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THE EFFECT OF WATER VAPOR ON THE CORROSION OF CARBON STEEL AT 65°C

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ABSTRACT

AISI 1020 carbon steel was exposed to air at various relative humidities at 65°C. A "critical relative humidity" (CRH) of 75-85% was determined. The CRH is the transitional relative humidity where oxidation/corrosion changes from dry oxidation to aqueous film electrochemical corrosion. Short term testing suggests that aqueous film electrochemical corrosion results in the formation of an inner oxide of Fe_3O_4, and an outer oxide of a powdery Fe_2O_3 and/or $Fe_2O_3 \cdot xH_2O$.

INTRODUCTION

The Yucca Mountain Site Characterization Project (YMP) is considering a strategy for isolation of spent nuclear fuel and vitrified high level radioactive waste in the potential repository at Yucca Mountain, Nevada that involves using the thermal output of the radioactive decay to modify the environment surrounding the waste packages such that the degradation of the waste packages (WP) is minimized. This concept involves keeping liquid water from the WP for as long as possible by configuring the waste packages in the repository so that their surface temperature remains above the boiling point of water for at least 1000 years. The WP would then be initially exposed to humid air. However atmospheres of humid air can be very corrosive to various metals under certain conditions [1]. Consequently there is a need to understand the conditions under which severe corrosion may occur, and the extent of the severity. It is also necessary to understand the corrosion / oxidation of the various metals under "non-aggressive" conditions. This information is necessary for the implementation of repository design to minimize corrosion of the WP.

A multi-barrier waste package for containment of radioactive waste is being considered. One implementation of this concept includes the use of a carbon or low allow steel as an outer barrier and an inner barrier made of a more corrosion resistant material, such as a Ti alloy, a Ni-Cr-Mo alloy, or a Ni-Fe-Cr-Mo alloy. The carbon or low alloy steel would be exposed to the humid air over a range of temperature. At lower temperatures, where water adsorption is possible, the metal alloys may be more susceptible to aggressive corrosion / oxidation.

This paper evaluates the corrosion / oxidation behavior of AISI 1020 carbon steel in air with varying relative humidities at temperatures where there is a potential for water adsorption on the material's surface. Atmospheric corrosion studies [1] indicate that "dry" oxidation occurs at low relative humidities, while aqueous electrochemical corrosion occurs in water films on the metal surfaces at high relative humidities. The water film corrosion rates can be 10 to 100 times faster than the "dry" oxidation rates at similar temperatures. The relative humidity where the corrosion process changes from "dry" oxidation to aqueous film corrosion has been termed the "critical relative humidity". This transition typically occurs over a range of relative humidities with the corrosion rate continually increasing with increasing relative humidity. The CRH can be arbitrarily defined as an enhanced corrosion rate above that of "dry" oxidation with all other conditions being equal. The CRH is dependent on several factors, such as, the type of metal, surface condition, surface contaminants, and gas-phase contaminants. Some of these factors that effect the CRH are discussed in the following sections.

The general characteristics of aqueous film electrochemical corrosion have been established at ambient atmospheric temperatures. What is not known is the effect of elevated temperatures on the aqueous film corrosion. Even though reaction kinetics may be accelerated with increasing temperature, other factors may cause corrosion rates to decrease. The solubility of oxygen in water decreases with increasing temperature and may decrease the reaction rate. On the other hand, since the water films are thin, oxygen transport through a film coupled with rapid resupply of oxygen from the surrounding air may compensate for the decrease in oxygen solubility. The higher temperatures may also change the morphology of the oxide layer, which may also affect the corrosion rates. Other temperature effects are discussed below.

This paper presents the results of the initial characterization of the CRH for carbon steel as a function of temperature. Other parameters affecting the CRH which will be studied include gas-phase contaminants, surface contaminants (such as, salts), and surface condition (e.g. previously oxidized, scratched).

BACKGROUND

Corrosion processes

The following is a brief discussion of the general characteristics of dry oxidation and aqueous film electrochemical corrosion. Dry oxidation leads to the steady build up of an oxide layer. Oxidation rates can be limited by adsorption and dissociation of oxygen on the oxide layer and / or transport of ions through the oxide layer. In general the thicker the oxide layer, the slower the subsequent oxidation rate; in other words, the oxide layer protects the underlying metal. Less protective oxide layers tend to be porous or cracked. Unless there is spalling of the oxide layer, the oxide layer will continue to grow. Because of the slow oxidation rates at low temperature, studies of the kinetics of oxidation processes are usually obtained at high temperatures

Electrochemical corrosion occurs in the aqueous film layers on metals. Depending on the metal or alloy, this type of process can have a greatly enhanced corrosion rate relative to dry oxidation. As discussed below, this type of corrosion is dependent on relative humidity and the presence of deleterious contaminants. Electrochemical corrosion can be very aggressive if the oxide layer formed is porous (that is, nonprotective). In addition to metal loss by formation of the oxide layer, metal can be lost by dripping of water off the material or washing the aqueous film off by water.

A partial explanation of the aggressiveness of aqueous film electrochemical corrosion is that soluble oxygen, which is consumed by the corrosion, is quickly replenished by gas phase oxygen and can be transported rapidly to a reactive surface because the diffusion path is short.

Factors affecting "critical relative humidity"

Factors which may affect the "critical relative humidity" of a particular metal include the surface condition, surface contaminants, and gas phase contaminants. Salts affect the CRH by their hygroscopic property and because they can accelerate electrochemical reactions (i.e. they are electrolytes).

It has been shown that the aggressiveness of salts deposited on a metal surface in humid air is related to the hygroscopic nature of the salts [2,3]. In particular it has been observed that aggressive corrosion occurs when the relative humidity of the air is near or exceeds the equilibrium relative humidity (or equivalently the water vapor pressure) above a saturated solution of the salt. This has been demonstrated at room temperature for numerous salts on carbon steel [3]. The salts tested included those with high equilibrium relative humidities, Na_2SO_4 (93% RH) and NaCl (78% RH), to those with low equilibrium relative humidities, NaI (43% RH) and LiCl (15% RH).

Duly [2] showed sea salt deposits were corrosive to mild steel even at relative humidities below the equilibrium RH, although at the lower relative humidities the corrosion was limited to the periphery of the salt deposits. Aggressive corrosion occurred when liquid water was visible on the metal surface; this occurred when the relative humidity was 80%.

It is of interest to know if the relationship between equilibrium RH and aggressiveness of salts deposits extends to higher temperatures. This will in part depend on the hygroscopic property of the salts at high temperature. Greenspan [4] has compiled equilibrium relative humidity data above saturated salt solutions for numerous salts. The data indicates that the equilibrium RH typically are within ± 20% of their value at room temperature. The exceptions are those salts that can decompose into volatile components, such as carbonates. The equilibrium RH were not reported at high temperatures for these salts.

Air contaminated with certain species, such as, SO_2 and CO_2, can also exhibit critical relative humidities. Brown and Masters [5] showed that steel at room temperature was aggressively attack by SO_2-contaminated air at relative humidities greater than 60%. Corrosion rates were 100 times greater than those at lower relative humidities. In contrast, SO_2-free air at 100% RH corroded at rates less than 10% of that for SO_2-contaminated air at 80% RH..

EXPERIMENTAL

Experiments were performed in an extensively modified commercial thermogravimetric analyzer (TGA) apparatus. The TGA is equipped with a very sensitive microbalance for measurement of specimen weight gain. The weight gain resolution of the TGA is approximately 60 µg.

The test chamber was a doubled walled glass cylinder heated with constant temperature silicone oil. With this arrangement, the centerline temperature of a test specimen could be maintained to ± 0.1°C and the temperature change across the length of a specimen was less than 0.5°C. The temperature and relative humidity in the reaction chamber were monitored with a combined temperature and humidity sensor .

Constant flow preheated humidified air was fed into the reaction chamber where it contacted the chamber wall before contacting the test specimen. The reactant air was purified house air that was humidified by bubbling it through a heated deionized water bath. (This bubbler arrangement was found to be ineffective for humidifying the air at temperatures greater than 60°C. It is being replaced with a micropump-vaporizer system which will supply a constant precise amount of vaporized water to a carrier gas (air), which is then fed into the reaction chamber.)

Test specimens were made of AISI 1020 carbon steel plate, which was machined into rectangular specimens (3.8 cm x 1.3 cm x 0.16 cm). The specimens were cleaned and degreased in isopropanol. Care was taken not to inadvertently contaminate the specimens prior to insertion into the reaction chamber.

The test parameters (time, temperature, specimen weight gain, and relative humidity) were recorded and stored electronically.

RESULTS AND DISCUSSION

The weight gain of specimens at 65°C was recorded as a function of time and relative humidity. The results are shown in Fig. 1. At relative humidities up to 75% weight gains were small and gradual, but did increase with increasing relative humidity. At relative humidities above 85% the weight gain was initially rapid, but then increased at a more gradual rate after the rapid rise.

These results indicate that at relative humidities above 75-85% aqueous film electrochemical corrosion is operational over the carbon steel surface. The value of the critical relative humidity in the 75 to 85% range is similar to that which has been determined for ambient temperature studies for carbon steels [1].

Visual examination of the specimens showed that those which were exposed to the higher relative humidities were covered with a uniform reddish-brown oxide, while those which were exposed to the lower relative humidities looked to be unoxidized. Examination with an optical microscope at higher magnification showed that for the specimen oxidized at RH > 85%, there were small uniformly scattered regions which were not oxidized to a significant extent and that underneath the reddish-brown oxide was a black oxide. For the specimens oxidized at RH < 75% the faces of the specimens showed no indication of oxidation, however the edges of the specimens tested at 65 and 75% RH had characteristics similar to those of the specimens oxidized at the higher RH, that is, an outer layer of the reddish-brown oxide and an inner layer of black oxide.

The reddish-brown oxide was powdery and non-adherent, and could be easily removed by light brushing of the surface. The inner black oxide appeared to be without cracks; however, it must be pointed out that black oxide was not continuous across the entire surface and the extent of oxidation was not extensive.

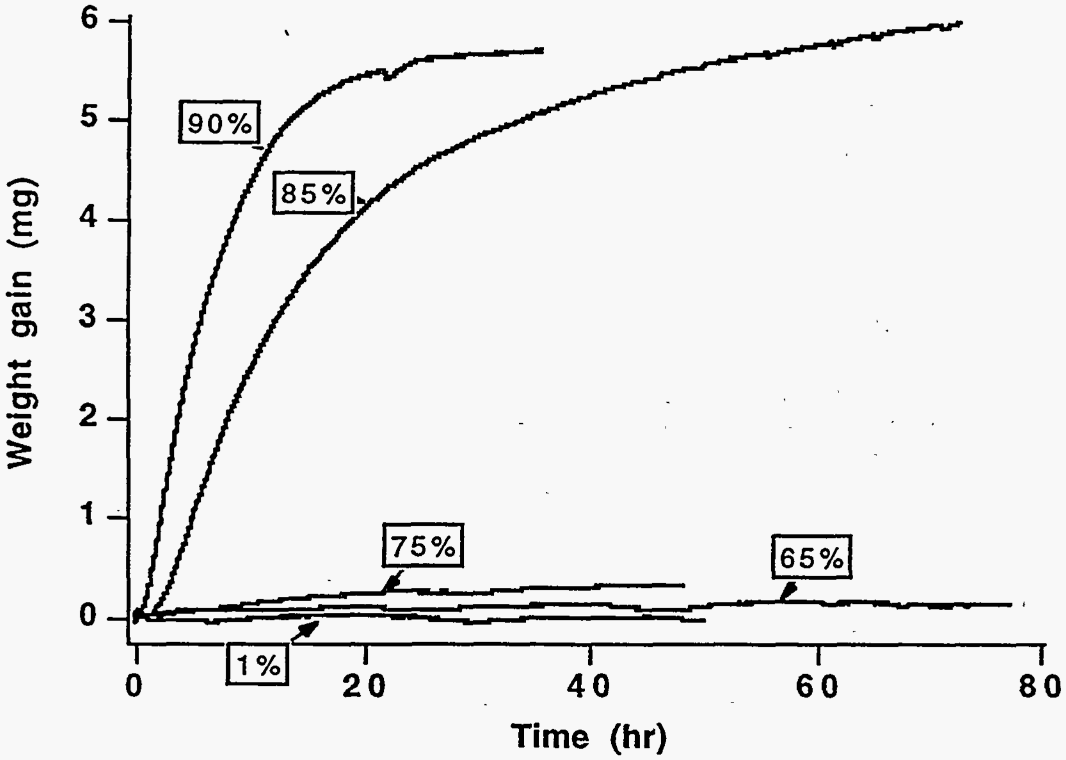

Figure 1. Weight gain of AISI 1020 carbon steel specimens as a function of time in atmospheres of air at various relative humidities at 65°C.

The inner oxide layer is assumed to be Fe_3O_4 and the outer layer Fe_2O_3 or $Fe_2O_3 \cdot xH_2O$. This identification is consistent with assignment by color; magnetite, Fe_3O_4, is black, Fe_2O_3 is reddish-brown to black, and $Fe_2O_3 \cdot xH_2O$. reddish-brown [6]. This assignment is also consistent with the higher oxidation state metal being at the gas oxide interface. Confirmation of this preliminary qualitative identification of the oxides by other surface analytical techniques is planned.

The slowing of the oxidation rate with time after the initial rapid oxidation for the RH > 85% indicates that the oxide formed was somewhat protective. The structure of the oxide layer suggests that the protective oxide is the black oxide, since the reddish-brown oxide has the powdery structure and would not be expected to be protective.

The susceptibility of the edges of specimens to more rapid oxidation/corrosion indicates that surface structure can enhance the susceptibility to oxidation. The faces of the specimens were polished to a finish of better than 64 microinches roughness average, while the edges were just deburred after cutting. The edges therefore will have a rougher texture with more potential sites for water adsorption, and hence greater susceptibility to aqueous film electrochemical corrosion. A more in depth investigation of surface texture on the critical relative humidity is planned.

CONCLUSIONS

This study was aimed at characterizing of the effect of water vapor on the oxidation / corrosion of carbon steel as a function of elevated temperature. In particular a "critical relative humidity" of 75-85% was determined at 65°C. The study suggests that surface roughness may lower the value of the critical relative humidity. The aqueous film electrochemical corrosion resulted in an oxide layer consisting of an inner layer of a black oxide (Fe_3O_4) and an outer layer of a reddish-brown oxide (either $Fe_2O_3 \cdot xH_2O$ or Fe_2O_3).

Future studies will include an extension of the characterization to temperatures up to 100°C and consideration of other factors that may affect the value of the critical relative humidity, such as, gas phase contaminants, surface contaminants (such as, salts), and surface condition (e.g. previously oxidized, scratched).

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