

Parametric investigation of nitriding and re-oxidation behaviors of pre-oxidized Zry-4

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1. Introduction

In air ingress scenarios, nitrogen has an active role on the cladding degradation mechanisms. New series of separate-effects tests were recently conducted to investigate the parameters that affect the nitriding and re-oxidation mechanisms. It has been known that an accelerated oxidation can occur in air due to the active role of nitrogen. The nitriding of pre-oxidized zirconium based alloys leads to micro porous and less coherent oxide scales due to a volume mismatch between oxide and nitride. Re-oxidation of nitrated pre-oxidized zirconium alloys leads to macro cracked oxide scales. In order to investigate the cladding degradation mechanisms by nitrogen during the nitriding and re-oxidation, a series of thermogravimetric tests was planned. Isothermal tests were conducted in a thermogravimetry system using fresh Zry-4 cladding samples. The samples were initially pre-oxidized in oxygen at different temperatures and oxidation degrees (with and without breakaway). The pre-oxidation was followed by a nitriding phase, where parameters like the temperature, the degree of pre-oxidation, prior breakaway during the oxidation phase and the duration of the nitriding period were studied. Finally, the effect of re-exposure of the cladding to oxygen was studied. These series of separate-effects tests were recently conducted to investigate the parameters that affect the nitriding and re-oxidation behaviors. This paper is based on a revised and considerably extended presentation given at the 21st International Quench Workshop [1].

2. Experimental details

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

Pre-oxidation (PO)			Nitriding (NT)		Re-oxidation (RO)	
900°C	$\alpha\text{-Zr(O)} + \text{ZrO}_2$	Breakaway regime	0.5 hr	2 hr (900°C)		
1000°C			1 hr	1 hr (1000°C)		
1050°C	$\alpha\text{-Zr(O)} + \text{ZrO}_2$	Non-breakaway regime	3 hr	20 min (1100°C)		
1100°C			6 hr	10 min (1200°C)		
1200°C			15 hr			

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

From numerous isothermal air oxidation tests data [2] and [3], no breakaway was observed above around 1050°C. The series of oxidation tests were performed in both breakaway regime (900 and 1000°C) and non-breakaway regime (1100 and 1200°C).

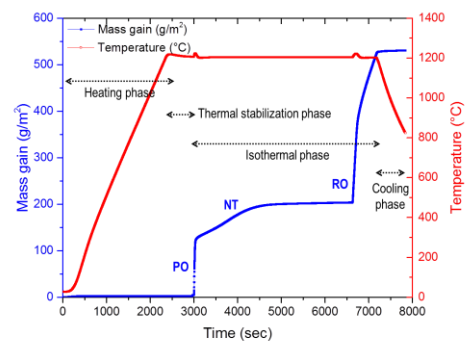


Fig. 2. Procedures of the series of PO-NT-RT tests

There were four phases for the thermal balance tests as shown in Fig. 2: heating phase, thermal stabilization phase, isothermal reaction phase and cooling phase. Firstly, the samples were heated to the target temperature with a heating rate of 30 K/min in argon atmosphere. After then they were thermally equilibrated for 10 min to prepare the stable isothermal condition. Afterward, reaction gases were supplied until the target mass gain or for a planned time. The tests were finished by turning off the reaction gases and cooling with a fast cooling rate in argon atmosphere. In the diagrams presented in the following chapters (x,y) were set to (0,0) at the begin of the isothermal reaction phase for better comparability.

3. Experimental results and discussion

As shown in Fig. 1, the series of PO-NT-RO tests were planned with various conditions: temperature, pre-oxidation duration, nitriding duration. Based on the test conditions, parameters that may affect the nitriding and re-oxidation behaviors are identified. The first step of the qualitative analysis is to separate each period. After then, each NT and RO mass gain is compared with the identified parameters: nitriding duration, annealing temperature and history of breakaway (i.e. if the breakaway was occurred, or not).

3.1 Effects on nitriding behaviors

Effects of each parameter on nitriding behavior are given in this section. Investigated parameters were nitriding duration, temperature and breakaway.

Parameter: nitriding duration

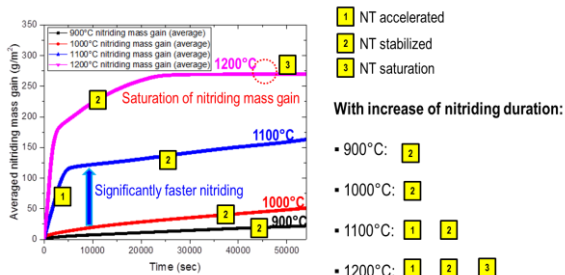


Fig. 4. Nitriding behaviors with increase of nitriding duration

As shown in Fig. 4, nitriding kinetics was different with increase of temperature and time. At 900 and 1000°C nitriding tests, only parabolic kinetic behaviors were shown for whole nitriding duration but 1100 and 1200°C nitriding tests showed totally different kinetics with the increase of nitriding duration. At 1100 and 1200°C, the nitriding kinetics was firstly accelerated and then stabilized, and finally it was saturated. In addition, nitride formation was different between two temperature groups as shown in Fig. 5.

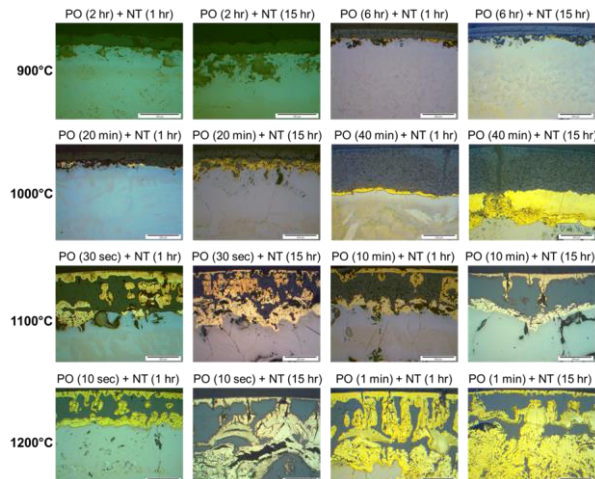


Fig. 5. Micrographs of the nitrided samples

At 900-1000°C, the nitride was observed at the oxide-metal interface. However at 1100-1200°C, the nitride was found at the external surface of the oxide scale and at the oxide-metal interface. In addition, the nitride precipitates were observed in the oxide scale.

Parameter: temperature

Fig. 6 shows the nitriding mass gain as a function of nitriding temperature. As shown in Fig. 6, higher

nitriding mass gain was observed with higher nitriding temperature.

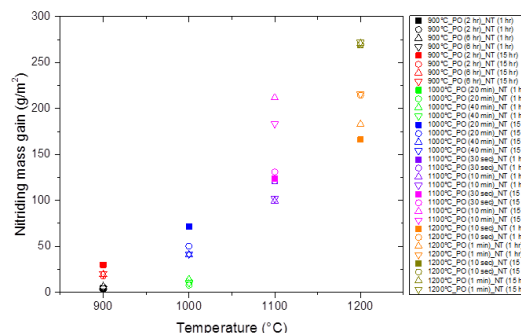


Fig. 6. Nitriding mass gain as a function of temperature

It seems that higher temperature may allow more energy for nitrogen to overcome the activation energy to initiate the nitriding.

Parameter: breakaway

To investigate the effect of breakaway on the nitriding behaviors, results of two sets of tests were compared. One is the pre-oxidation without breakaway condition (20 min pre-oxidation at 1000°C) and the other is with breakaway condition (60 min pre-oxidation at 1000°C). Fig. 7 shows the nitriding mass gain of both non-breakaway (red) and breakaway (blue) tests at 1000°C.

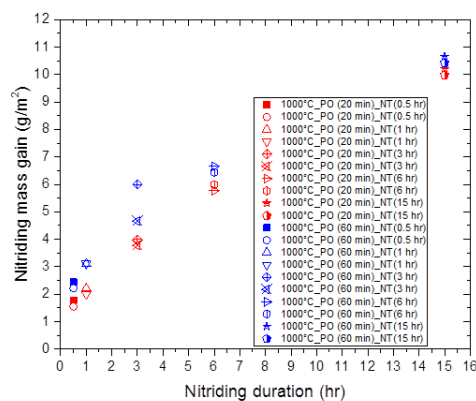


Fig. 7. Nitriding mass gain as a function of breakaway

As shown in Fig. 7, slightly higher nitriding mass gain in prior-breakaway oxide was observed than in non-breakaway oxide. It seems that during nitriding, N₂ gas might access easily to the oxide-metal interface through the radial cracks which were developed by the prior-breakaway. For this reason, the more chance of nitriding would be happened in the prior-breakaway oxide than in the non-breakaway oxide. To understand better the effect of breakaway on the nitriding, the relative difference of nitriding mass gain is shown in Fig. 8. The relative difference of nitriding mass gain was calculated as a ratio of {(NT mass gain of prior-breakaway) – (NT

mass gain of non-breakaway)) and (NT mass gain of non-breakaway) in percentage.

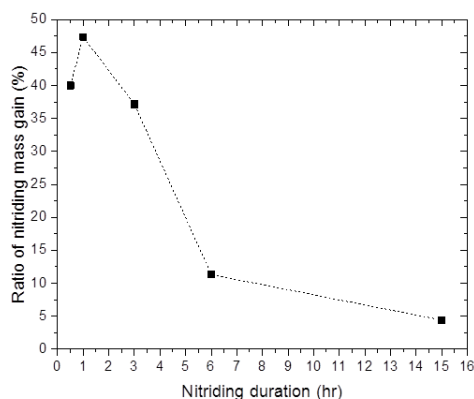


Fig. 8. Relative difference of nitriding mass gain as a function of breakaway

As shown in Fig. 8, the relative difference was non-negligible. However, as the nitriding duration increased the effect of breakaway decreased. It seems that firstly nitriding was promoted due to an enhanced diffusion through the radial cracks that were formed by a prior-breakaway, but it was slowed-down as the nitride layer thickened with the increase of nitriding duration. Since, nitrogen needed to diffuse through a thick nitride layer to reach the oxidized metal below the nitride layer.

3.2 Effects on re-oxidation behaviors

Effects of each parameter on re-oxidation behavior are given in this section. Investigated parameters were nitriding duration, temperature and breakaway. The analysis of each effect of parameter is given in the following.

Parameter: nitriding duration

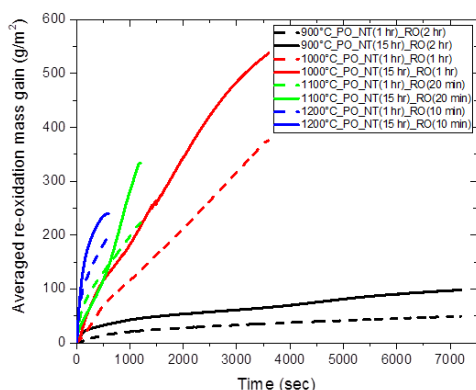


Fig. 9. Re-oxidation behaviors with increase of nitriding duration

As shown in Fig. 9, higher re-oxidation mass gain was observed with longer nitriding duration. With the

increase of nitriding duration, higher amount of nitride was formed as shown in Fig. 5. This formed nitride during nitriding period would be re-oxidized by oxygen in the beginning of re-oxidation period. For this reason, more promoted re-oxidation kinetics was observed in a long nitriding (15 hr) tests than in a short nitriding (1 hr) tests. In addition, a nitride was converted to an oxide during re-oxidation period. Due to a molar volume difference between oxide ($21.7 \text{ cm}^3/\text{mol Zr}$) and nitride ($14.8 \text{ cm}^3/\text{mol Zr}$), a significant molar volume expansion would occur during a transformation from nitride to oxide. For this reason, the oxide scales may be severely degrade as shown in Fig. 10.

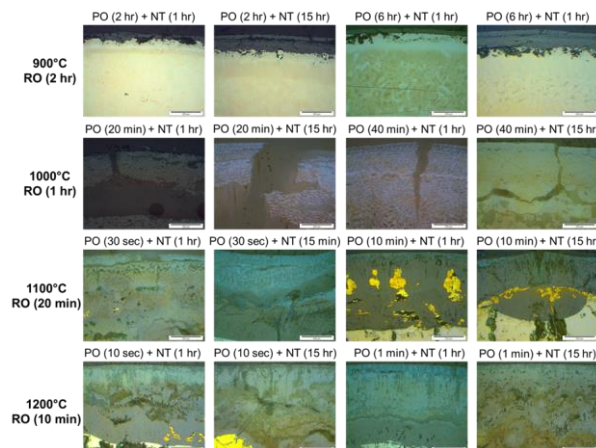


Fig. 10. Micrographs of the re-oxidized samples

Parameter: temperature

Fig. 11 shows the re-oxidation mass gain for the beginning 10 min as a function of re-oxidation temperature.

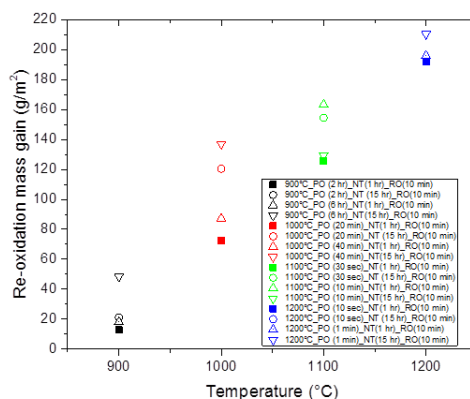


Fig. 11. Re-oxidation mass gain for 10 min at 900-1200°C

As shown in Fig. 11, higher nitriding mass gain was observed with higher re-oxidation temperature. As discussed in the section of analysis of temperature effect on the nitriding, higher temperature may allow more energy for oxygen to overcome the activation energy to initiate the re-oxidation of nitride and further oxidation

of the remained metal. For 10 minute of re-oxidation, re-oxidation mass gain difference between each temperature looked linearly-increased.

▪ **Parameter: breakaway**

Fig. 12 shows the re-oxidation mass gain of tests with prior-breakaway (blue) and without prior-breakaway (red) during pre-oxidation period.

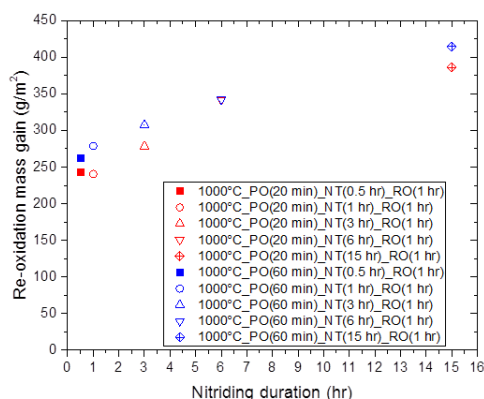


Fig. 12. Re-oxidation mass gain as a function of breakaway

As shown in Fig. 12, slightly higher re-oxidation mass gain was observed in the tests with prior-breakaway than in without prior-breakaway. Unlike the effect of the breakaway on the nitriding behavior, this prior-breakaway effect on the re-oxidation behavior seems not significant. O₂ diffusion through the oxide/nitride scale during the re-oxidation period could be enhanced not only by the breakaway but also by the volume expansion from the phase transformation from nitride to oxide. During the breakaway by a phase transformation from tetragonal to monoclinic ZrO₂, molar volume expansion would be 4.65%, but it would be 46.62% by a significant molar volume differences between nitride and oxide during the re-oxidation of nitride. For this reason, the effect of breakaway on the re-oxidation behavior would give an additional enhancement of re-oxidation kinetics.

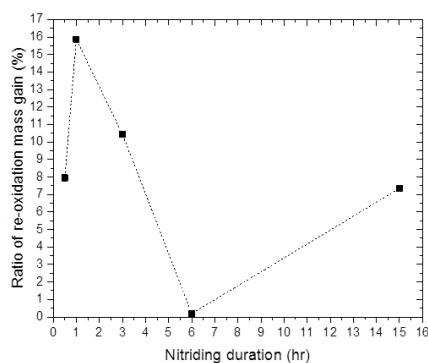


Fig. 13. Relative difference of re-oxidation mass gain as a function of breakaway

It is expected that the additional enhancement would be ca. 10% (4.65/46.62) by taking into account the molar volume expansion during the breakaway and the re-oxidation of nitride, respectively. Fig. 13 shows the relative difference of re-oxidation mass gain. The relative difference of nitriding mass gain was calculated as a ratio of $\{(\text{RO mass gain of prior-breakaway}) - (\text{RO mass gain of non-breakaway})\}$ and $(\text{RO mass gain of non-breakaway})$ in percentage. As shown in Fig. 13, relative ratios were scattered around 10% and an average of the relative mass gain is 8.4% that is close to the expected value of 10%.

4. Conclusions

A series of pre-oxidation – nitriding – re-oxidation tests were conducted to understand a nitriding and re-oxidation behaviors at 900-1200°C. Behaviors of nitriding and re-oxidation were qualitatively investigated by three parameters: nitriding duration, temperature and breakaway. To understand better the behaviors, a semi-quantitative analysis was also performed. The semi-quantitative analysis consists of mass balance analysis and optical microscope image analysis. This paper only presents a qualitative analysis of nitriding and re-oxidation behaviors. The present study will contribute developing a nitriding and re-oxidation model for nuclear reactor system analysis codes.

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