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Matrix Composition of Zircaloy-4

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Abstract — The matrix composition of two experimental Zircaloy-4 cladding tube materials has been analysed. The two materials have undergone different heat treatments and have vastly different corrosion properties. In both materials the matrix is markedly depleted of alloying elements. However, atom probe analyses show a significant difference in Fe content by a factor of five. This suggests that the matrix composition is of importance for the corrosion properties but more analyses have to be made in order to understand the underlying reasons.

I — Introduction

Zircaloy-4 is a zirconium-tin alloy containing approximately 1.5 wt% tin and small additions of oxygen (0.1 wt%), iron (0.2 wt%) and chromium (0.1 wt%). It is used as a fuel cladding material in nuclear pressurized water reactors (PWR). A tendency to use higher service temperatures and longer service times than predicted when the Zircaloy grades were developed has created a great interest amongst tube and fuel producers as well as amongst power companies in the long time corrosion properties of Zircaloy-4.

Since the early seventies extensive studies have been made of the corrosion properties both after long time experiments in reactor environment and after simulations in autoclave. The composition of Zircaloy-4 is standardized and cannot be significantly changed, but the heat treatment is not specified. Attempts to vary the corrosion properties by use of different heat treatments have led to the assumption that the matrix content of alloying elements is of importance for the corrosion properties [1]. Since this content is very small a method of analysis is needed which
both has the sensitivity required, and sufficient lateral resolution to avoid sampling a very fine dispersion of intermetallic particles shown in figure 1. The atom-probe seems to fulfill these requirements.

Experiments on high purity zirconium in an environment of water at 260-360 °C and water vapor at 400 °C have shown that in general the oxide growth rate increases with increasing impurity content [2]. Especially nitrogen has a bad influence. Further investigations have shown that additions of tin can suppress the oxidation caused by the nitrogen. Also the presence of Fe, Ni and to some extent Cr lead to better corrosion properties. These observations led to the development of the Zircaloy family of alloys. An additional problem with corrosion of Zr in a water- or water-vapor-environment is the large amount of hydrogen which is formed in the process. Zr has a high tendency to pick up hydrogen and form hydride precipitates. These lead to severe embrittlement which may decrease the service life of the fuel elements. Hydride formation has been found to increase with increasing Ni content. Therefore, in Zircaloy-4 which is made especially for PWR-reactors, Fe is substituted for Ni.

Studies of the oxidation of Zircaloy-4 in water (360 °C) made by Bryner [3] show that the oxidation rate is cyclic. In each cycle the oxidation rate decreases as the cubic root of time. The cycles can be seen in the oxide microstructure as 2 µm thick layers of dense oxide with thin layers of porous oxide in between. The reason for this oxidation behavior is not known but one theory which has been proposed is that the mismatch in the oxide metal interface will lead to mechanical stresses which at a certain oxide thickness will be sufficiently large to break up the protective layer and allow for a new cycle to begin.

Long time studies of Zircaloy-4 corrosion in PWR-reactors have conveyed an oxide structure which essentially agrees with the experiment of Bryner [4]. Microanalysis of the oxide has shown that the content of alloying elements is the same for metal and oxide except for the outermost layer where Fe and Cr is enriched.

II — Experimental

In this investigation two materials with vastly different corrosion properties have been studied. The gross composition of the materials is shown in table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Material I wt%</th>
<th>Material II wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>1.56</td>
<td>1.49</td>
</tr>
<tr>
<td>Fe</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>Cr</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>O</td>
<td>0.14</td>
<td>0.12</td>
</tr>
<tr>
<td>C</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Zr</td>
<td>bal.</td>
<td>bal.</td>
</tr>
</tbody>
</table>

*Table 1. Gross composition of the two materials analysed*
The materials were cut into bars with a cross section of 1 mm$^2$. These were electropolished in three steps in accordance with [5]:

1. The bars were polished to a cylindrical shape with Ø 0.5 mm using 5% perchloric acid, 35% n-butanol and 60% methanol, 12 V and room temperature.
2. A neck was formed by electropolishing in the same electrolyte, 8-10 V using a circular gold cathode.
3. The final polishing was done in 2% perchloric acid, 98% ethylene-glycol-monobutyl-ether, 15 V and room temperature, using a device which automatically switches off the voltage on large gradients in the current e.g. when the neck is polished through. An optional delay time was set to 35 ms so the tip would be slightly rounded off after the neck had been polished through.

If the tip was not clean and sharp after this step it could often be improved by back polishing using 5% sulphuric acid and 95% methanol, cooled to -30°C, 15-40 V and polishing times of 0.5-1.0 ms in accordance with [6].

During electropolishing an anodic oxide is formed on the specimen. This oxide can cause severe problems during atom-probe analysis. If it is too thick no field evaporation at all takes place before the specimen fails. More often it is possible to tear away or even field evaporate away the oxide before starting the analysis but other problems may occur. Quite often during analysis the carbon and oxygen content may increase simultaneously to absurd values. We believe that this happens when the field strength is too low and thus residual CO is allowed to adsorb and dissociate on the tip surface. Furthermore, since the evaporation field of the oxide is higher than that of the metal, after some field evaporation the oxide surrounding the evaporated surface will protrude and screen off the field. Analysis can not continue until the surrounding oxide is ripped of (obviously it can not be evaporated off) and this usually results in specimen failure. Rather extensive efforts have been made to find a way to minimize the thickness of the oxide film on the samples. The sample preparation method described above is the result of these efforts. It is not fully reproducible but often leads to useful samples. Figure 2 shows specimens made with the above described method. In the dark field image the oxide can be seen as a bright contrast.

The atom-probe used in this investigation has been described previously [7,8]. Before each analysis the specimen was imaged using neon as imaging gas. All analyses were made at 80 K.

III — Results

Due to the low content of alloying elements in the matrix at least 10000 ions from each material had to be collected in order to obtain acceptable statistics. The difficulty was increased since large parts of the analyses, where the field strength had been to low, had to be excluded. Out of totally 69550 ions from both materials 44545 ions remained for evaluation, 33263 ions from material I and 11282 ions from material II. The result of all analyses is shown in table 2.
Table 2. Atom-probe analyses of the matrix composition of two different heat treatments corresponding to very different corrosion properties. The error limits are given as ± 2 standard deviations.

The Sn contents from the gross compositions have been used as a reference. This can be done safely since Sn is distributed homogeneously in the matrix and does not participate in the precipitation. The procedure eliminates possible errors due to preferential evaporation of Zr between pulses and loss of Zr due to simultaneous impact of ions on the detector.

In both materials the matrix is markedly depleted of alloying elements. Nevertheless material II has an iron content which is a factor of five higher. The analyses also indicates that there is a difference in chromium content but this is within the statistical errors.

IV — Discussion

Most high resolution work on Zircaloy-4, done previously, has focused on the fine dispersion of intermetallic particles. Andersson and coworkers [1] studied them by SEM and AEM. The particles were shown to consist of hexagonal Zr(Fe,Cr)₂ with a Cr-to-Fe ratio which varied between 0.44 and 0.53. Figure 3 shows the main steps in the manufacturing process of experimental Zircaloy-4 cladding tubes. At high temperatures in the intermediate annealings both the precipitate and matrix grain sizes increases. At long annealing times the precipitate grain size increases and the number of precipitates decreases due to Ostwald ripening.

Corrosion experiments, made by the same authors, showed a decrease in corrosion rate with increasing temperature and time of the intermediate annealings until a point was reached where no further nucleation of precipitates occurred i.e. the concentrations of alloying elements had reached their equilibrium values and only Ostwald ripening was responsible for the precipitate grain growth.

The results of Andersson et al. suggest that the content of alloying elements in the matrix is more important for the corrosion properties of Zircaloy-4 than the particle size and the density of particles. Our results are consistent with the results of Andersson et al. However, in order to understand the reasons for the corrosion behavior more analyses of different heat treatments have to be made.
V — Conclusions

- The matrix composition has been analysed in two experimental Zircaloy-4 cladding tube materials with vastly different corrosion properties.

- The matrix is markedly depleted of alloying elements in the two materials investigated.

- The Fe content differs by a factor of five between the two materials.

- Our results support the theory that the matrix content of alloying elements is of importance for the corrosion properties of Zircaloy-4.

- More analyses of different heat treatments have to be made and correlated to the corrosion properties in order to understand the reasons for this behavior.

VI — Acknowledgements

This work has been financially supported by AB Sandvik Steel. Dr. T. Thorvaldsson, AB Sandvik Steel, is thanked for providing the micrograph in figure 1.

VII — References


Figure 1. TEM micrograph showing the fine dispersion of intermetallic particles in Zircaloy-4.

Figure 2. Bright field and dark field images of specimens made with the electropolishing method described above. In the dark field image the oxide film can be seen in bright contrast.

Figure 4. The main steps in the manufacturing process of experimental Zircaloy-4 cladding tubes used by Andersson et al. [1].