The Application of Noble Metals in Light-Water Reactors

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Corrosion potential is a primary determinant of the stress-corrosion cracking susceptibility of structural materials in high-temperature water. Efforts to minimize stress-corrosion cracking in light-water reactors include adding hydrogen. In some plants' out-of-core regions, the hydrogen required to achieve the desired corrosion potential is relatively high. In-core, more hydrogen is needed for an equivalent reduction in corrosion potential. Additionally, side effects of high hydrogen-addition rates, including increased 11N turbine shine and 6Co deposition, have also been observed in some cases. An approach involving noble-metal coatings on and alloying additions to engineering materials dramatically improves the efficiency with which the corrosion potential is decreased as a function of hydrogen addition, such that very low potentials are obtained once a stoichiometric concentration of hydrogen (versus oxygen) is achieved.

INTRODUCTION

The important influence of the corrosion potential on stress-corrosion cracking (SCC) (Figure 1), irradiation-assisted SCC (IASCC) (Figure 2), flow-assisted corrosion of carbon steel (FACCS), and other facets of boiling-water reactor (BWR) operation is well established. Early attention was focused on the relationship between the corrosion potential and SCC, which resulted in the discovery that SCC can be markedly suppressed if the potential is maintained below about -0.25 V_{acc} thereby reducing the thermodynamic driving force for crack advance.4,5

While many other factors (e.g., metal properties, temperature, irradiation, flow characteristics, aqueous impurities, etc.) are involved in establishing the corrosion potential, the redox properties of the coolant water are usually of primary importance. Under normal water chemistry (NWC) conditions, oxidants such as dissolved oxygen, hydrogen peroxide, and chromate ions are in stoichiometric excess of reductants (primarily hydrogen). This results in relatively high corrosion potentials, often ≥0.10 V_{acc}. Hydrogen water chemistry (HWC), in which hydrogen is injected into the feedwater, has subsequently been adopted at numerous BWRs to shift the redox balance in favor of lower potentials. Under unirradiated conditions, some plants were found to require comparatively high hydrogen-addition rates to shift the corrosion potential into the desired range (less than -0.23 V_{acc}). In-core, more hydrogen is needed for an equivalent shift in corrosion potential. Apart from cost, undesirable side effects of high hydrogen-addition levels have also been observed in some cases, including turbine shine from 11N carry-over and 6Co deposition, both of which increase the radiation level in parts of the plant.

Noble metals have long been recognized as recombination catalysts for oxygen and hydrogen dissolved in water. However, it was recently found that the corrosion potential of a surface containing noble metals dropped to very low values when hydrogen was present in stoichiometric amounts (or greater), even in the absence of complete volume recombination of O2 and H2 in the water.6,8 This was first evaluated during studies of the corrosion potential of types 304 and 316 stainless steel coupons in high-temperature water containing stoichiometric excess of hydrogen with varying levels of dissolved oxygen. Under these conditions, it was proposed that the effectiveness of hydrogen was limited by the irreversibility of the hydrogen/water half-reaction on oxidized stainless-steel surfaces, and that it should be possible to achieve lower corrosion potentials more readily if the catalytic properties of the stainless-steel surface were enhanced for this reaction.6

Details of this hypothesis were reported and confirmatory data obtained using electrochemical studies and constant extension rate tests (CERTs) in

Figure 1. Observed and predicted crack growth rate as a function of corrosion potential for furnace-sensitized type 304 stainless steel at 27.5-30 MPa/m in 288°C water over the range of solutions conductivities of 0.1 to 0.5 μS/cm. Data points at elevated corrosion potentials and growth rates correspond to irradiated water chemistry conditions in test or commercial reactors.5,6

Figure 2. The dependence of IASCC on corrosion potential as measured in slow strain tests at 3.7 x 10^{-7} s^{-1} in 288°C water on types 304 and 316 stainless steel pre-irradiated to several specific fluences.

Figure 3. Schematic E (potential) vs. log i (absolute value of current density) curves showing the interaction of H2 and O2 on a catalytically active surface such as platinum or palladium. The quantity i0 is the exchange current density, which is a measure of the reversibility of the the reaction. Above i0, activation polarization (Tafel behavior) is shown in the sloped, linear regions. The quantity iL is the limiting current densities for oxygen diffusion, which vary with mass transport rate (e.g., oxygen concentration, temperature, and convection). The corrosion potential in high-temperature water containing oxygen is usually controlled by the intersection of the O2 reduction curve (O2 + 2H2O + 4e- → 4OH-) with the H2 oxidation curve (H2 → 2H+ + 2e-).
Conversely, FACCS is markedly enhanced when the corrosion potential falls below -0.6 V_sh, as hydrogen is added to the feedwater. This type of attack, associated with regions of high and/or disturbed flow, stems in part from the less protective corrosion film on carbon steel versus stainless steel.\(^7\) In deaerated high-temperature water, carbon steel tends to depassivate more readily than stainless steel, and hence develops corrosion potentials in the active corrosion range (e.g., -0.8 V_sh versus -0.5 V_sh for stainless steel in deaerated pure water). Once in this region, corrosion of carbon steel can occur, balanced by water reduction and oxygen reduction reactions. Because of the high overvoltage (poorly catalyzed) hydrogen-evolution reaction on the oxidized-steel surface, corrosion potentials can fall to -0.80 V_sh.\(^10\) At such low potentials, the solubility of magnetite increases as “reductive dissolution”\(^11\) occurs and enhances corrosion. The presence of a catalytically active palladium or platinum coating can raise the potential to that of the reversible hydrogen/water reaction (e.g., about -0.55 V_sh) where a protective passive film may form or, at least, “reductive dissolution” would be lessened. In addition, palladium or platinum coatings may form a mechanically protective layer that also aids in mitigating corrosion.

These important, interrelated behaviors are now the focus of in-depth studies designed to achieve a better understanding and thereby better control of the processes. These studies include the investigation of possible side effects of the noble-metal coatings on turbine shine from \(^1^4\)N carry-over and \(^6\)Co deposition.

**BEHAVIOR OF STAINLESS STEEL**

It is useful to consider the behavior of the corrosion potential (mixed potential) with the aid of schematic Evans diagrams. Figure 3 represents the behavior of hydrogen and oxygen on catalytically active metals such as platinum. A high exchange-current density \(i_0\) is shown for the hydrogen/water reaction and a somewhat lower one for the oxygen/water reaction. In both cases, Tafel (activation polarization) behavior has been assumed with a transition to diffusion control \(i_0\) at higher current densities for the oxygen reduction reaction. When hydrogen is in stoichiometric excess (HWC conditions), several limiting oxygen reduction-rate curves \(i_0\) can be shown that correspond to different oxygen concentrations and, hence, different rates of mass transport of oxygen to the electrode. In this system, over a wide range of oxygen concentrations, the intersection of the oxygen reduction curves with the hydrogen oxidation curve occurs below the Tafel region for the hydrogen reaction, and little deviation in corrosion potential from the reversible hydrogen/water potential occurs; this potential is -0.25 V below the accepted range of the “critical” potential for protection from SCC.

Figure 4 shows the more complex situation for stainless steel, wherein the exchange current density for both the hydrogen/water and oxygen/water reactions is smaller than platinum or palladium. Also indicated on this figure is a polarization curve for oxidation of stainless steel in high-temperature water. This has been drawn with only a small maximum in the active region before the current decreases to a somewhat lower passive value that is shown as essentially constant over a wide potential range.

If hydrogen is in stoichiometric excess with respect to oxygen and the mass transport conditions are similar to those in Figure 3 for platinum, stainless steel exhibits much different behavior. The exchange current density \(i_0\) for the hydrogen/water reaction is much lower than stainless steel; thus, the Tafel regime for this reaction begins at much lower current densities. The intersection of this curve with the limiting current densities for the oxygen/water reaction \(i_0\) begins to deviate from the reversible hydrogen potential even at relatively low

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**Figure 4.** Schematic E (potential) vs. log \(i_0\) (absolute value of current density) curves showing the interaction of \(H_2\) and \(O_2\) on a catalytically inactive surface such as stainless steel.

**Figure 5.** The corrosion potentials of platinum, stainless steel, and stainless steel with palladium coatings on cleaned or preoxidized stainless steel vs. dissolved oxygen content in 285°C water containing 150 ppb \(H_2\). The palladium-coated stainless steels exhibit catalytically active behavior just like platinum, and maintain a low corrosion potential despite elevated dissolved oxygen concentrations, provided stoichiometric excess hydrogen is maintained.

**Figure 6.** The corrosion potentials of type 316 stainless steel and palladium-coated type 316 stainless steel in 285°C water containing 300 ppb \(O_2\), and various amounts of \(H_2\). At about the stoichiometric \(H_2\) concentration, the corrosion potentials of the catalytically active specimens drop to approximately -0.5 V_sh.

**Figure 7.** The corrosion potentials of platinum, type 304 stainless steel, and type 304 stainless steel alloyed with 1 wt.% Pd and 3 wt.% Pd in 285°C water containing 350 ppb \(O_2\), and various amounts of \(H_2\).