

Air oxidation kinetics of zircaloy-4

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1. Introduction

Air ingress scenarios could occur in reactor and spent fuel pool accidents. For example, in reactor sequences air could be admitted through the broken reactor vessel at the late phase of a severe accident after the reactor vessel has been breached. In addition, spent fuel assemblies could be directly exposed to air in a postulated complete loss of coolant accident in a spent fuel pool.

Several separate effect tests have been performed at KIT [1] and IRSN [2] to study the air oxidation of zirconium alloy cladding. In this study, air oxidation of zircaloy-4 cladding was conducted in 600-1600°C to investigate the breakaway kinetics.

2. Experimental results and discussions

The macro samples are shown in Fig. 1.



Fig. 1 Macro samples of air oxidized zircaloy-4

As shown in Fig. 1, the samples of 850, 950, 1000°C were severely degraded after the air oxidation. Because there was a breakaway phenomenon during the air oxidation test for those highly degraded samples.

At 600-1000°C, this temperature regime was the 'breakaway oxidation regime'. The breakaway is an abrupt kinetic change from the parabolic to linear kinetic rate law. Fig. 2 shows the mass gain curves of

the air oxidation tests in the temperature of breakaway oxidation regime.

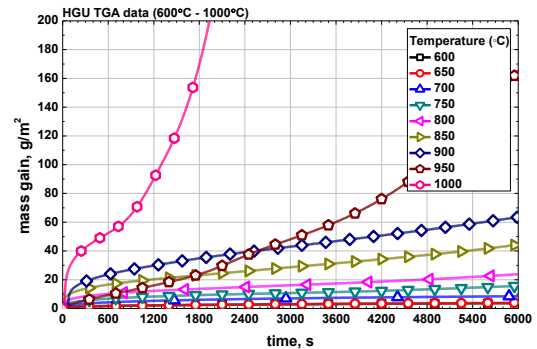


Fig. 2 Mass gain curves of air oxidation tests at 600-1000°C (breakaway temperature regime)

As shown in Fig. 2, the abrupt kinetic transition clearly was observed in the mass gain curve of air oxidation test at 650°C.

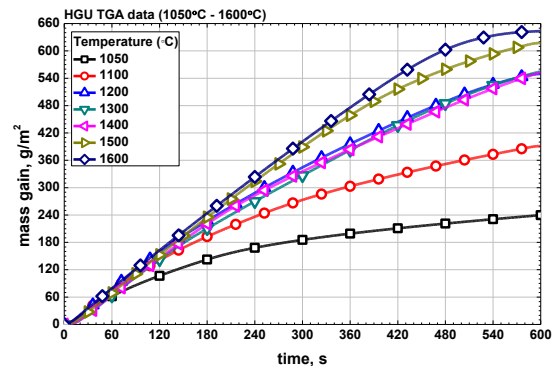


Fig. 3 Mass gain curves of air oxidation tests at 1050-1600°C (non-breakaway temperature regime)

On the other hand, the breakaway phenomenon was not observed in the air oxidation tests at 1050-1600°C. These temperature regime is called 'non-breakaway regime'. Fig. 3 shows the mass gain curves of air oxidation tests in the temperature of non-breakaway regime.

As shown in Fig. 3, only parabolic kinetics curves were observed in the temperature of non-breakaway regime.

For the breakaway, there is a global stress relaxation mechanism during the tetragonal to monoclinic phase transformation.

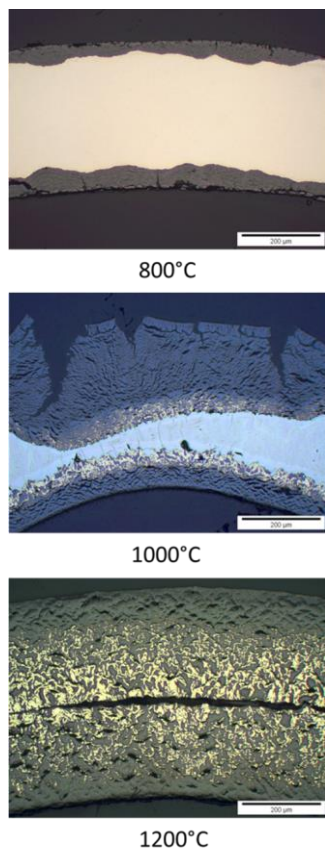


Fig. 4 Zircaloy-4 air oxidation scale at 800°C (after 6h), 1000°C (after 1h) and 1200°C (after 15 min) [3]

The tetragonal thin layer locates near the interface. If the volume-free energy difference between t-ZrO₂ to m-ZrO₂ becomes greater than the compressive strain energy at critical thickness, the t-ZrO₂ transforms to m-ZrO₂ with 4.56% molar volume expansion [4]. Once the oxide thickness exceeds the critical thickness, the stress built in this outer layer from the critical level does no longer sufficiently stabilize the t-ZrO₂ near the interface [5]. Thus, t-ZrO₂ transforms to the thermodynamically stable m-ZrO₂ near the interface. Because of the larger volume of the m-ZrO₂ than the t-ZrO₂, the m-ZrO₂ applies the emergent tensile stress to the underlying t-ZrO₂ and this tensile stress causes the cracks to be triggered. This crack tips propagate to the Zr/ZrO₂ interface as the oxidation proceeds due to the successive formation of the m-ZrO₂ at the crack tips [6]. For this reason, the compressive stress is relieved at the free surface and hence the radial cracks initiate from the free surface toward the interface along the grain boundaries. This cracking in the oxide layer could result in the reduced diffusion distance of the air to the metal. Through cracks, air could access easily to the metal and that leads to higher rates of oxidation. The cracking behaviors according to the temperature are shown in Fig. 4.

As shown in Fig. 4, small circumferential cracks were developed locally at 800°C. In case of 1000°C, the radial cracks were observed more frequently than those of 800°C and the larger circumferential cracks were observed, as well. However, no macro radial cracks were observed at 1200°C. Only large circumferential cracks (with interconnected pores) were observed.

Consequently at high temperature above 1050°C, a stress release to the metal and the stability of t-ZrO₂ would bring no kinetic transition by global tetragonal to monoclinic transformation. It seems that the macro radial cracks could be initiated by the tetragonal to monoclinic transformation below 1050°C. For this reason, the main driving force of the breakaway would be the tetragonal to monoclinic transformation below 1050°C. This allotropic transformation would attribute to the global stress relaxation by initiating the macro radial cracks from the free surface to the interface.

3. Conclusion

In summary, the breakaway phenomenon was observed in the temperature range of 600-1000°C by the phase transformation from the tetragonal to monoclinic ZrO₂ at the interface. Above 1050°C, there was no phase transformation and no breakaway kinetics was observed. For the future work, the nitrogen-assisted breakaway phenomenon will be investigated to identify the role of nitrogen in the breakaway kinetics.

ACKNOWLEDGEMENT

This work was supported by the Nuclear Safety Research Program through the Korea Foundation Of Nuclear Safety (KOFONS), granted financial resource from the Nuclear Safety and Security Commission(NSSC), Republic of Korea (No. 1603011-0116-SB110).

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