A new quantitative analysis on nitriding kinetics in the oxidized Zry-4 at 900-1200°C

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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. In air ingress scenarios, nitrogen has an active role on the cladding degradation. Two major roles of nitrogen on the zirconium based cladding degradation were identified: mechanical degradation of the cladding, and the additional chemical heat release.

It has long been known that accelerated oxidation can occur in air due to the nitrogen. In addition, significant uptake of nitrogen can also occur. The nitriding of pre-oxidized zirconium based alloys leads to micro porous and less coherent oxide scales. This paper aims to quantitatively investigate the nitriding mechanism and kinetics by proposing a new methodology that is coupled with the mass balance analysis and the optical microscope image processing analysis.

A new quantitative analysis methodology is described in chapter 2 and the investigation of the nitriding kinetics is performed in chapter 3. The experimental details are previously reported in [1]. Previously only qualitative analysis was performed in [1], and hence the quantitative analysis will be performed in this paper.

A series of pre-oxidation (PO) – nitriding (NT) tests were performed in coupled thermal balance system and an exhaust gas analyzer in the temperature range of 900-1200℃ as shown in Fig. 1.

Fig. 1. Overview of the series of PO-NT-RT tests

2. A new quantitative analysis methodology

A quantitative analysis consists of mass balance analysis and optical microscope image analysis. Two main results from the oxidation tests were the mass gain curves and the optical microscope images from the metallography. The first quantitative analysis is to use the results of mass gain curves by calculating mass balance of each test period. The second semi-quantitative analysis is to use the results from the metallography by processing the optical microscope images to quantify each phase in the post-test sample. An overview of the qualitative and semi-quantitative analysis is shown in Fig. 2.
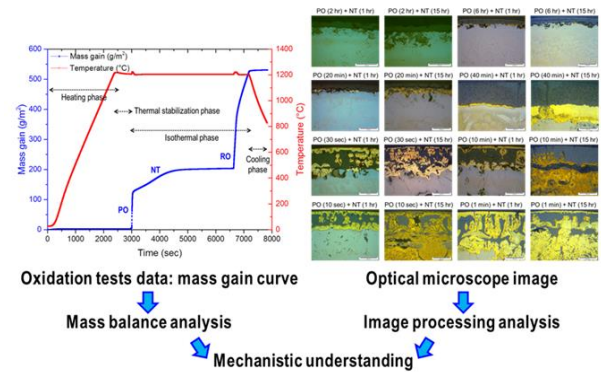

Fig. 2 Overview of a new quantitative analysis

A mechanistic understanding of the nitriding kinetics and mechanism could be obtained from both mass balance analysis and image processing analysis. From the oxidation tests, mass gain was recorded in real time. This recorded mass gain with time is a mass gain curve as shown in Fig. 2 left side. By using mass gain curve, a mass balance analysis is possible to understand in more detail the reactions during the pre-oxidation/nitriding tests. From the oxidation tests, the initial values for the mass balance analysis are given as follows:

▫ Mass of Zry-4 sample: Zr
▫ Mass gain of pre-oxidation (O2 mass gain): PO
▫ Mass gain of nitriding (N2 mass gain): NT

The bold symbols above will be used as an abbreviation to refer to each mass. Zry-4 is a zirconium based alloy cladding with main alloying component with Sn (ca. 1.3%), but the mass of Zry-4 will be assumed a mass of Zr metal in the mass balance analysis.

Based on the initial values and a molar mass of each component, the methodology of mass gain analysis is proposed in each pre-oxidation, nitriding and re-oxidation period in the following.

▫ Pre-oxidation: α-Zr(O) stabilization and ZrO_2 development

α-Zr(O) stabilization: $Zr + O2 \rightarrow$ α-Zr(O) (assumed to be saturated 6.5 wt.%)

ZrO_2 development: $Zr + O_2 \rightarrow ZrO_2$

▫ Nitriding: $2Zr(O) + N2 \rightarrow 2ZrN(O)$; An oxidized Zr(O) is nitrided. Oxygen is assumed to be trapped in the oxide/nitride scale and no O_2 is released out of the oxide/nitride scale.

The final products of mass balance analysis are the mass of remained Zr metal after the test, mass of ZrO2 and ZrN after the test, as well. From the mass balance analysis, the mass percentage of Zr metal and ZrO_2 and ZrN can be calculated. Using density of each component, the mass percentage can be converted to the volume percentage. With a negligible penetration depth of the each component by the optical microscopy, the volume percentage from the mass balance analysis can be compared with the results of the optical microscope image processing analysis. Fig. 3 shows an overview of the optical microscope image processing analysis.
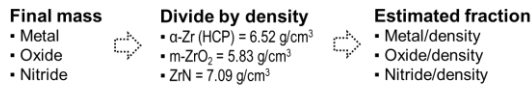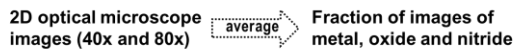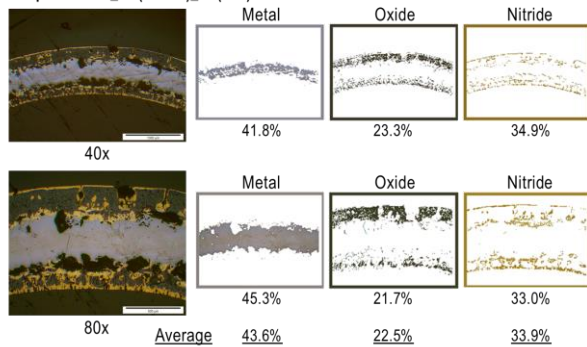

Fig. 3 Overview of an optical microscope image processing analysis

As shown in Fig. 3, two different magnifications micrographs were analyzed by calculating each color of phase with very high precision (200 pixels of resized widths) to quantify the percentage of each component. The optical microscope image processing analysis was focused on the nitrided sample to understand better the nitriding behaviors. A comparison between the results of mass balance analysis and optical image processing analysis is given in the following. Fig. 4 shows the comparison between the results of mass balance analysis and optical image processing analysis of the pre-oxidation/nitriding tests performed in the thermal balance system of STA-409 (hereinafter, STA).
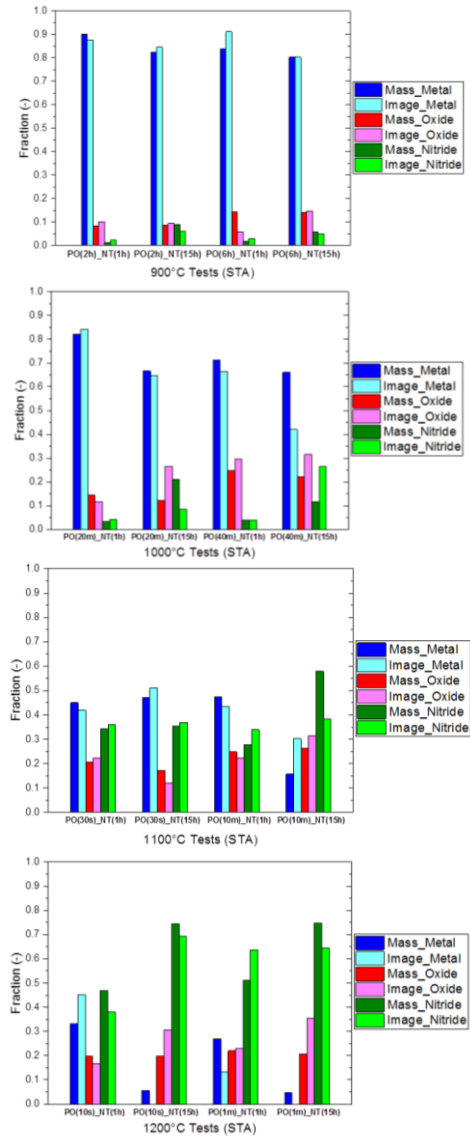

Fig. 4 Comparison between the results of mass balance analysis and optical image processing analysis of the tests at 900-1200°C

As shown in Fig. 4, for metal, oxide and nitride, both fractions from the mass balance analysis and the optical microscope image processing analysis were quite comparable. However, few samples show some inconsistencies due to the following reasons:

▪ During the metallography, the post-test samples may lose some of their inclusions (e.g. metal, oxide and nitride).

▪ Only 2 optical micrographs were used to determine the fraction of each phase.

In addition to understand the nitride formation behavior, the different locations of nitride were analyzed by an optical microscope image processing analysis as proposed in Fig. 5. In this optical microscope image processing analysis, these different locations of nitrides were divided as follows:

▪ External nitride (E): nitride on a top of oxide scale
▪ Nitride precipitates (P): nitride within the oxide scale
▪ Internal nitride (I): nitride at the oxide-metal interface
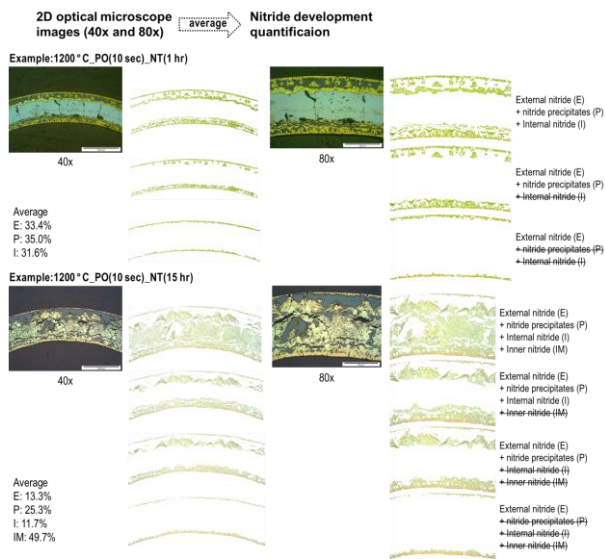▪ Inner nitride (IM): nitride below the oxide-metal interface

Fig. 5 Overview of an optical image processing analysis to quantify a nitride development

As shown in Fig. 5, only nitride phase was taken from two different magnifications of optical micrographs and quantified into the each nitride formation according to its location. Based on the quantitative analyses of the pre-oxidation/nitriding tests, nitriding and behaviors are analyzed in the following chapter.

3. Quantitative analysis on nitriding behaviors

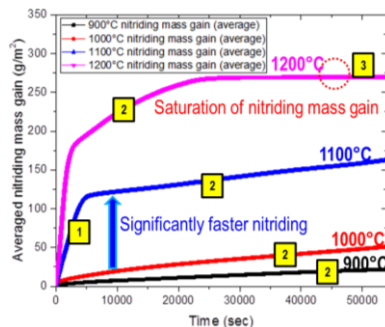As shown in Fig. 6, nitriding kinetics was different with increase of time at 900-1200℃.

Fig. 6 Nitriding kinetics at 900-1200℃

At 900 and 1000℃ nitriding tests, only parabolic kinetic behaviors (2 in Fig. 6) were shown for whole nitriding duration but 1100 and 1200℃ nitriding tests showed totally different kinetics with the increase of nitriding duration. At 1100 and 1200℃, the nitriding kinetics was firstly accelerated (1) and then stabilized (2). Finally it was saturated (3) at 1200℃.

From the optical microscope image processing analysis to quantify the nitride development according the locations, the fraction of external nitride (E), nitride precipitates (P), internal nitride (I) and Inner nitride (IM) were calculated and compared with the fraction of NT accelerated and stabilized in Fig. 7.
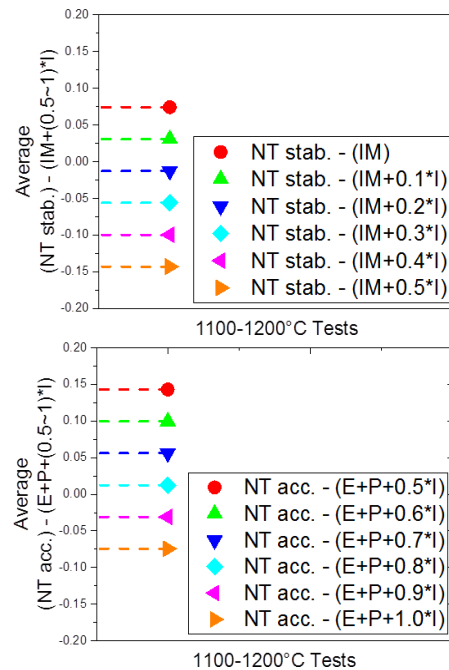

Fig. 7 Nitride development and nitriding kinetics

The sum of fraction {E + P + (0.5-1.0)•I} and the sum of fraction {IM + (0.1-0.5)•I} were compared with the fraction of NT accelerated and NT stabilized, respectively. As shown in Fig. 12 the lowest averaged difference for both NT accelerated and stabilized phases are as follows:

▪ NT accelerated = E+P+0.8•I
▪ NT stabilized = 0.2•I + IM

It seems that an external nitride, nitride precipitates and 80% of internal nitride may be formed during the NT accelerated phase by nitriding the initial stabilized α-Zr(O) that might be re-distributed throughout the oxide scale during the NT accelerated phase. Due to the development of external α-Zr(O) layer, nitrogen might directly access the α-Zr(O) and hence it may give an accelerated kinetics.

After the NT accelerated phase, nitrogen may need to penetrate the external nitride layer and a protective oxide layer to react with 20% of re-distributed initial stabilized α-Zr(O) and to react with the further stabilized α-Zr(O) below the oxide-metal interface. Due to oxide/nitride scale formed during before the NT stabilized phase, nitrogen may need to diffuse to react with oxidized metal. This nitriding kinetics would be a diffusion controlled reaction.

In addition, Fig 6 shows a nitriding saturation after the NT stabilized phase at 1200℃. To investigate the NT saturation, concept of DoR (Degree of Reaction) is adopted from [2]. This paper defines the DoR by considering two binary system reactions as follows:

▪ Pre-oxidation (PO): O_2 mass gain (Zr + O_2 → ZrO_2)
▪ Nitriding (NT): N_2 mass gain (Zr + ½ N_2 → ZrN)

A DoR can be derived as follows:

$$\frac{\Delta m(O_2)}{100} = \frac{M_{O_2} \cdot f_{O_2}}{M_{Zr}} = \frac{31.9988 \cdot f_{O_2}}{91.224} \Rightarrow f_{O_2} = \frac{91.224 \cdot \Delta m(O_2)}{3199.88} \quad \text{(eqn 1)}$$

$$\frac{\Delta m(N_2)}{100} = \frac{M_{\frac{1}{2}N_2} \cdot f_{N_2}}{M_{Zr}} = \frac{14.0067 \cdot f_{N_2}}{91.224} \Rightarrow f_{N_2} = \frac{91.224 \cdot \Delta m(N_2)}{1400.67} \quad \text{(eqn 2)}$$

$$\mathbf{DoR} = \left(\mathbf{f_{O_2}} + \mathbf{f_{N_2}}\right) \cdot \mathbf{100} \, [\%]$$

When the DoR approaches 100%, the nitriding takes no longer. The DoR of each test at 1200℃ reached almost 100% and it means that no further nitriding would occur after reaching the 100% of DoR.

4. Conclusion

In this paper, the nitriding kinetics and mechanism were quantitatively analyzed by the new proposed analysis methods: the mass balance analysis and the optical microscope image processing analysis. Using these combined methods, the mass gain curves and the optical microscopes are analyzed in very detail, and the mechanisms of nitriding accelerated, stabilized and saturated behaviors were well understood. This paper has two very distinctive achievements as follows:

▪ Development of very effective quantitative analysis methods only using two main results of oxidation tests: No detailed analytical sample measurements (e.g. TEM, EPMA and so on.) were required. These methods can effectively reduce the cost and effort of the post-test investigation.

▪ The first identification of the nitriding behaviors and its very accurate analysis in a quantitative way. Based on this quantitative analysis results on the nitriding kinetics, these new findings will contribute significantly the understanding the air oxidation behaviors and model development.

REFERENCES

[1] S. Park, Parametric investigation of nitriding and re-oxidation behaviors of pre-oxidized Zry-4, Transactions of the Korean Nuclear Society Spring Meeting, May 12-13, 2016, Jeju, Korea.
[2] M. Steinbrück, "High-temperature reaction of oxyegen-stabilized α-Zr(O) with nitrogen", Journal of Nuclear Materials 447(1-3), pp. 46-55 (2014)