High temperature oxidation experiments with sponge base E110G cladding

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Abstract

High temperature oxidation experiments with sponge base E110G alloy were performed in wide range of parameters to investigate the oxidation behaviour of this fuel cladding in steam and in hydrogen rich steam environment; furthermore to study the susceptibility of this alloy to breakaway phenomenon. These tests are part of a systematic investigation of E110G cladding in order to facilitate the licensing of new cladding for Paks Nuclear Power Plant, in Hungary. The oxidation tests were carried out in the temperature range of 600–1200 °C under isothermal conditions. The new and the traditional types of cladding ring were compared. The experimental results showed similar behaviour of E110G and E110 samples in most of the temperature. However, the oxidation of E110 was significantly faster at 900 and at 1000 °C due to the breakaway oxidation. The oxide layer of the E110 cladding became spalling in contrast to the intact oxide layer of the new E110G cladding. The hydrogen content of the oxidised claddings was measured. Only a very small amount of hydrogen (below 100 wppm) was detected in samples of E110G, because the absorption of hydrogen was limited by the compact oxide layer. The presence of breakaway oxidation was investigated in steam atmosphere by on-line hydrogen detection between 800 and 1200 °C. No breakaway oxidation of E110G was observed during the tests up to 2700 s. Test series was carried out in steam-hydrogen mixture in the temperature range of 900–1100 °C. Hydrogen rich environment had no significant effect on the E110G oxidation.

Keywords: Zirconium alloys, steam oxidation, high temperature behaviour
1. Introduction

The E110 alloy is used as fuel cladding material in Paks nuclear power plant (Paks NPP) in Hungary. It has excellent corrosion resistance during normal operation, especially at higher burnup levels. However, it is important to investigate the oxidation behaviour of this cladding under accident conditions. For this reason, hundreds of separate and combined effect tests have been performed at the Hungarian Academy of Sciences Centre for Energy Research (MTA EK) with E110 alloy. These test results were compiled in an electronic database [1].

The Russian fuel supplier intends to introduce a new technology for the production of cladding tubes. The tubes will be produced from sponge material (E110G) instead of the currently used electrolytic method (E110). The chemical composition of the alloy remains the same, but the tolerance of the quantity of the components changed. Furthermore, the behaviour of the cladding under accident conditions is affected by many other factors [2]. The systematic investigation of E110G alloy in wide range of parameters has been initiated. The aims of these experiments were to support the licensing of this new cladding material in Hungary and to compare the high temperature behaviour of the traditional and new type of claddings.

Preliminary data on high temperature behaviour of E110G alloy from fuel supplier indicated better oxidation behaviour compared to E110 [3], [4].

2. Experimental Procedures

Oxidation tests were carried out with sponge base E110G fuel cladding specimens. 8 mm long rings were cut from the original E110G tubes with 9.13 mm outer diameter. The rings were cleaned in acetone and air-dried. The original tubes were obtained directly from fuel supplier by the experts of Paks NPP. The chemical composition of the alloy was determined by mass-spectrometry. Table 1. shows the content of the main alloying elements of the E110G and E110 alloy. The new alloy contained more iron and less hafnium than the traditional one. On the basis of a Russian paper [5] the sponge base alloy contains half the amount of impurities (70 ppm C, Si, Ni, P, Cl, N, F, Al) compared to E110. The authors emphasized that the surface roughness of the alloys did not differ substantially.

Three different series of oxidation tests were performed at high temperature (600 – 1200°C) under isothermal conditions. The tests were conducted in steam and in hydrogen rich steam environment. The purposes of the experiments were to study the oxidation kinetics of E110G cladding in steam, to study the effect of hydrogen in the steam environment on the oxidation and to investigate the presence of breakaway phenomenon during steam oxidation.

The schematic figure of the equipment used for oxidation experiment is shown in Fig. 1. The experimental facility consisted of a steam generator, a three-zone tube furnace with temperature control system and a condenser. Steam flow rate (2.8 – 4.0 mg/cm²/s) was evaluated by measuring the weight of the condensed water. After reaching the required temperature and steam flow the sample was pushed into the heated zone of the furnace. At the end of oxidation the sample was withdrawn to the cold part of the equipment.
The same equipment was used for investigation of the breakaway phenomenon, but it was attached to a thermal conductivity detector (TCD). This detector measured the hydrogen concentration of the outlet gas during the steam oxidation. The method is the following. After sample insertion into the furnace, the formation of hydrogen starts due to the zirconium-steam reaction. The sample partly absorbs the hydrogen and the rest of it goes into the gas phase with the argon gas. At the beginning of oxidation a protective oxide scale starts to develop [2], thus the oxidation rate and the hydrogen production decreases. In case of crack formation the hydrogen production starts to increase again, because there is a free path for the steam to reach the fresh metal surface. The on-line hydrogen detection can give information about the formation of cracks in the oxide.

3. Results

The first test series was carried out in the temperature range of 600 – 1200 °C, in steam – argon mixture including 12 vol.% argon gas. The equivalent oxidation (ECR%) was calculated as follows:

\[ \text{ECR} \% = \frac{A_{Zr} \cdot \Delta m}{M_{O_2} \cdot m_i} \cdot 100 \]  

Where:
- \( A_{Zr} \) (g/mol) – molar mass of zirconium
- \( M_{O_2} \) (g/mol) – molar mass of oxygen
- \( m_i \) (g) – initial mass of the Zr sample
- \( \Delta m \) (g) – mass gain after oxidation

Fig. 2 illustrates the extent of oxidation versus oxidation time at 600 °C, 700 °C, 800 °C, 900 °C and at 1000 °C, 1100°C, 1200 °C, respectively.

Fig. 3 shows the oxidation rate of E110G and E110 as a function of the reciprocal temperature. The triangular symbols represent the oxygen mass gain rate of E110G, the circular symbols indicate the mass gain rate of E110 alloy. Comparing the results of the sponge base and the standard cladding, there was only slight difference between the oxidation kinetics of these two alloys at 600 °C, 700 °C, 800 °C, 1100 and 1200 °C. The oxidation of E110 was much faster at 900 and at 1000 °C due to the breakaway oxidation.

In line with this, the oxide layer of the E110 cladding became spalling. The oxidised E110G samples were lustrous and black in all cases.

The hydrogen content of the oxidised claddings was measured by hot extraction (high temperature desorption) method. The E110G samples contained less than 100 wppm hydrogen, because the hydrogen absorption during steam oxidation was limited by the compact oxide layer. In case of E110 cladding, the hydrogen absorption was accelerated after the breakaway phenomenon. The hydrogen content of E110G and E110 alloys oxidised at 1000 °C is shown in Fig. 4.
During the second test series the specimens were oxidized in a controlled, mixed steam – hydrogen atmosphere between 900 and 1100 °C. The hydrogen content in the steam was 65 vol.%. Fig. 5. represents the oxidation kinetics of E110G and E110 in pure steam and in hydrogen rich steam at 900 °C and 1100 °C. The filled symbols indicate the samples oxidised in pure steam, the empty markers show the samples oxidised in steam – hydrogen mixture. We can conclude that the hydrogen rich environment does not influence significantly either the E110G or the E110 cladding oxidation.

The breakaway oxidation behaviour of the sponge base E110G cladding was studied in steam atmosphere between 800 and 1200 °C. The tests were terminated after 2700 seconds. Fig. 6. illustrates the TCD signal during steam oxidation at different temperatures versus oxidation time. This signal of the TCD is directly proportional to the hydrogen concentration. The solid line shows the hydrogen release during standard E110 oxidation with secondary maxima typical of breakaway. During E110G oxidation (dashed lines) the hydrogen production smoothly decreased, indicating that breakaway oxidation did not take place.

4. Conclusions

The oxidation behaviour of E110G cladding produced by new technology was investigated in high temperature experiments. The results were compared to the currently used E110 alloy’s results. More favourable behaviour of oxidised E110G was observed regarding the oxidation kinetics, breakaway oxidation and hydrogen uptake. The steam oxidation of E110G was much slower at 900 and 1000 °C, otherwise it was similar. The presence of hydrogen in the steam environment had no significant effect on the oxidation kinetics. Although the standard E110 is susceptible to breakaway oxidation, the E110G oxidation process was characterized by the lack of breakaway phenomenon. Because of the protective oxide layer formed on the surface of E110G, very low hydrogen content was found in these samples. Our former database [1] was extended with new experimental data that give information on the E110G cladding behaviour under accident conditions.
5. References


Table 1. Main alloying elements of the E110G and E110 alloy (wt ppm), balance: Zr

<table>
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<tr>
<th></th>
<th>Nb</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
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<tr>
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<td>15</td>
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<td>100</td>
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Fig. 1. Schematic of the equipment for oxidation experiments
Fig. 2. Oxidation kinetics of E110G alloy in steam at different temperatures

\[ y = 64.24e^{-0.8173x} \]

for 600°C - 900°C

\[ y = 8948.4e^{-1.4014x} \]

for 900°C - 1200°C

Fig. 3. Oxygen mass gain rate constants of E110G and E110 alloys as a function of the reciprocal temperature

\[ y = 8948.4e^{-1.4014x} \]

for 900°C - 1200°C

\[ y = 64.24e^{-0.8173x} \]

for 600°C - 900°C
Fig. 4. The hydrogen content of E110G and E110 alloys oxidised at 1000 °C.

Fig. 5. Oxidation kinetics of E110G and E110 in pure steam and in hydrogen rich steam at 900 °C and 1100 °C.
Fig. 6. Hydrogen release during oxidation of E110G (and E110) samples at different temperatures