Oxidation of AISI 304L and 348 Stainless Steels in Water at High Temperatures

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Oxidation of AISI 304L and 348 stainless steels was investigated in water at 1000 – 1350 °C by TGA, SEM, EDS, and Raman spectroscopy. Linear-Parabolic kinetics and multilayer oxide scales with voids were found for both alloys. Based on the experimental results, AISI 304L presented higher oxidation resistance and higher activation energy. Zircaloy-4 kinetic results were used for validation and performance comparison. In severe accidents conditions, stainless steel might lead to a faster hydrogen production comparing to Zircaloy.

Keywords: Stainless steel, Oxidation, Hydrogen, AISI 348, AISI 304L.

1. Introduction

The nuclear industry with universities and research institutes are making great efforts to improve the safety in nuclear reactors by developing Accident Tolerant Fuels (ATF). Although austenitic steel clad operated reliably in Pressurized Water Reactors (PWR), its thermal neutron absorption cross section is a factor of 12–16 times higher than Zircaloy. Therefore, the fuel enrichment penalty incurred by the use of Stainless Steel (SS) cladding became the primary driver for the replacement of stainless steel cladding by Zircaloy cladding in commercial reactors.

Nowadays, zirconium based alloys enjoy a monopoly for the primary driver for the replacement of stainless steel cladding material in Light Water Reactors (LWR). However, the continuous interest on nuclear safety improvement in Nuclear Power Plants (NPP) demands the evaluation the of low-probability events consequences, called Severe Accidents (SA), such as Three Mile Island in 1979 and more recently, Fukushima Daiichi in 2011.

During severe accidents, core cooling might be interrupted. The decay heat and metal-water reaction enthalpy drive the core temperature upward. As the water level decreases and core becomes uncovered, the heat transfer processes become less efficient and the fuel assemblies start to experience physical and chemical degradation, or even melting. Physical degradation occurs first (700–1000 °C) and involves swelling (ballooning) and burst of the thin-walled fuel rod cladding tube. Chemical degradation occurs on higher temperatures (mainly above 1000 °C), depending on the cladding material) and it is dominated by water oxidation reaction, which is highly exothermic.

Once the cladding temperature reaches values above 1204 °C, US-NRC (Nuclear Regulatory Commission) specified Peak Cladding Temperature (PCT) under design basis Loss-of-Coolant Accidents (LOCA), the temperature rises rapidly in the fuel. This rapid increase is due to the very high oxidation rate of zirconium based alloys above 1200 °C in water.

Despite presenting the advantage of neutron economy, zirconium-water reaction generates substantially more energy (-1560 kcal/kg) than stainless steel (from -144 up to -253 kcal/kg). Due to stainless steel higher oxidation resistance, especially at temperature range that could possibly take place in Design-Basis Accidents (DBA), it may present safety advantages. As the melting point of stainless steel is approached at 1370 – 1500 °C, its oxidation rate can become much higher comparing to zirconium based alloys. However, prolonged core uncovery would probably be required to achieve these temperatures.

Many authors have studied the oxidation of stainless steel under high temperature conditions. However, few works have been carried out at temperatures above 1200 °C and in water. The 304 SS appears as the most commonly studied alloy in the literature. When these alloys are exposed at high temperatures, an initial fast period of reaction is followed by a reduction in reaction rate due to the development of a corrosion resistant scale. Considering the application as cladding material, this period of rapid oxidation is important for alloy design and selection.

It is generally observed that the presence of water significantly accelerates the oxidation rate comparing to dry air. Oxidation of Fe-Cr-Ni alloys is highly dependent on Cr content. Chromium levels greater than 20% led to the formation of a protective oxide scale with the associated low diffusion rates through the scale and hence low oxidation rates, comparable with that of pure chromium. Pint et al. showed that 25% Cr was needed to form a protective Cr₂O₃ scale at 1200 °C. Thus, both 304 and 348 SS cannot be considered as an ATF candidate.
Using stoichiometric calculations\textsuperscript{10,17}, hydrogen generation curves may be derived from weight gain models. This study presents kinetic results of AISI 348 oxidation in water at high temperatures and compares its performance against other materials commonly applied in nuclear reactors. The obtained oxidation kinetics model is applicable to predict hydrogen generation in the calculation of a hypothetical LOCA in a LWR employing 348 SS cladding.

2. Experimental

2.1 Sample preparation

Samples in disc formats of AISI 304L, 348 and Zr-4 with dimensions of 22 mm (diameter) x 2 mm (thickness) were studied. Chemical compositions in weight % are given in Table 1.

2.2 Oxidation exposures

Flowing steam was generated by pumping approximately 1.33 mL/min of distilled water into the heating device at 300 °C. Isothermal water oxidation experiments were carried out in a Lindberg/Blue M\textsuperscript{®} furnace connected to a steam generator. During all experiments, the furnace heating rate was set as 15 °C/min. When the furnace temperature achieved the desired value for the test, it remained at this temperature for at least 5 h before the beginning of the experiment.

The weight gain data of the Thermal Gravimetric Analysis (TGA) was obtained by a Shimadzu\textsuperscript{®} analytical balance placed above the furnace. A nickel chrome wire hanged a high alumina crucible where the samples were exposed to water. Once the nitrogen flow was interrupted, the steam was introduced immediately and the oxidation exposure time started to count. All tests had the same duration of 90 min. After oxidation, the steam flow was switched off and the samples were cooled down to room temperature.

3. Results and Discussion

3.1 Oxidation kinetics

The oxidation kinetics results are shown in Figures 1, 2 and 3. Figure 1 shows that AISI 348 presented significant weight

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|}
\hline
Chemical Element & AISI 304L & AISI 348 & Zr-4 \\
\hline
Fe & 71.65 & 68.63 & 0.20 \\
Cr & 18.50 & 17.45 & 0.10 \\
Ni & 8.30 & 10.94 & - \\
C & 0.008 & 0.052 & 0.01 \\
Si & 0.13 & 0.42 & - \\
Mn & 0.90 & 1.61 & - \\
P & 0.008 & 0.017 & - \\
Cu & 0.36 & - & - \\
V & 0.02 & - & - \\
Ta & <0.05 & <0.005 & - \\
Co & 0.05 & 0.023 & - \\
Nb & <0.01 & 0.83 & - \\
S & 0.0025 & 0.003 & - \\
B & 0.0008 & 0.0007 & - \\
N & 0.0055 & 0.018 & - \\
O & - & - & 0.13 \\
Sn & - & - & 1.36 \\
Zr & - & - & 98.20 \\
\hline
\end{tabular}
\caption{Chemical composition in weight %.}
\end{table}

Figure 1. Evolution of the weight gain for AISI 348 at 1100 °C, 1200 °C, 1300 °C and 1350 °C in water.

Figure 2. Evolution of the weight gain for AISI 304L at 1100 °C, 1200 °C, 1300 °C and 1350 °C in water.

Figure 3. Evolution of the weight gain for Zircaloy-4 at 1100 °C, 1200 °C, 1300 °C and 1350 °C in water.
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Table 2. Kinetic parameters of 304 SS models and the proposed model for AISI 348.

| Material / Kinetic Parameter | AISI 348 | 304L SS | 304 SS | 304 SS |
|-----------------------------|----------|---------|--------|--------|
| This study                  |          | Brassfield et al. (1968) | Ishida et al. (1968) | Ishida et al. (1968) |
| 1000 °C ≤ T ≤ 1350 °C       |          | 1000 °C ≤ T ≤ 1375 °C | 900 °C ≤ T ≤ 1200 °C | 1200 °C ≤ T ≤ 1350 °C |
| \( A_0 \) (kg/m²/s)         | 4.85 x 10⁷ | 2.40 x 10⁸ | 7.34 x 10⁹ | 1.85 x 10¹ |
| \( E_A \) (kJ/mol)          | 333-354  | 343-363 | 240-277 | 442-498 |

Table 3. Kinetic parameters of Zircaloy models.

| Material / Kinetic Parameter | Zr-4 | Cathcart-Pawel (CP) | Baker-Just (BJ) |
|-----------------------------|------|---------------------|-----------------|
| This study                  | 119  | 36.22               | 409.97          |
| \( A_0 \) (kg/m²/s)         |      |                     |                 |
| \( E_A \) (kJ/mol)          | 176  | 167                 | 190             |

gain at 1200 °C, whereas Figure 2 shows that AISI 304L presented higher oxidation resistance comparing to AISI 348 at the same temperature. On the other hand, Figure 3 shows that Zircaloy-4 already presented significant oxidation at 1100 °C.

Both SS followed a linear rate law in the in the first 10-30 minutes. After this early linear stage, the oxidation kinetics gradually changed to parabolic. The parabolic scaling kinetics provides indications that local equilibrium was achieved at the scale/gas interface and solid diffusion process tended to be the rate-controlling step.

The data obtained in the experiments with AISI 348 oxidation yielded the parabolic model given by Equation 1.

\[
\frac{\Delta w}{A} = \frac{4.85 \times 10^{7}}{T} \cdot \exp \left( \frac{-41338 \pm 1257}{T} \right) \cdot t
\]

Where \( \Delta w/A \) is mass-gain per unit area (kg/m²), \( t \) is time (s), and \( T \) is temperature (K). For a better fit in the initial 30 minutes, the linear model given by Equation 2 should be used.

\[
\frac{\Delta w}{A} = \frac{1.13 \times 10^{3}}{T} \cdot \exp \left( \frac{-23247}{T} \right) \cdot t
\]

Kinetic models are available in the literature for 304 SS oxidation in water10,15-17. The results for AISI 304L are in accordance with those obtained by Ishida et al.16, where two parabolic equations were proposed to describe the oxidation.

The metal-water kinetics of Zircaloy has been investigated by many authors10,17,20-23. The results for Zr-4 are in accordance with those obtained by Baker-Just (BJ)20 and Cathcart-Pawel (CP)21,23. The slightly higher activation energy and parabolic constants might be due to the higher enthalpy of reaction that could have increased locally Zr-4 temperature accelerating reaction kinetics. Nevertheless, a very similar correlation was found.

The aim of the experiments conducted with 304 SS and Zircaloy was to compare against literature correlations in order to validate the experimental methodology. Tables 2 and 3 compare the kinetic parameters of SS models and Zircaloy models, respectively.

The Arrhenius plot presented in Figure 4 shows that AISI 348 and AISI 304L both have higher activation energy comparing to Zircaloy-4. Figure 5 shows another Arrhenius plot with the proposed model for AISI 348 and its confidence intervals, considering a confidence level of 90%, and compares the results against BJ20 model for Zircaloy metal-water reaction. The results clearly show that due to its higher activation energy, AISI 348 oxidation rate beyond 1200 °C can surpass zirconium based alloys10,11.

3.2 Characterization

After oxidation, samples were cooled down to room temperature and photographed. Figures 6, 7, and 8 show, respectively, the samples of AISI 304L, AISI 348, and
Zircaloy-4 after 1.5 h of oxidation in water at four different temperatures. Despite presenting the highest oxidation resistance at 1100 °C, AISI 304L also showed scale spallation. The spallation debris are highly undesirable as they might accumulate inside the reactor core and block water flow channels during the reflood phase. On the other hand, at 1350 °C, Zircaloy samples broke off during their removal from crucible, indicating embrittlement. Thus, at the temperature that stainless steel would start to melt (1400 °C), Zircaloy might start to lose its integrity.

Cross-section SEM image of AISI 304L oxidized in water at 1300 °C is shown in Figure 9. It shows multilayer oxide scales with voids, containing chromia, spinel, iron and nickel oxides. The innermost spinel thick layer, which is separated from the external magnetite layer by voids, shows excellent contact at the scale/metal interface. On the other hand, the magnetite layer, identified by Raman spectroscopy, might break off due to scale spallation.

The Cr content plays an important role on the oxidation resistance of stainless steels. The diffusion of Cr from the steel bulk to the oxide scale is temperature dependent. Fine grain size improves oxidation resistance by increasing the supply of Cr to the surface. The ability of an alloy to endure Cr vaporization without losing the protective properties of the oxide is expected to be dependent on the rate of supply of Cr from the alloy to the oxide scale. Austenitic steels, such as 304 and 348 can experience accelerated Cr loss and oxidation rates due to the formation of a volatile oxy-hydroxide, CrO\(_2\)(OH)\(_2\). Although both AISI 304L and 348 contains ~18% Cr, these alloys are unable to form a protective Cr-rich oxide in water at these temperatures. EDS maps for Fe, Cr, and Ni may be visualized in Figures 10 and 11 for AISI 348 samples exposed in steam at 1100 °C and at 1300 °C, respectively. Both show that neither Cr nor Ni were observed in the external layer. Thus, oxidation kinetics reflects the rapid reaction of iron oxides formation rates. This fact is also in accordance with other studies.

Nevertheless, AISI 304L showed higher activation energy and also better oxidation resistance comparing to AISI 348, due to its higher Cr content. After the exposures, AISI 304L non-reacting nucleus still presented a slightly higher Cr content comparing to AISI 348 samples.

SEM was also used to investigate the surface morphology with subsequent chemical analysis by EDS to identify alloying elements (up to a given depth) in the outermost layer. The results showed that the outward grown magnetite had lower density of grain boundaries (large grain size) and higher Cr depletion in the more oxidized samples.
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For example, due to the higher oxidation resistance of AISI 304L up to 1200 °C, it was possible to identify other alloying elements than Fe in surface of a sample oxidized at 1200 °C. However, at 1300 °C and beyond, a very thick Fe (II,III) oxide rich layer did not allow Cr and Ni identification.

### 3.3 Hydrogen generation

Although the experimental apparatus did not measured hydrogen generation, it is possible to derive hydrogen generation curves using weight gain results, by considering the relation given by Equation 3.

\[
\frac{H_2}{A} = 2 \frac{M_{H_2}}{M_{O_2}} \left( \frac{\Delta w}{A} \right)
\]

Where \(H_2/A\) and \(\Delta w/A\) are in the same unit; \(M_{H_2}\) and \(M_{O_2}\) are the molecular weights of hydrogen and oxygen, respectively; and 2 is the number of hydrogen moles produced for each mole of oxygen reacted.

**Figure 9.** Cross-section SEM image of AISI 304L layers after 1.5 h at 1300 °C oxidation. The outer magnetite layer is highlighted in red.

**Figure 10.** EDS maps of AISI 348 sample after 1 h oxidation at 1100 °C showing (a) Fe, (b) Cr, and (c) Ni profiles. The outer layer is on the left side.

**Figure 11.** EDS maps of AISI 348 sample after 5 min oxidation at 1300 °C showing (a) Fe, (b) Cr, and (c) Ni profiles. The outer layer is on the left side.
Figure 12 presents the hydrogen generation curves of AISI 348, comparing the experimental results and the predictions given by the mixed linear-parabolic model. Figure 13 shows that the upper interval with a 90% confidence level of the parabolic model is sufficient for a conservative prediction of hydrogen generation from AISI 348 by metal-water reaction in severe accidents. As the experiments did not measure hydrogen generation and there might be loss of mass (part of the non-adherent oxide layer), it is reasonable that the model presents significant uncertainty. Nonetheless, other authors reported similar level of uncertainty in the activation energy\textsuperscript{15,16} and the prediction model for AISI 348 hydrogen generation is in agreement with the experimental results obtained by other laboratories\textsuperscript{10}.

AISI 348 proposed model upper confidence interval seems like Brassfield et al.\textsuperscript{15} correlation. This fact is in accordance to Pint et al.\textsuperscript{2}, where typical 18-8 stainless steels (e.g., 304L, 321L, 347) all performed similarly in TGA experiments.

In SA conditions, where cladding temperature can be higher than 1200 °C, stainless steel cladding might lead to a faster hydrogen production comparing to Zircaloy. Even thought, it presents a better performance at lower temperatures. Thus, it can be considered a better option regarding hydrogen generation only in Design Basis Accidents (DBA)\textsuperscript{11}.

4. Conclusions

Oxidation of AISI 304L and 348 in water was studied at 1000 – 1350 °C in terms of kinetics and scale composition. Based on obtained results, the following conclusions can be made:

1. Oxidation of both alloys followed mixed linear-parabolic rate kinetics. Multilayer scales with voids, consisting mainly of Fe (II,III) oxide and Fe-Cr spinels were observed.
2. From the obtained data, a kinetic model is proposed to predict the oxidation of AISI 348. It presented lower activation energy and lower oxidation resistance comparing to AISI 304L.
3. For design basis LOCA, stainless steel clad presents lower hydrogen generation comparing to Zircaloy.
4. For an accident of the severity of Fukushima, stainless steel clad offers no significant advantage over Zircaloy concerning hydrogen generation.

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