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Corrosion of Aluminum Alloys in Simulated Dry Storage Environments (U)

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CORROSION OF ALUMINUM ALLOYS
IN
SIMULATED DRY STORAGE ENVIRONMENTS

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ABSTRACT

The effect of temperature and relative humidity on the high temperature (up to 150°C) corrosion of aluminum alloys was investigated for dry storage of spent nuclear fuels in a closed or sealed system. A dependency on alloy type, temperature and initial humidity was determined for 1100, 5052 and 6061 aluminum alloys. Results after 4500 hours of environmental testing show that for a closed system, corrosion tends to follow a power law with the rate decreasing with increasing exposure. As corrosion takes place, two phenomena occur: (i) a hydrated layer builds up to resist corrosion, and (ii) moisture is depleted from the system and the humidity slowly decreases with time. At a critical level of relative humidity, corrosion reactions stop, and no additional corrosion occurs if the system remains closed. The results form the basis for the development of an acceptance criteria for the dry storage of aluminum clad spent nuclear fuels.

Keywords: spent nuclear fuel, aluminum alloys, corrosion, dry storage, humidity, temperature

INTRODUCTION

Many research and test reactors including the Savannah River Site production reactors are operated using aluminum clad nuclear fuel elements. Following irradiation, the spent fuel is put in wet basin pools for storage and to cool. Various options exist for interim storage of the spent fuel prior to ultimate disposition in a geologic repository. One option is storage in a dry cask until a final decision is made on its ultimate disposition path. This option is being studied within the U.S. Although some zircaloy clad commercial power reactor spent fuel is being stored using this method, aluminum clad fuel has been placed in dry storage only on a limited basis. A technical basis for dry storage of commercial zircaloy clad fuel has been established; however, they are not applicable to the high enriched aluminum clad fuels from either research and test reactors or from Savannah River production reactors due to differences in the characteristics of the fuels. A technical basis is thus required in order to establish the acceptance criteria for long-term interim storage of aluminum clad fuels.[1-4]

Degradation of the spent fuel due to corrosion of the aluminum cladding alloy is a major concern for dry storage when corrosive environments exist. Under ideal conditions, where all moisture and oxygen are excluded from a sealed storage container and the temperature is limited, aluminum fuels can be stored without oxidation. Achieving and maintaining these ideal conditions would be economically prohibitive and virtually indefensible; therefore, limited degradation of the aluminum cladding must be part of any dry storage acceptance criteria. The state of the fuel must be predictable from corrosion models to establish that the degradation is within acceptable limits for the extended storage periods. Further, any spent fuel storage facility in today's regulatory environment will require validation and verification that acceptable conditions exist and can be maintained throughout the storage period. Consequently a corrosion surveillance program will be an integral part of any dry storage acceptance criteria.

This paper details the corrosion behavior of aluminum alloys in various conditions of temperature and humidity in sealed systems. Tests were conducted wherein 1100, 5052 and 6061 aluminum alloy coupons were exposed to temperatures of 120 and 150^{o} C in air with 20% to 100% relative humidity. Exposure times were up to about 4500 hours. The corrosion behavior was characterized qualitatively and quantitatively and the results incorporated into the development of the dry storage acceptance criteria.

BACKGROUND

General Corrosion: General or uniform corrosion is affected by the chemical composition of the corrosive medium, relative humidity, temperature and alloy composition. Water, one of the major components in the atmosphere, condenses on the surface of metals and serves as the electrochemical path for corrosion reactions. The water or moisture content in air can be expressed by its relative humidity (Rh) which is defined as the ratio of the water vapor pressure to the saturation vapor pressure at a given temperature. It is generally expressed as a percent. Water from a humid environment can be deposited on the surface of a metal by condensation and adsorption. The amount of moisture adsorbed varies with the relative humidity and temperature. Volpe[5] determined that, at 20^{o}C in moderately humid atmospheres of about 30% Rh, more than 10 monolayers of water are present on the surface. At 100% relative humidity, the adsorbed layer more than doubled. Investigators[6,7] have also found that there is a critical humidity, between 40% and 70%, below which practically no corrosion occurs at room temperature. The critical value for the relative humidity appears to depend on the electrolyte composition, the previous amount of corrosion and temperature-pressure (as shown in this investigation).

Although aluminum is a very reactive metal, it generally has good corrosion resistance. In air, its stability is primarily due to a thin layer of amorphous or crystalline aluminum oxide which forms rapidly on exposed aluminum surfaces. The molecular volume of the oxide is 1.5 times the volume of aluminum consumed which puts the oxide surface in compression and allows some deformation of the surface without rupturing the oxide film[8]. On continued exposure, a layer of hydrated oxide grows and can have several different crystalline phases depending on the reaction temperature and the presence of water. For example, at temperatures less than about 80^{o}C bayerite ($Al_2O_3.3H_2O$) forms while above 80^{o}C boehmite ($Al_2O_3.H_2O$) forms on the surface of aluminum. These hydrated oxides are reported to be highly porous compared to the layer of amorphous Al_2O_3 [9]. Furthermore, oxygen in air is not necessary for corrosion in a water environment.[10]

Water, present as vapor in the atmosphere, can cause continuous corrosion of aluminum especially at high humidities and temperatures. Water in the atmosphere contains both dissolved solids and gases, particularly in industrial areas. Aluminum compounds that have been found in the corrosion layers include oxides and hydrated variants of sulfates and chlorides. Nitrates have not been detected on surfaces of aluminum exposed to natural environments[11]. The most likely reason is because all nitrates are water soluble and would be leached from the surface by excess water. Also, Nguyen and Foley[12] found that the nitrate ion is reduced by aluminum but not aluminum oxide; thus, interaction with the aluminum substrate occurs when there is a defective oxide surface.

Corrosion Models: The basic corrosion process is well understood at high temperature. Ionic compounds have appreciable ionic conductivity due to Schottky and/or Frenkel defects. Metal cations diffuse interstitially or by diffusion to vacancies in the oxide lattice. Oxidation continues as metallic ions move through the film to the oxide/oxygen interface where they combine to form the metal oxide. The growth rate for general corrosion is related to the weight gain of the material and is proportional to the ion concentration gradient. From this relationship, the general power law follows:

$$W = (C\,t)^n \qquad (1)$$

where W is the oxide thickness or weight gain, C is a constant depending on ion concentration, t is the exposure time, and n is an exponent theoretically equal to 0.5 for parabolic growth. The constant C is related to the concentration of the diffusing species so that its effects may be modeled using the Arrhenius relationship[13]. The resulting equation becomes:

$$W = A\,e^{-Qn/RT}\,t^n \qquad (2)$$

where A is a constant dependent on the material and humidity, Q is the activation energy, R is the universal gas constant, and T is the absolute temperature. Other models used to describe low temperature oxidation include models based on logarithmic and inverse logarithmic laws.

EXPERIMENTAL MATERIALS

The materials used in this study included 1100, 5052 and 6061 Aluminum alloy, respectively. Results from x-ray fluorescence analysis of the 1100, 5052 and 6061 aluminum alloys are compared to the nominal Aluminum Corporation of America (ALCOA) limits in Table I. The 1100 aluminum alloy is a commercially pure material containing basically iron, silicon and copper with other trace impurities. This material has been used as a cladding material for heavy water reactor target elements at the Savannah River Site. Alloy 5052 contains typically 2.5% magnesium and 0.25% chromium. This high magnesium alloy contains alloying elements similar to materials used by some European fuel fabricators for foreign research reactor fuel. Aluminum 6061 is a precipitation hardening alloy containing typically about 1% magnesium, 0.6% silicon and 0.3% chromium. The alloy is used as a cladding material for the HFIR fuel elements in the US and for cladding on other research reactor fuel elements made by Babcock and Wilcox.

The aluminum coupons used in the corrosion tests were obtained from Metal Samples[1]. They were machined from 1100-H14, 5052-H32 and 6061-T6 sheet material and ground on a belt sander to give a 600 grit surface finish. Optical photomicrographs of the three alloys in the as-received condition are shown in Figure 1. The etching solution to bring out the microstructure was a mixture of 90 ml of water and 10 ml of hydrofluoric acid. Elongated grains in the cold worked microstructure for the 1100 and 5052 alloys can be seen in (a) and (b) while equiaxed grains of the solution annealed and aged 6061 are evident in (c). Scanning electron microscopy and energy dispersive x-ray spectroscopy was used to identify the basic composition of the precipitates.

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[1] Metal Samples Co., Munford, AL, 36208

Precipitate compositions consist of (1) aluminum-iron-copper in the 1100 Al, (2) aluminum-iron-chromium in the 5052 Al and(3) aluminum-iron-copper-chromium in 6061 Al alloy respectively.

EXPERIMENTAL METHODS

Corrosion Tests in Capsules: To simulate a dry stainless steel storage cask, corrosion tests were carried out in stainless steel capsules made from 1 1/2 inch diameter pipe caps. The top and bottom caps were machined to fit together for the electron beam (EB) closure weld. Three pins were placed in the bottom cap to hold the aluminum coupons in an upright position, as shown in Figure 2, and to make contact with the capsule. A 1/8 inch diameter stainless steel tube, about 4 inches long, was gas-tungsten-arc (GTA) welded to the top cap so water solutions could be added to the vessel before completely sealing. A square rod about 1/2 inch long was GTA welded to the bottom cap on the outside to hold the capsule in a vice when cutting apart to remove the coupons for corrosion analysis.

A statistical sample of the capsules was helium leak checked prior to sealing and corrosion testing. All of the welded capsules were pressure tested at 200 psi for safety before adding water and final sealing. The proof pressure is greater than twice the expected pressure during corrosion testing at the temperature of 150^{o}C. The volume of the machined pipe caps was measured by filling with water using a burette. The combined cap volumes varied from 67.6 to 74.4 ml. From the volume measurements, the amount of water added to the capsules was determined for starting relative humidities at the test temperature. The calculated water volume ranged from 0.0276 to 0.1617 ml.

Condensate water was used so atmospheric impurities, characteristic to the Savannah River Site, could be included in the test matrix. The water from the atmosphere was obtained using a condensing coil and was collected in a polyethylene bottle. Instrumental chemical analysis for elemental impurities was done using Inductive Coupled Plasma (ICP). Anion analysis was done by Ion Chromatography. The results for elements detected as significant are given in Table II along with pH and conductivity measurements.

All coupons were cleaned before beginning the test using acetone to remove oils and then rinsed thoroughly in distilled water and alcohol before air drying. No attempt was made to remove the oxide layer from the as-received aluminum coupons before corrosion testing. One each of the three types of aluminum samples was put inside a capsule; hence, they were exposed to the same environment. Only one sample was tested at each condition. After assembling and welding the capsules, the appropriate amount of water solution was injected, using a micro-syringe, into the capsules through the stainless tube. To verify that the correct amount of condensed water had been added, each capsule was weighed before and after filling to four-place accuracy. The fill tube was then crimped, and the end of the tube was GTA welded to completely seal the capsule. Also, weighing of the capsules before and after removal from the furnace was used to determine if leaks occurred during testing. For a closed system, the weight must remain the same.

The tests were conducted for 500, 2000 and 4500 hours at 120^{o}C and 150^{o}C, respectively. After removal of the capsules from the resistance heated oven shown in Figure 3, the caps were separated using a pipe cutter and the coupons removed with plastic tip tweezers. A bottom cap was placed in the oven and weighted along with the capsules each time a set was removed to adjust for any changes in capsule weight due to heating. The coupon was placed in a dessicator for about 15 minutes before weighing. This procedure was used to dry residual water from the sample surface. Each aluminum coupon was weighed three separate times on a 5 place microbalance. The weights were averaged and subtracted from the original weight to obtain weight gain data. Standards were weighed before each sample to verify balance accuracy.

RESULTS AND DISCUSSION

Humidity Conditions for a Closed System: Using the experimental weight gain equations at 100% relative humidity for the aluminum alloys, the change in water vapor and pressure inside a 70 ml vessel was calculated as a function of time at 150 °C.[14] The effect of changing humidity over time was not modeled in this calculation, but corrosion was assumed to take place according to the model developed for a constant 100% relative humidity.[14] It also was assumed (i) that only moisture reacted with the aluminum and (ii) that one coupon each of 1100, 5052 and 6061 aluminum was inside the vessel. Corrosion of the aluminum alloys took place according to the reaction:

$$2Al + 4H_2O \dashrightarrow Al_2O_3.H_2O + 3H_2(gas) \qquad (3)$$

The water vapor and hydrogen gases were assumed to obey the perfect gas law and Dalton's law of partial pressure. The results of the calculations are shown in Figure 4. The water vapor and the relative humidity inside the closed system decreased as a function of exposure time while the hydrogen gas pressure increased to about 3.9 kg/cm^2 (55 psi). After 5.6 years, all of the moisture is depleted from inside the vessel if corrosion reactions continue and eventually corrosion of the aluminum due to moisture stops. Oxygen in the air also contributes to corrosion, but its effect was not modeled in the calculation. At higher temperatures, the time required to deplete the water vapor would be less because of increased corrosion of aluminum.

Corrosion Behavior: The general corrosion, reported in this paper, occurred over about 4500 hours (6 months) of testing in condensed water environments. No pitting corrosion has been observed on the aluminum coupons. X-ray diffraction of the oxide has confirmed that boehmite formed both at 120°C and at 150°C on all test samples.

Weight gain data (micrograms/dm2) for the 1100, 5052, and 6061 aluminum alloys are plotted as a function of time at various initial humidities in Figures 5, 6, and 7, respectively. In the figures, solid curves represent results for different beginning water vapor environments, and the dashed curves represent weight gain calculated for a constant saturated water vapor condition (100% relative humidity) throughout the test.[14] At 100% humidity, the amount of corrosion is clearly less for long exposure times in the capsules (closed systems) when compared to corrosion at constant 100% Rh. Reduced corrosion is due to decreasing humidity with time.

For aluminum alloys, the amount of corrosion is less at lower humidities. For 1100 aluminum, the weight gained, which is a function of the oxide layer growth, was 48,000, 32,000, 4,000 and <500 $\mu gm/dm^2$ for initial relative humidities of 100, 80, 50, and 20% after 4500 hours at 150°C. A value of 1000 $\mu gm/dm^2$ is the uncertainity in the weight gain measurements. This level of uncertainity is consistent for the 20% weight gain measurements. With increasing exposure time, the corrosion rate decreases due to: (i) the formation of a hydrated film to slow corrosion[14] and (ii) the decrease in relative humidity due to the consumption of water in the corrosion reaction.

The effect of temperature on the corrosion of Al alloys was examined. Experimental data for 120°C and 100% initial relative humidity is well below similar data for 150°C in the figures. The results show that corrosion susceptibility decreases from 1100, 5052 to 6061 at these test conditions. It should be noted that there is practically no corrosion of 1100 and 6061 aluminum alloys at 20% relative humidity while only 400 µg/dm2 occurs for 5052 aluminum.

It is also observed that the critical humidity level is lower at 150°C than the reported critical range of 40% to 70% at room temperatue. Corrosion in humid environments is strongly influenced by adsorbed water on the surface film. In a high temperature-pressure system, the partial pressure of water vapor is greater than at room temperature for the same relative humidity. This leads to a larger amount of water adsorbed at a given humidity in the high tempreature-pressure system. Thus the critical humidity where comparative corrosion occurs is lowered in the high tempreature-pressure system.

The metallurgical results from the present study show that a uniform film of boehmite, characteristic of general corrosion, forms on aluminum alloys at 120°C and 150°C in water vapor environments. Uniform growth of the oxide thickness is expected to continue, but it is effected by decreasing humidity inside the closed system. It has been observed that spallation of the oxide takes place when the thickness is greater than about 50 microns.[15]

Corrosion of aluminum alloys in water vapor environments is a function of material type, humidity, and temperature. Decreasing the temperature and humidity lowers the amount of corrosion at any given exposure time. Corrosion reactions deplete the sealed system of water vapor thus continually reducing the relative humidity with time. There exists a critical level of humidity such that corrosion reactions are not significant. Calculations for specific storage conditions (i.e 100% relative humidity, 70 ml volume and 150°C), indicate that the relative humidity could reach 20% after about 3.8 years.

High temperature corrosion of aluminum is reported to follow the power law equation (2). Models fit to the data allow long term predication of corrosion behavior for long term storage of aluminum clad fuel elements. Analysis and extrapolation of this data helps establish that dry storage of Aluminum clad spent nuclear fuel can be safely implemented with a temperature limit of 150°C in high humidity environments. Testing is continuing to define the shape of the corrosion curves so critical parameters in the corrosion model can be determined.

CONCLUSION

Corrosion experiments were performed on 1100 Al, 5052 Al, and 6061 Al alloys at 120°C and 150°C under various relative humidity conditions. The corrosion tests on these materials were conducted for up to 4500 hours. The effects of humidity, temperature and alloy type on corrosion of the aluminum alloys was established. These conditions represent the worst case for storage of spent nuclear fuel where the fuel is stored in a humid air environment. Calculations using experimental data for constant 100% relative humidity conditions show that the corrosion essentially stops after aluminum reactions deplete all moisture from inside a closed vessel. Prior to full consumption of the water species, a critical humidity level occurs which appears to be alloy dependent. For 5052 Aluminum alloy, the critical value is less than 20%; for1100 and 6061 Aluminum alloy, the critical value is greater than 20% but less than 50%.

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Table I

X-RAY FLUORESCENCE ANALYSIS OF ALUMINUM ALLOY MATERIALS FOR CORROSION TESTING AND ALUMINUM COMPANY OF AMERICA COMPOSITION LIMITS

	Element Weight Percent												
Alloy	Si	Fe	Cu	Mn	Cr	Ni	Zn	Ti	V	Ga	Zr	Mg	Al
1100	0.104	0.521	0.128	0.005	0.007	0.009	0.009	0.007	0.008	0.011	0	0.012	99.17
1100 Limits	1.0		0.05 - 2.0	0.05	-	-	-	0.1	-	-	-	-	Bal.
5052	0.116	0.284	0.014	0.022	0.188	0.012	0.011	0.019	0.012	0.013	0.001	2.522	96.78
5052 Limits	0.45		1.0	0.10	0.15 - 0.35	-	-	-	-	-	0.10	2.2 - 2.8	Bal.
6061	0.613	0.497	0.30	0.031	0.228	0.012	0.024	0.012	0.016	0.012	0	1.019	97.23
6061 Limits	0.4 - 0.8	0.7	0.15 -0.4	0.15	0.04 - 0.35	-	0.25	0.15	-	-	-	0.8 - 1.2	Bal.

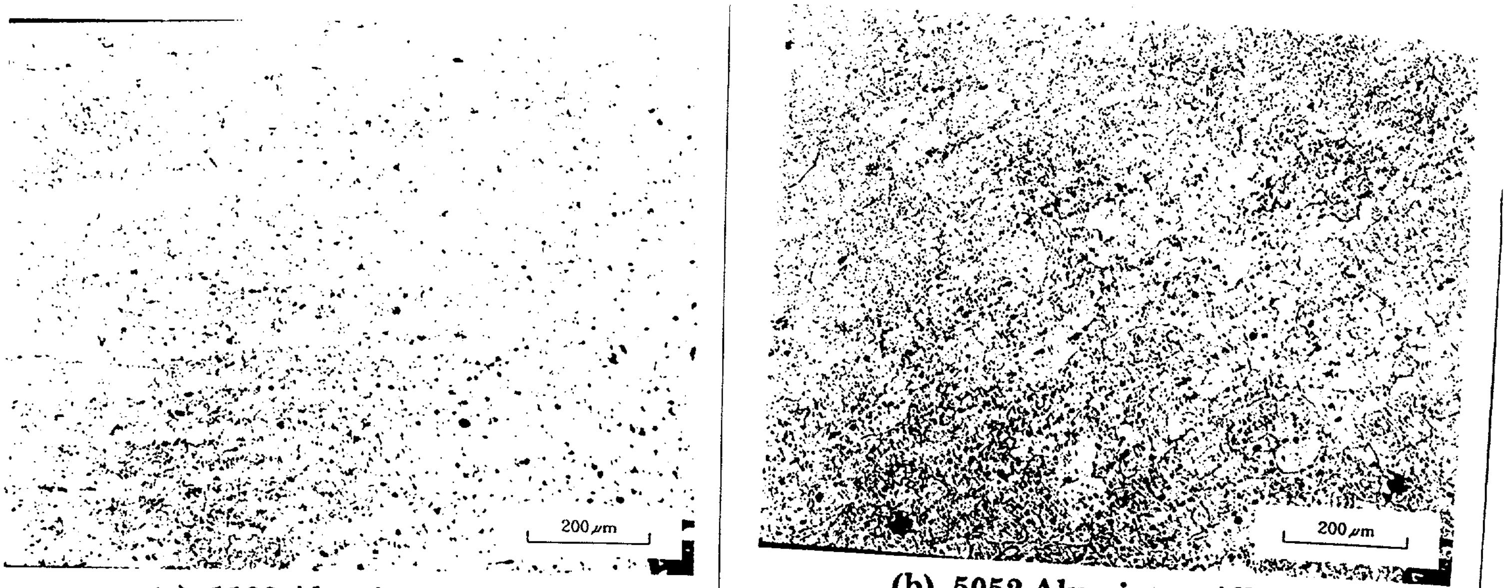
Table II

CHEMICAL ANALYSIS OF CONDENSATE WATER USED IN CORROSION TESTING

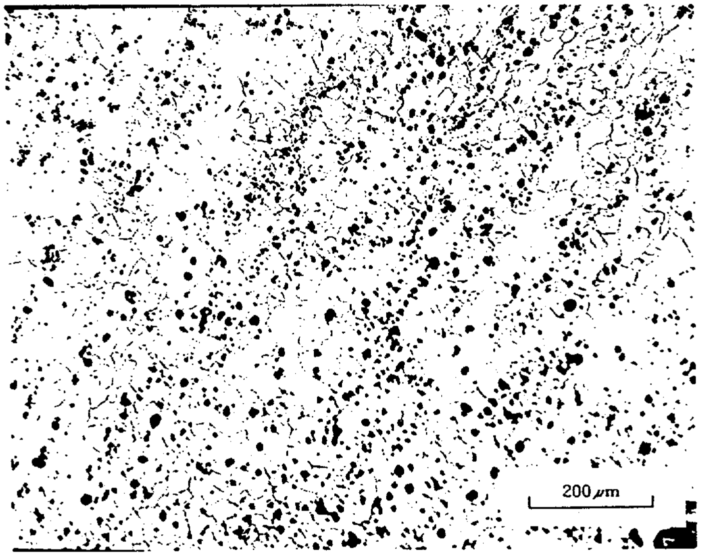
Major Elements	Concentration, ppm
Calcium	1.812
Magnesium	0.423
Manganese	0.131
Zinc	0.493
Iron	0.021
Sodium	7.577
Phosphorus	4.904
Silicon	0.557

Anion	Concentration, ppm
Chloride	1.25
Formate	2.85
Nitrate	<1.5
Sulfate	7.49

Conductivity µmhos/cm	52
Acidity (ph)	6.80



(a) 1100 Aluminum Alloy **(b) 5052 Aluminum Alloy**



(c) 6061 Aluminum Alloy

Figure 1: Optical Micrographs of as-received (a) 1100 Al, (b) 5052 Al, and (c) 6061 Al alloys.

Figure 2: Top and bottom caps of the stainless steel capsules prior to electron beam welding.

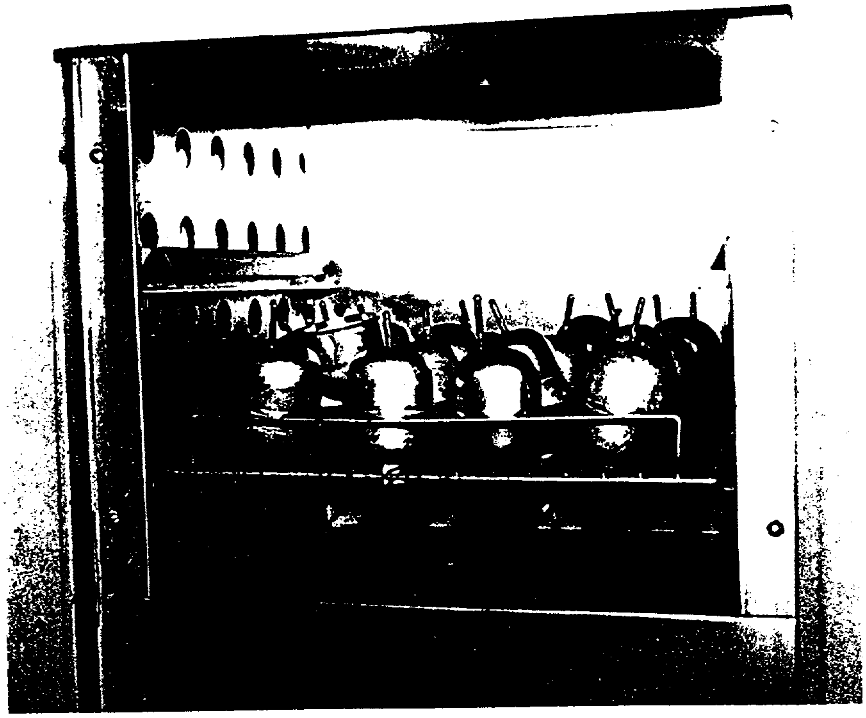


Figure 3: Capsules in the oven during corrosion testing.

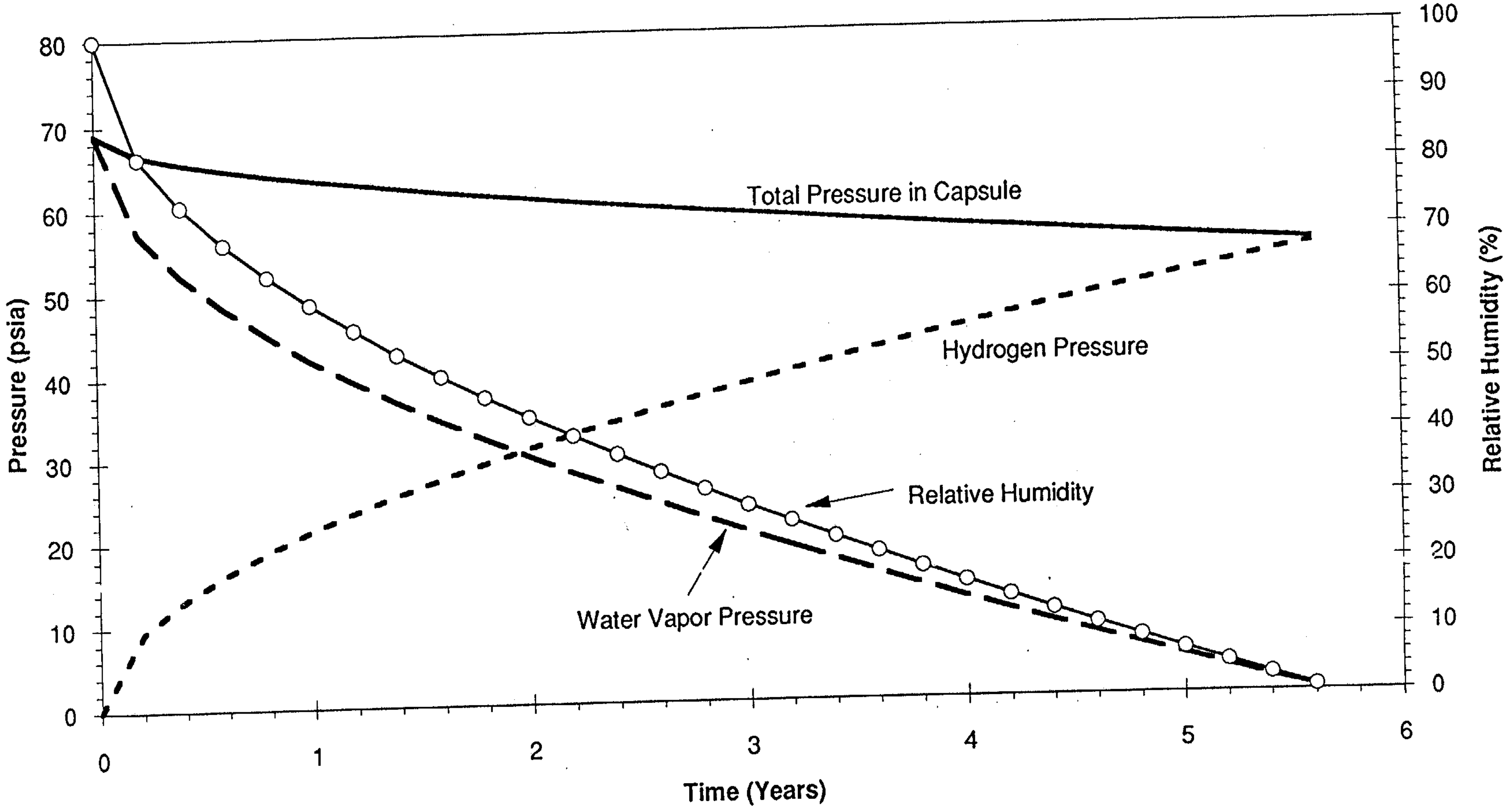


Figure 4: Calculation showing changes in relative humidity, water vapor pressure, and hydrogen pressure due to aluminum corrosion in a sealed capsule.

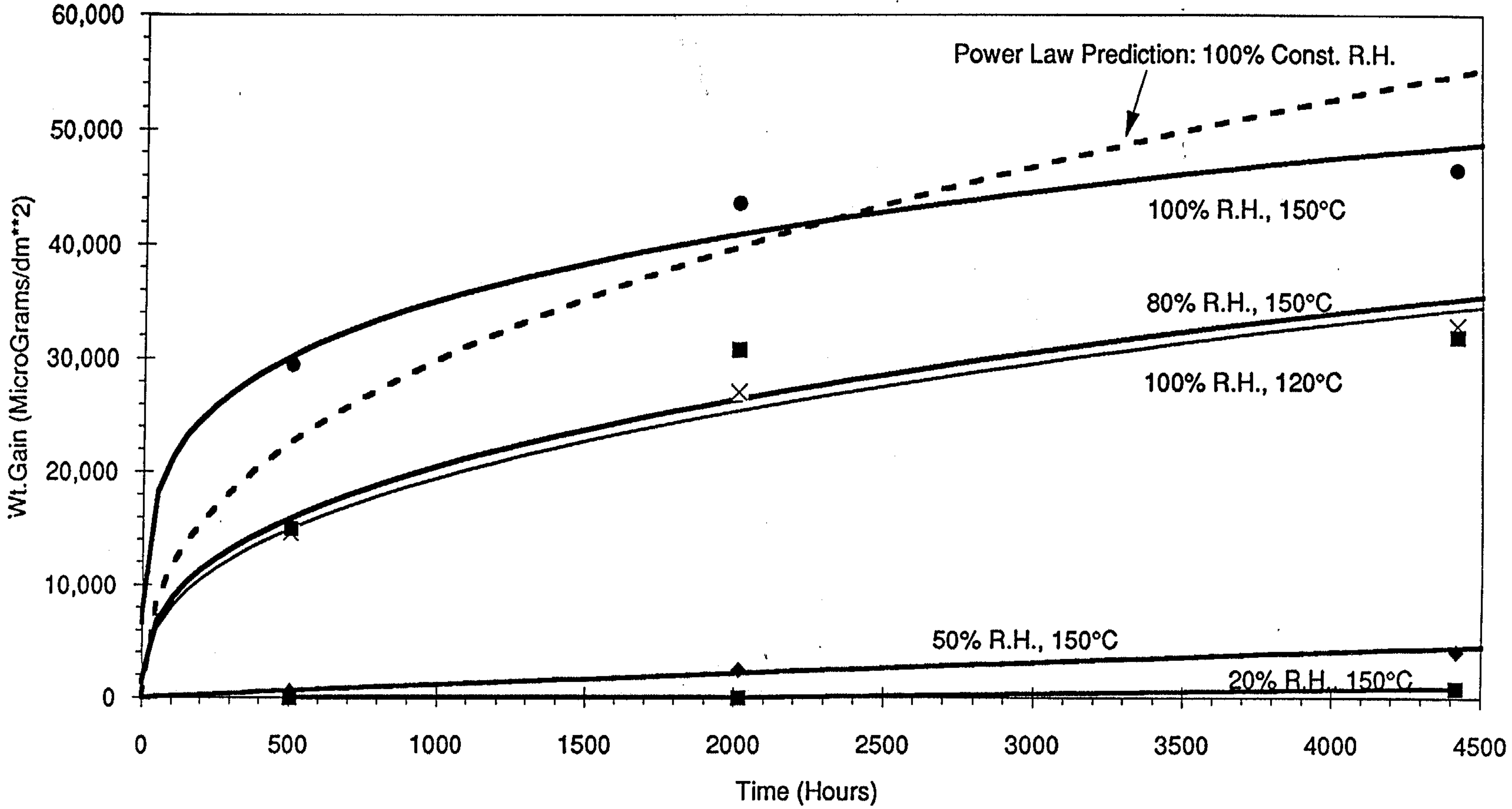


Figure 5: Corrosion of 1100 Aluminum alloy at 20%, 50%, 80% and 100% starting relative humidity in a sealed capsule.

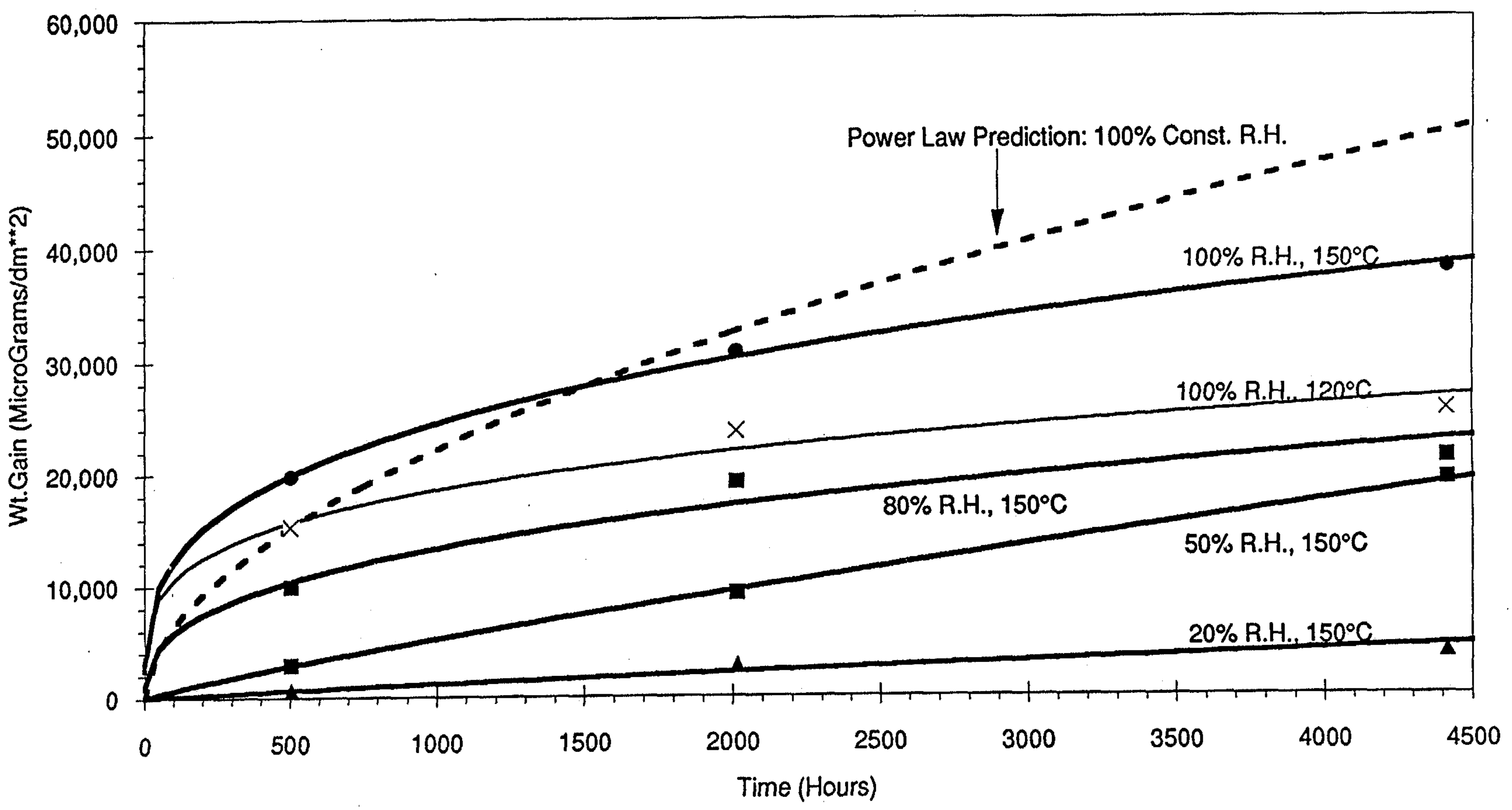


Figure 6: Corrosion of 5052 Aluminum alloy at 20%, 50%, 80% and 100% starting relative humidity in a sealed capsule.

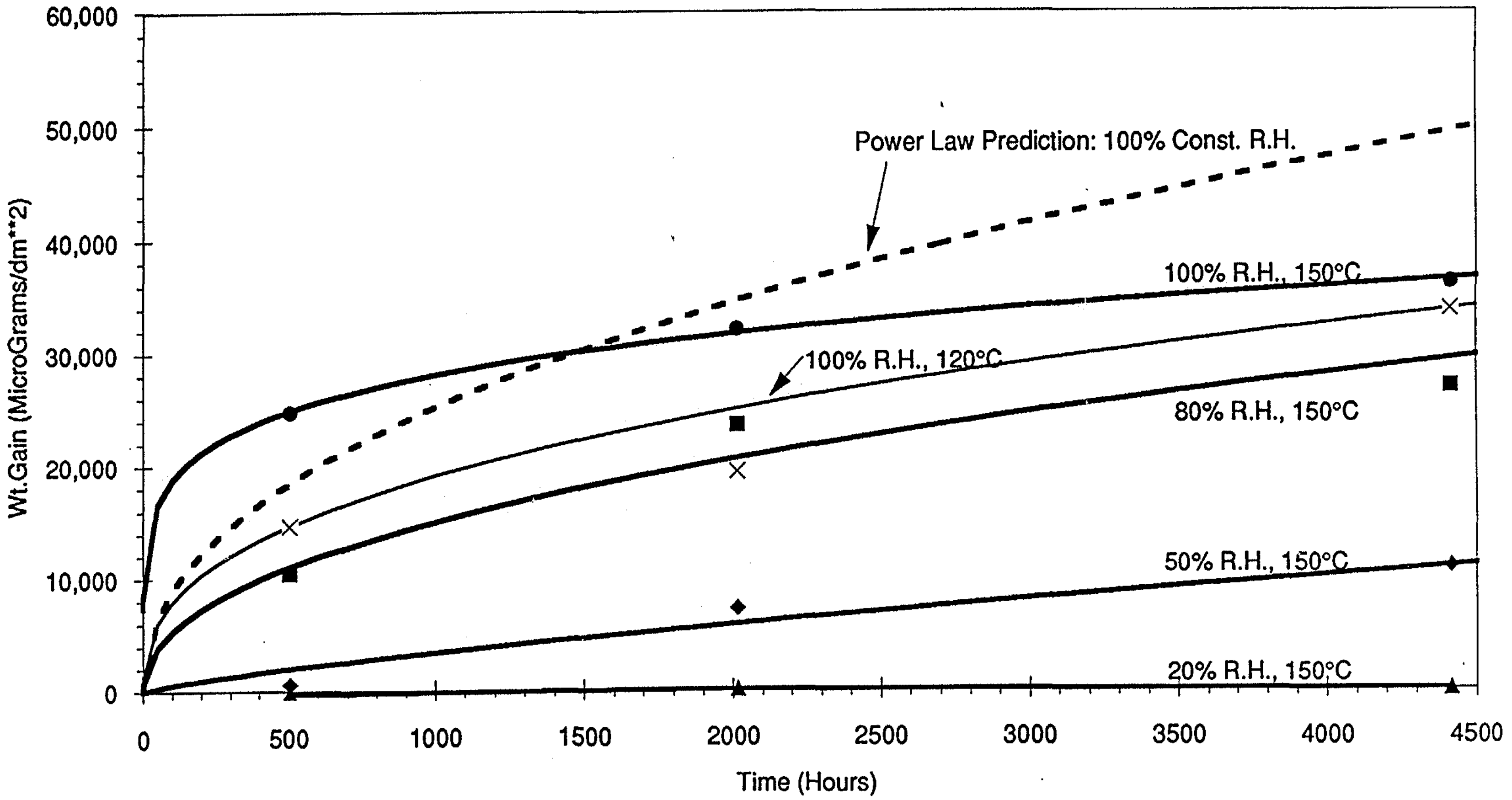


Figure 7: Corrosion of 6061Aluminum alloy at 20%, 50%, 80% and 100% starting relative humidity in a sealed capsule.