1}$. Polarization curves were recorded over the potential range 0.1-0.4 V and 10 min was allowed at each potential to ensure steady-state was achieved. The potentials were applied stepwise and an impedance measurement was performed at each potential. In dissolution experiments, an anodic potential between 0.20 and 0.35 V, was held for 1 hour before the solution was sampled and an ICP-AES analysis (inductively coupled plasma atomic emission spectroscopy) performed for dissolved uranium in solution. The SEM (scanning electron microscopy) was performed before and after anodic oxidation of the electrode.

3. Results and discussion

Two SIMFUEL electrodes, one doped with only rare earth elements (RE) and one with both rare earth elements and ε-particles (RE+ε), were held at constant anodic potentials (0.1-0.4 V) in H_2O_2 solutions containing low carbonate concentrations. As shown in Fig. 1, the steady-state current on the RE+ε electrode was slightly higher than that on the RE electrode for E<0.25 V, while for more positive potentials, a significant difference was observed. The anodic current on RE was suppressed at high overpotentials ($E>0.25$ V), which was attributed to a passive film formed on the electrode surface. For RE+ε, the current reached a plateau between 0.2 and 0.3 V and then increased again. The difference was due to the effect of ε-particles, either accelerating UO_2 dissolution or H_2O_2 oxidation.

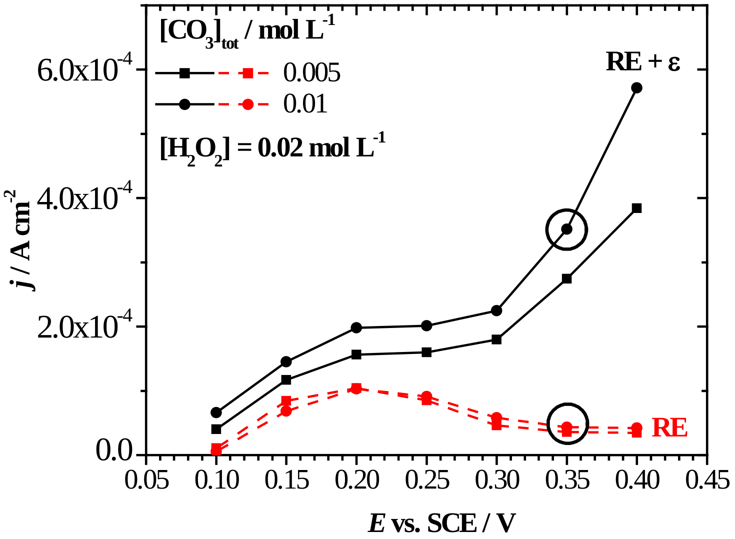

Fig. 1. Steady-state currents as a function of potential recorded on 3at.% SIMFUEL electrode with (RE+ε) and without (RE) ε-particles in 0.1 mol.L^{-1} NaCl + 0.02 mol.L^{-1} H_2O_2 solution containing different carbonate concentrations at pH 9.7, ω=16.7Hz. $[CO_3]_{tot}$: (■) 0.005 mol.L^{-1}; (●) 0.01 mol.L^{-1}.

It is unlikely that the increased current at high potentials on RE+ε was mainly due to UO_2 dissolution, for the following reasons:

1) The same experiment was repeated in higher carbonate concentrations up to 0.2 mol.L^{-1}, since carbonate can accelerate the dissolution of UO_2 by complexation leading to an increased anodic current. However, the anodic current at E>0.35 V was increased <5% even for the highest $[CO_3]_{tot}$.

2) The SEM images in Fig.2 were taken before and after anodic oxidation at E=0.35 V for 1 hour. The oxidation currents are indicated by the circled data points in Fig.1. Fig. 1 also shows that the oxidation current on RE+ε was much higher than that on RE, the difference in the integrated charge of 1 hour being ~1 C. At higher pH and carbonate concentration, a similar amount of anodic charge (~1 C) caused visible damage on the surface (not shown). However, the SEM images in Fig.2 were similar before and after oxidation suggesting little damage (due to dissolution) to the surface. This result indicated that both the UO_2 surfaces were passivated at high anodic potential and little dissolution occurred.

3) The ICP-AES test for dissolved uranium concentration is currently ongoing.

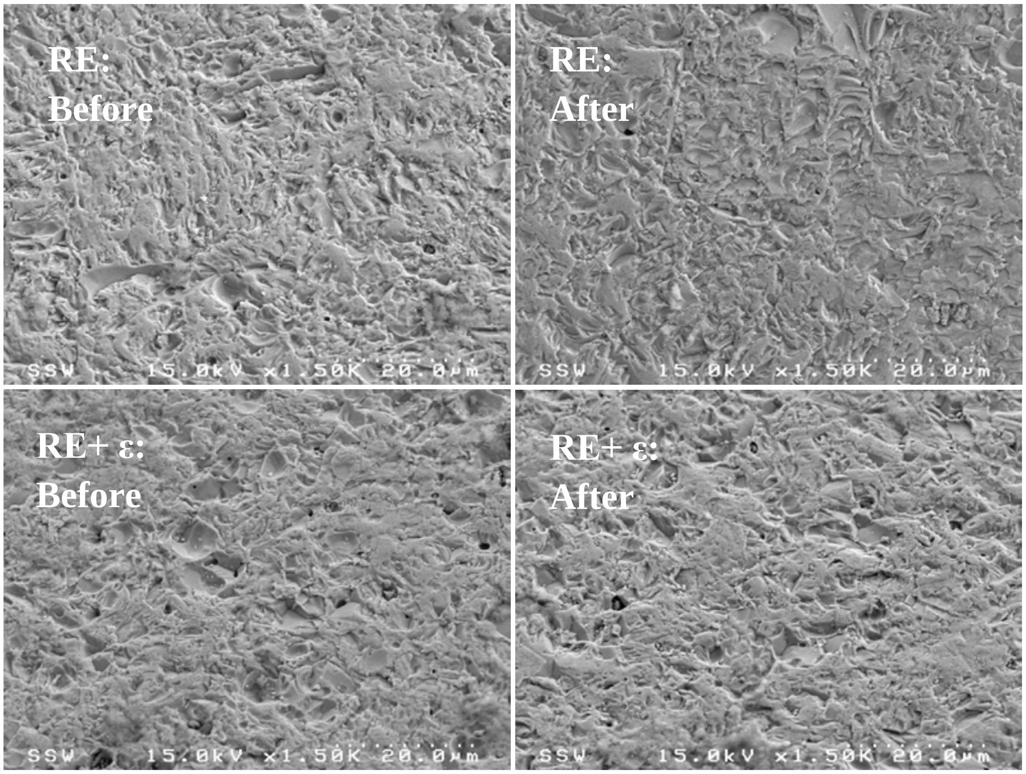

Fig. 2. SEM micrographs of SIMFUEL specimens after oxidation at *E*=0.35 V for 1 hours in 0.1 mol.L^{-1} NaCl + 0.02 mol.L^{-1} H_2O_2 + 0.01 mol.L^{-1} $NaHCO_3$ at pH 9.7.

These results imply that most of the extra anodic current on RE+ε was due to H_2O_2 oxidation. In a previous study on palladium (primary constituent of the ε-particles) electrode [9], the oxidation of H_2O_2 was demonstrated to commence at *E*=0.2 V and to increase rapidly at higher potentials. Thus at *E*<0.2 V, H_2O_2 was not expected to undergo a predominant oxidation on ε-particles, consistent with the observation in Fig.1 that the currents of RE and RE+ε were close to each other at this potential. At E>0.3 V, the electrode doped with RE+ε had a much higher current than RE, and the different behaviours can be attributed to H_2O_2 oxidation on ε-particles at E>0.2 V. The magnitude of the H_2O_2 oxidation current was consistent with previous studies on Pd or Pt electrodes [9-11]. This claim is also supported by EIS data.

4. Conclusion

The anodic dissolution of simulated spent fuel has been studied electrochemically. The fission products, specifically the noble metal particles, were found to have a significant effect on the corrosion behaviour. It was observed that H_2O_2 oxidation can be largely accelerated at high potentials. H_2O_2 decomposition instead of UO_2 corrosion is expected to be the dominant reaction at high H_2O_2 concentrations.

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