STEEL CORROSION IN SUPERCRITICAL WATER: AN ASSESSMENT OF THE KEY PARAMETERS

D. Guzonas[1], J. Wills[1], H. Dole[2], J. Michel[2], S. Jang[2], M. Haycock[2], M. Chutumstid[2]
[1] Atomic Energy of Canada Limited
Chalk River Laboratories, Chalk River, ON, K0J 1J0
[2] Co-op or summer student, Chalk River Laboratories

Abstract

The key variables identified to date that influence corrosion in supercritical water (SCW) are temperature, density (pressure), water chemistry (dissolved oxygen concentration, pH control additives), surface finish and irradiation. Work carried out at Chalk River Laboratories over the past few years has focussed on assessing the relative significance of these variables, excluding irradiation. In particular, the work focussed on studying those variables (e.g., density, chemistry, and surface finish) that had not been examined in detail in the supercritical water-cooled reactor (SCWR) literature. A large matrix of tests were performed using 304 stainless steel.

The data suggest that surface finish can have as large an effect as temperature on the corrosion rate. The magnitudes of the effects of varying the water chemistry (including oxygen concentration and pH) and water density are similar, and smaller than those of surface finish and temperature. These results are being used to develop strategies for further, longer-term testing.

1. Introduction

The idea of using a supercritical water (SCW) coolant in a water-cooled nuclear reactor dates back to the 1960s [1, 2], although no such reactor was ever built. More recently, two types of supercritical water-cooled nuclear reactor (SCWR) concept have evolved from existing light water reactor (LWR) and pressurized heavy water reactor (PHWR) designs: (a) a number of designs [3-5] consisting of a large pressure vessel containing the reactor core, analogous to conventional pressurized water reactor (PWR) and boiling water reactor (BWR) designs, and (b) designs with distributed pressure tubes or channels containing fuel bundles, analogous to conventional CANDU® nuclear reactors [6]. The balance-of-plant is typically a direct-cycle design (although indirect concepts have also been considered) and the out-of-core portions of both concepts are similar to existing fossil-fired power plants.

The SCWR will have core outlet temperatures well above the thermodynamic critical point of water (374ºC, 22.1 MPa), with an operating pressure of 25 MPa and an outlet water temperature up to 620ºC (Figure 1). Peak fuel cladding temperatures could be as high as 850ºC in some designs [7]. Aside from the design concept itself, the most important technical issues to be overcome in the development of an SCWR are likely to be the identification of materials for in-core and out-of-core components and the identification of an appropriate coolant chemistry. In the various SCWR concepts, the coolant passes through the critical point at some location in the reactor core. The corrosivity of SCW varies widely depending upon the values of properties such as the density, ion product and dielectric constant, as well as on the nature of any solutes present (impurities, dissolved oxygen) and their concentrations [8]. At the low coolant density (~0.1 g/cm^3) expected at the core outlet of an SCWR, SCW is a weakly polar solvent able to dissolve gases such as oxygen to complete miscibility. While the solubility of ionic species is expected to be extremely low under these conditions, the formation of neutral complexes increases with temperature, and can become important under near-critical and supercritical conditions.

A substantial number of studies of material behaviour under proposed SCWR conditions have been carried out in the past few years. There have been a number of reviews of corrosion and stress corrosion cracking (SCC) in SCW (for example, see Reference [9]), and therefore a detailed review will not be given here. In addition, there has been significant industry experience with the use of SCW in non-nuclear power generation, with about 269 GWe (462 units) of installed capacity in fossil-fired SCW power plants worldwide as of 2004. Based on experiences from LWRs, PHWRs, fast reactors and supercritical water-cooled fossil fired plants [10], candidate alloys for an SCWR include austenitic stainless steels, corrosion-resistant ferritics (e.g., HT-9), advanced ferritic/martensitics such as oxide dispersion strengthened (ODS) alloys, and precipitation-hardened Ni-based alloys. Recently, data from corrosion studies on T23, P91, P92, MARB2, SAVE 12, VM12, Alloy 214, 347HFG, 304H, SUPER304H, Alloy 800HT, Nimonic 263, 20-25+Nb, CCA617, SAVE 25, Alloy 230, HR6W, Alloy 740, RA602CA, HR-120, and 310HCbN have been reported [11]. In addition to the operating experience and research in support of fossil-fired SCW plants, a large amount of data on materials degradation in SCW was acquired in the development of supercritical water oxidation (SCWO) processes. While the chemistry conditions in these tests are generally not of direct relevance to an SCWR, typically being acidic with high concentrations of aggressive species such as chloride, these data do provide some insights into the key parameters affecting corrosion phenomena in SCW [8]. A recently compiled database of all of the relevant corrosion data [12] contains some data for about 90 alloys. However, in spite of information available from current reactor designs, modern boiler technologies and research in support of SCWO, significant gaps still exist in our understanding of the corrosion properties of materials under proposed SCWR operating conditions.

2. An Assessment of the Key Variables

Table 1 lists the key variables identified to date that influence corrosion in SCW. Our recent work has focussed on assessing the relative significance of these variables, in particular those that had not been examined in detail in the SCWR literature (e.g., density, chemistry, surface finish). Over 20 experiments have been performed to characterize the corrosion of type 304 stainless steel under various test conditions; although this alloy is not a primary candidate for in-core materials, it is a good model alloy and has a corrosion rate in SCW sufficiently high to obtain a measurable corrosion response in a relatively short period of time. Note that the effects of irradiation have not been studied in this work.

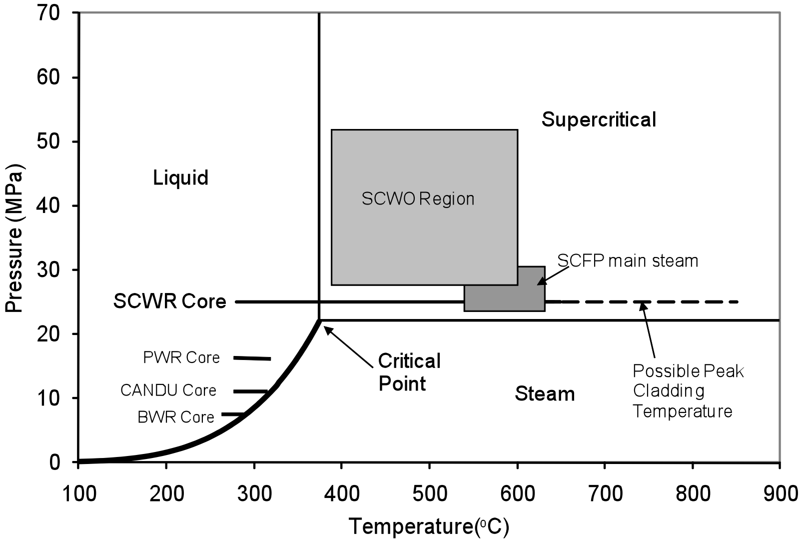

Figure 1: Temperature-pressure phase diagram of water. The operating regions of present BWR, PWR and CANDU plants and of proposed SCWR designs are indicated. Also shown are the main steam conditions for supercritical fossil-fired boilers (SCFP), and operating conditions for supercritical water oxidation (SCWO) processes. Adapted from [13].

Table 1
Key variables identified to date that affect corrosion in SCW

Variable	**Comments**
Temperature	280 – 650ºC
Water density (pressure)	0.1 – 0.8 kg/m^3
Dissolved oxygen concentration	0-8 ppm (saturation concentration at room temperature in air; the concentration will be higher in SCW)
Water conductivity	Neutral water, various additives (see next item)
Concentrations of additives	e.g., pH control agents (NH_3, LiOH)
Surface finish	e.g., mechanical polishing, shot-peening
Irradiation	-

The tests were performed in one of two static autoclaves: a 260 mL Hastelloy C autoclave suitable for operation up to 500°C, or a 500 mL Alloy 625 autoclave rated for operation at temperatures up to 650°C. The coupons were suspended on electrically insulating coupon trees. When required, the water was purged with helium to remove oxygen. Additional details on the test methods can be found in [14].

Figure 2 plots all of the weight change data from these experiments using 304 SS as a function of the test temperature. Although there is considerable variation among the data, there is a clear increase in the weight gain with increasing temperature. It is also clear that the temperature and surface finish have the strongest effect on the weight gain relative to the other variables studied (density, water chemistry).

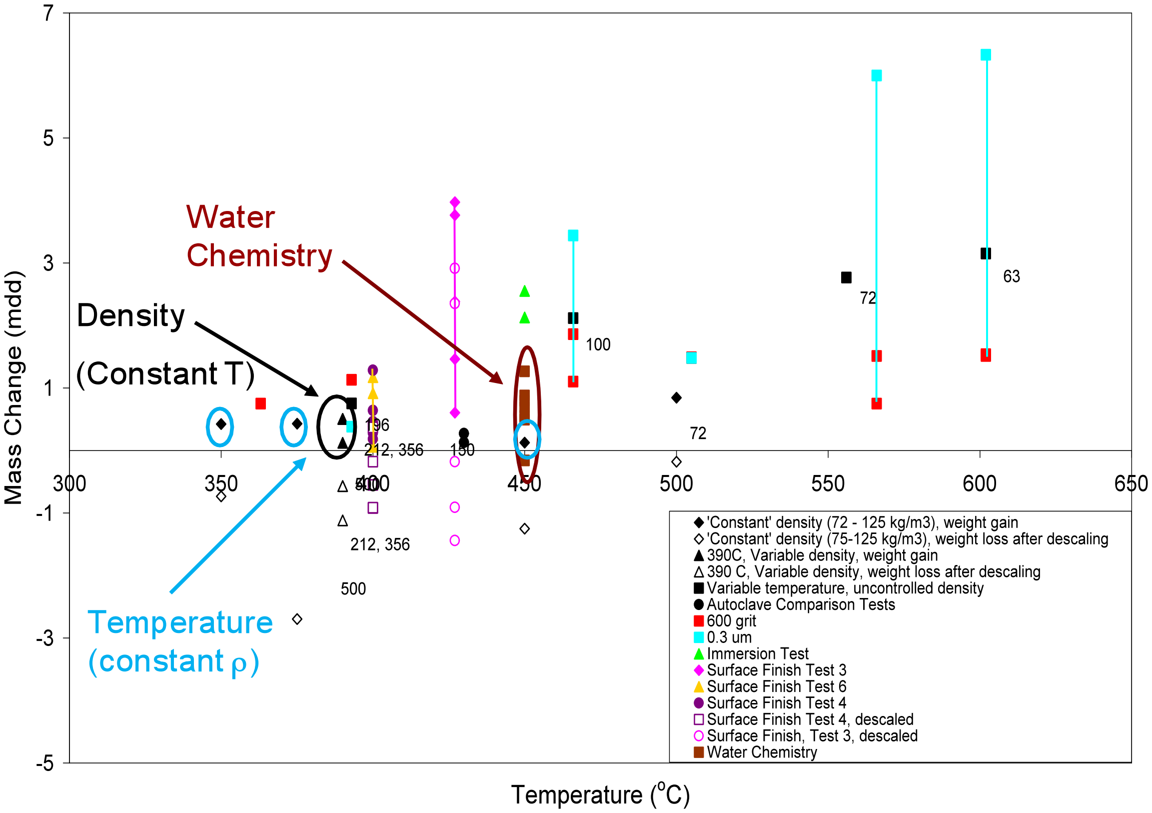

Figure 2 Mass change versus temperature from all experiments at AECL using 304 SS, in units of mg/dm^2/day (mdd). Filled symbols are weight change before descaling; open symbols are weight change after descaling.

Temperature

Of the variables listed in Table 1, temperature has been the most extensively studied, and a detailed exposition of the effect of temperature on corrosion in SCW can be found in [9]. Generally, temperature has been found to have the greatest influence on oxidation/corrosion of materials. With an increase of exposure temperature, the weight gain associated with oxidation typically increases significantly. However, in most of these studies the SCW density was not controlled, making it difficult to separate the effects of temperature (increase in the reaction rate) from those of water density (change in solvent properties). While corrosion studies performed in support of the development of SCWO systems suggested a maximum in the corrosion rate at temperatures around the critical point, where the water density changes significantly [15], most measurements of the corrosion rate under SCWR conditions do not clearly show this effect. However, the data presented in Figure 2 suggest that the weight loss may pass through a local maximum around the critical temperature.

Density

Figure 3 shows the variation of the density of water as a function of temperature at a pressure of 25 MPa. The density of SCW decreases rapidly at temperatures around the pseudo-critical temperature; above about 450ºC, the density can be considered to be constant. As a result, the dependence of the corrosion behavior of materials on the density is only important for in-core components.

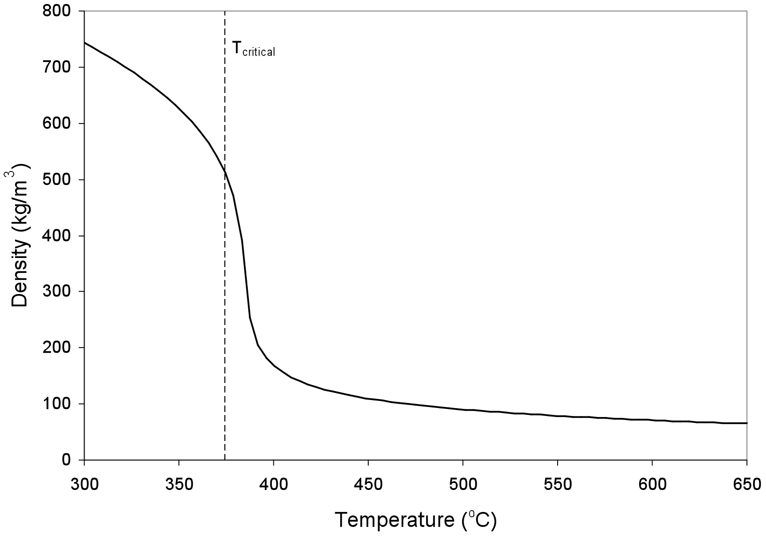

Figure 3 Variation in water density as a function of temperature at a pressure of 25 MPa.

Figure 4 shows the effect of water density on the corrosion of 304 SS at a temperature of 390ºC. Both the weight change and the weight loss of the descaled coupons are shown. The data suggest that the corrosion rate changes little at densities between 200-300 kg/m^3, but increases at higher densities. This may be due to a change in corrosion mechanism (Figure 5). At higher water densities (and higher dielectric constants), an electrochemical mechanism, involving the formation and dissolution of a surface film, is expected to dominate [16, 17]. Below some threshold water density, it has been proposed that the dominant mechanism changes to one based on molecular interactions of the metal with oxygen and/or water and the transport of cation and anion defects in the oxide. Betova et al. [18] concluded that at temperatures up to 500ºC, the oxidation of stainless steels proceeds in a manner analogous to that in high temperature sub-critical water, whereas at higher temperatures the oxidation kinetics seems to be closer to that observed in water vapour. The data shown in Figure 4 are consistent with that conclusion. Yi et al. [19] concluded that corrosion in SCW was similar to corrosion under gaseous conditions, where oxide formation occurs without metal dissolution.

In addition to possible changes in corrosion mechanism, the solubility of the corrosion film may change as the density changes. Although the dependence of the solubility on pressure is generally very weak in the subcritical region, the effect of pressure on the solubility of corrosion products can be significant in SCW. In general, the solubility of oxides usually increases with increasing SCW density [20].

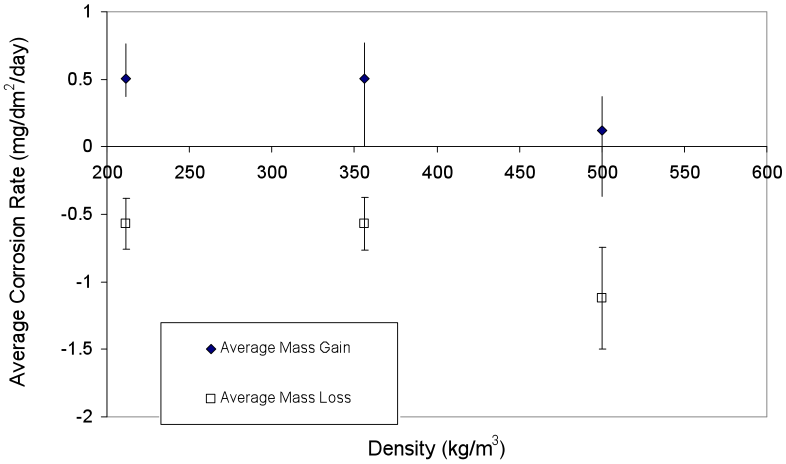

Figure 4 Measured weight gain and weight loss after descaling as a function of water density at a constant temperature of 390°C (variable pressure).

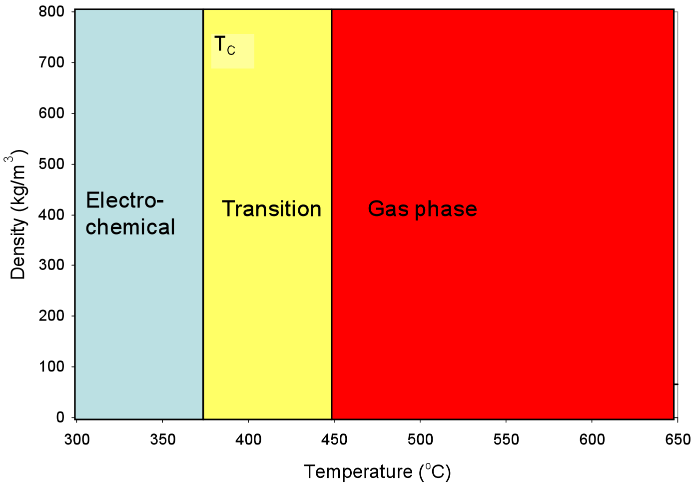

Figure 5 Postulated changes in corrosion mechanism in SCW as a function of temperature and SCW density. The corrosion mechanism(s) in the transition region near the critical temperature (T_c) have not been studied in detail.

Water Chemistry (Including the Effect of Dissolved Oxygen Concentration)

Potential water chemistry issues in an SCWR have recently been reviewed [21, 22]. The dissolved oxygen concentration in fossil-fired SCW plants is controlled to minimize the corrosion of feedwater components. Several water chemistry regimes are typically used in fossil-fired SCW plants [23, 24, 25, 26]: ammonia-hydrazine, hydrazine only, neutral pH plus added oxygen (oxygenated treatment (OT)), and the combined treatment, consisting of injection of oxygen or hydrogen peroxide into the feed water to give 50-300 µg/kg dissolved oxygen plus addition of ammonia to give a pH between 8.0 - 8.5 at room temperature. Most recent materials testing for the SCWR have used neutral water and low concentrations of dissolved oxygen, similar to the oxygenated treatment use in fossil-fired SCW plants. In addition to control of feedwater oxygen, it will be important to control (or at least, predict) the dissolved oxygen concentration in an SCWR to minimize corrosion of downstream components.

There are some data on the effects of dissolved oxygen concentration on the oxidation behavior of candidate SCWR materials. For the ferritic-martensitic alloy HCM12A, the weight gain at 500°C decreases with increasing dissolved oxygen concentration between 10 and 200 ppb. At much higher dissolved oxygen concentrations (2000 ppb), the weight gain increases considerably above that experienced between 10 and 200 ppb [9]. This dependence of oxidation on dissolved oxygen concentration is exploited in the fossil-fired energy industry; OT chemistry control [23, 26] involves addition of small amounts of oxygen to the feedwater. The effect of dissolved oxygen concentration on oxidation of austenitic steels does not demonstrate such a clear trend.

To assess the possible use of other water chemistries in an SCWR, AECL has performed a series of experiments to examine the effects of water chemistry on the corrosion of 304 SS in SCW. The test conditions examined are listed in Table 2.

Table 2: Test matrix used in the AECL water chemistry studies

Water Chemistry	pH (25°C)	Details
Low Oxygen[a]	-	Neutral pH, < 300 ppb dissolved oxygen
High Oxygen	-	Neutral pH, ~8 ppm dissolved oxygen
Hydrazine + Ammonia	8.5 - 9.0	Contains 0.7 - 1 mg amine/kg
Hydrazine + Ammonia	9.1 - 9.5	Contains 0.7 - 1 mg amine/kg
Combined mode	8.0 - 8.5	< 300 ppb dissolved oxygen plus ammonium hydroxide
LiOH	9.0	< 300 ppb dissolved oxygen

[a] – similar to the oxygenated treatment

Figure 6 shows the corrosion rate (from weight change) measured for each of the chemistries studied. The lowest weight change was obtained using the combined mode chemistry. Note that the concentration of dissolved oxygen had only a small effect on the corrosion.

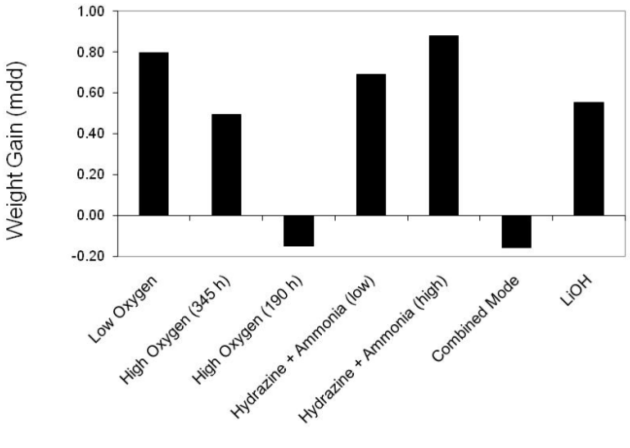

Figure 6 Weight change (not descaled) for 304 SS in SCW at 450ºC in various water chemistries (listed in Table 2).

Figure 7 shows the metal release from the autoclave and suspended coupons for several of the chemistries studied. The highest metal release was obtained using water chemistries that contained ammonia, possibly due to the formation of iron-ammonia or nickel-ammonia complexes in solution [27]. There appeared to be a linear relationship between the oxide thickness (as determined by Scanning Auger Microscopy (SAM)) and the concentration of ammonia (Figure 8). Note that there was not a large difference in the weight change for oxygenated versus deoxygenated SCW. It should be noted that LiOH may be a viable pH control agent in an SCWR [27].

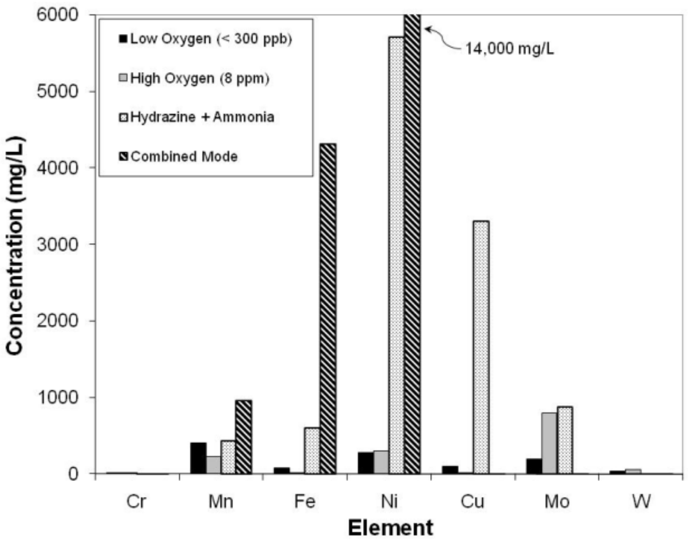

Figure 7 Metal release from 304 SS coupons and Hastelloy C autoclave in SCW at 450ºC in various water chemistries (listed in Table 2). The surface area of the autoclave exposed to SCW is much larger than the surface area of the corrosion coupons.

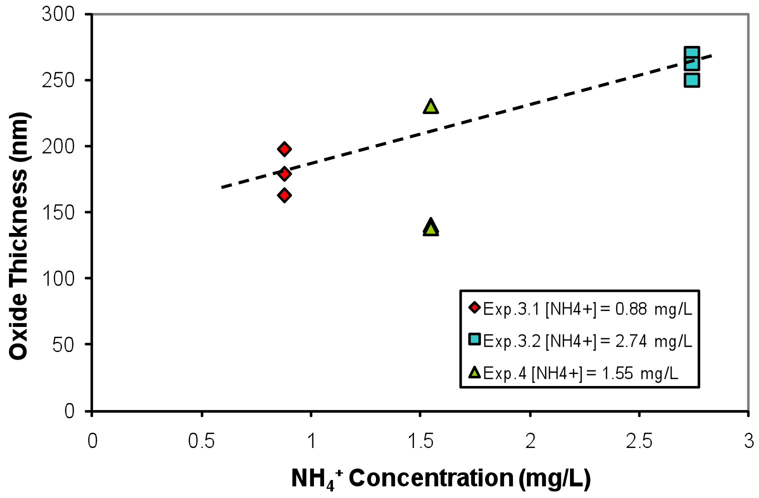

Figure 8 Correlation between oxide thickness (determined using SAM) and the concentration of NH_4^+ (determined after the experiment by ion chromatography).

2.1 Surface Finish

The effects of the method of surface preparation of corrosion coupons on the corrosion rate in SCW has received only limited attention in recent investigations, although the effect has been known for decades. For example, Ruther et al. [28] reported that surface preparations that left a strain-free surface resulted in much higher corrosion in superheated steam than surface preparations that severely work the surface. This effect was attributed to higher chromium diffusivity for mechanically worked surfaces.

Tan et al. [29] reported the effects of surface finish on corrosion. They noted that since diffusion is critical to oxide growth and grain boundaries are fast diffusion pathways, one way to influence oxidation rates is to change the grain size. They found that the weight gain was reduced by about 30% by both Equal Channel Angular Processing and shot-peening treatments, and the oxide layer formed by corrosion was thinnest in those regions where the bulk metal grains were the smallest. Sarver [11] reported that mechanical surface treatments were the most effective treatments in improving the steamside oxidation behavior of candidate alloys for 4000 h exposures to supercritical steam. Both methods, shot peening and deep rolling, cold work the surface of the materials. The resulting cold-worked microstructure permits fast diffusion paths to the surface of the material, allowing a thin, protective chromium oxide to form quickly. Low-chromium, iron-based austenitic materials given a shot peening or deep roll treatment exhibited greatly reduced oxidation rates and no oxide exfoliation.

Figure 9 shows the preliminary results from the current study on the effects of surface finish on corrosion rate. With the exception of the as received coupons, all coupons were initially polished using 600 grit polishing paper to remove an approximately 30-micron thick layer from all surfaces, using deionized water as the lubricant. Final finishing was as described in Table 3.

Table 3: Details of the surface finishes studied in this work

Experiment ID	Surface Finish
600 grit	As received
1200 grit	Polished using 1200 grit polishing paper.
1 micron	Polished with 1200 grit polishing paper followed by 1-micron alumina.
Autoclave oxide	Coupons finished as above for the 1-micron coupon, then exposed to sub-critical water in an autoclave at 200ºC and ~100 psi for 3 days.
Air oxide	Coupons finished as above for the 1-micron coupon, then placed in a 50ºC oven for three days in air.
Electropolish	As per ASTM A380-06.

After polishing, all coupons were ultrasonically cleaned with acetone and propanol. To prevent further oxide growth prior to use coupons were stored in propanol. Since the polishing process removes any protective surface oxide, some coupons were prefilmed by heating in air at 50°C, by heating in water at 200°C, or by electropolishing. Three sets of tests were performed, with different exposure times in SCW. The coupons that had been prefilmed showed the least variation in corrosion rate with exposure time, while the polished coupons showed a decrease in corrosion rate as a function of exposure time, as the protective film reformed. Further studies of the effects of surface finish are underway.

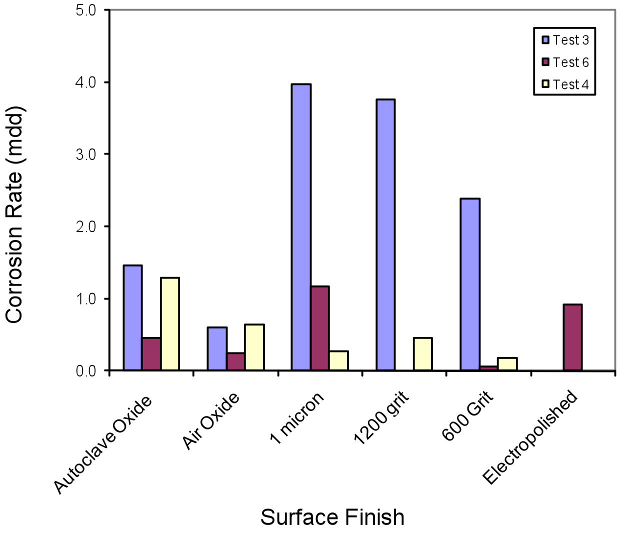

Figure 9 Results of preliminary tests at AECL to examine the effects of surface finish on the corrosion rate of 304 SS. The data are shown in order of increasing exposure time (Test 3 – 170 h, Test 6 –240 h, Test 4 – 336 h).

3. Conclusions

Based on the data presented, the various parameters listed in Table 1 can be ranked as follows, in descending order of relative importance to general corrosion in SCW:

Temperature = Surface Finish > Water Chemistry > Water Density

Note that water conductivity and oxygen concentration are included under water chemistry. In addition, as the effect of irradiation was not studied in this work, it is not included in the ranking. The data suggest that surface finish can have as large an effect as temperature on the corrosion rate. This is consistent with work reported by Sarver [11], who noted a decrease in corrosion rate by a factor of 10-100 for materials that were shot peened or deep rolled. The effects of water chemistry (including oxygen concentration) and water density appear to be of similar magnitude. It should be noted that the effect of fluid velocity on corrosion rate has not been studied systematically in SCW; under very oxidizing conditions the protective chromium oxide film may be unstable, and flow-accelerated corrosion may become possible. Additional, longer duration testing of the effects of all of these variables is required.

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