Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 17-18, 2012

Quantitative Measurement of Displacement and Strain Fields in the ZrO_2 Layer during the Transition in Oxidation Kinetics

Dong Jun Park*, Byoung Kwon Choi, Jeong Yong Park
LWR fuel Technology Division, Korea Atomic Energy Research Institute, 1045 Daedeok-daero, Yuseong-gu, Daejeon 305-353, Korea
***Corresponding author: pdj@kaeri.re.kr**

1. Introduction

A number of excellent properties, such as high resistance to corrosion by water, small cross-section for capture of thermal neutrons, adequate strength, and formability are required for Zr based alloys to be used as fuel cladding in light water reactors (LWRs). Among those properties, corrosion behavior of Zr based fuel cladding is a key concern since it could greatly affect both the operating performance during normal operation and the safety margins under transient or accident conditions. Therefore, corrosion tests under various conditions should be performed to predict the long term corrosion behavior and improve understanding of corrosion mechanism of Zr based alloys. In this respect, corrosion behavior of Zr based alloy has been extensively studied.

Interestingly, despite various test conditions in different research groups, transition in oxidation kinetics was a common characteristic of all Zr base alloys, regardless of the oxidizing condition, temperature, and their composition [1].

The transition can be explained as an abrupt change in the oxidation kinetics of Zr based alloys from an approximately parabolic to a linear rate law. The representative phenomena observed after transition are nodular and breakaway oxidation. Nodular oxides having a lenticular shape are formed at local region on the surface of uniform ZrO2 layer while whitish oxides are eventually developed in the entire surface in case of breakaway oxidation. These two phenomena have different appearance and reasons for their occurrence but they exhibit very similar post-transition characteristics in several points.

Once the nodular or breakaway oxidation occurred after the transition point, several changes are observed in the oxide layer on the surface of the Zr based alloy metals. The superficial layer of Zr oxide changes color from the black to the white. In both cases, Zr oxide layer formed after transition lost its protectiveness. Oxygen deficient and non-stoichiometric ZrO2-x is the main species in initial black uniform oxide, while stoichiometric ZrO2 is the main oxide species in the whitish oxide. Another noticeable change during transition to breakaway is crystalline structure of oxide layer. The proportion of oxide with metastable tetragonal phase decreases, and most of tetragonal phase is replaced by the monoclinic form in the end. Recrystallized microstructure in oxide layer, micro-pores [2], and cracks [1] can be also observed in the oxide layer formed after transition point.

Even though several mechanisms with different explanation for the occurrence of nodular corrosion or breakaway oxidation have been proposed in a number of literatures, controversies remain, and it is still unclear how these abnormal corrosion behaviors occur. Mechanical failure of a protective oxide layer under the compressive stresses generated during oxidation is one of the reliable causes for initiation of transition in oxidation kinetics among a number of plausible theories [3].

In this report, microstructural characterization and mechanism of nodular oxide were investigated by using high resolution transmission electron microscopy (HRTEM) and strain in the oxide layer was analyzed by geometric phase analysis (GPA) method.

2. Methods and Results

In this section, GPA methods used to analyze strain filed in the oxide layer during the transition and some of remarkable results obtained from TEM analysis for microstructural characterization.

2.1 GPA method

High-resolution transmission electron microscopy (HRTEM) is one of most powerful tool for microstructural study of various materials because of its atomic scale resolution. Recently, the development of quantitative image analysis methods made it possible to analyze the strain field with the atomic scale using HRTEM images. Geometric phase analysis (GPA) is one of such techniques [4]. The GPA can be applied to wide range of systems. According to study reported by Hy¨tch *et al.*, the accuracy of the technique demonstrated was 0.003 nm. In this study, the GPA was applied to quantitative measurements of strain field of ZrO2 layer formed before and after transition point [5].

2.2 HRTEM analysis

A HRTEM image obtained from the nodular ZrO_2 formed after transition. Fast Fourier transformed (FFT) image in the Fig. 1(b) indicates that the direction of incident beam is parallel to the ZrO_2 $[0\,\bar{1}\,1]$ and crystalline structure is monoclinic.

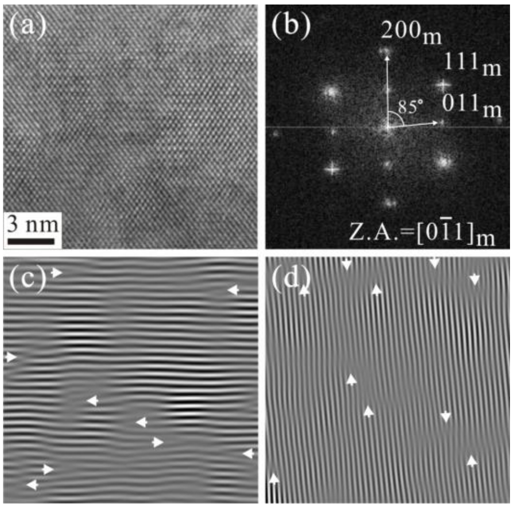

Fig. 1. (a) Cross-sectional HR TEM image taken from the white nodular oxide layer and (b) its Fast-Fourier-transformed patterns. Fourier-filtered image using the ZrO (c) (200) and (d) (011) reflection.

The extra half planes can be seen in Figs. 1(c) and 1(d), which is a Fourier-filtered image of Fig. 1(a) using the ZrO_2 (200) and (011) reflections. The cores of edge dislocation can clearly be seen by arrows. Dislocations have strain fields arising from distortions at their cores and strain drops radially with distance from dislocation core. Edge dislocations introduce compressive and tensile strain their above and below slip plane.

2.3 Geometric Phase images

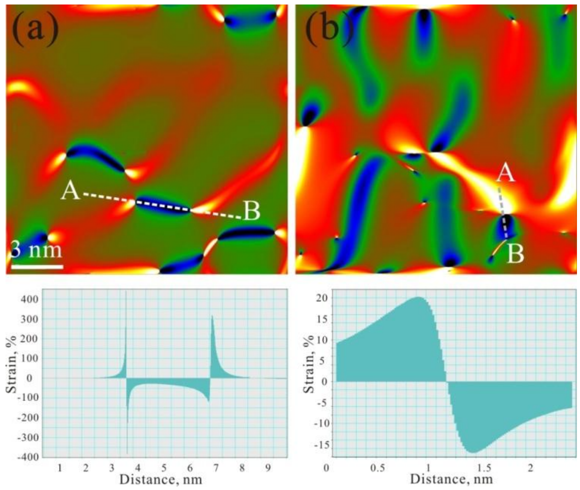

Fig. 2. (a) ε_{yy} and (b) ε_{xx} strain field obtained from geometric phase image analyzed with (200) and (011) reflections of Fig 3(a). Simulated strain corresponding to dotted line from A to B is shown in the bottom of each image as a function of distance.

GPA for the ZrO_2 (200) and (011) lattice fringes was conducted by using HRTEM image of Fig 1(a) and corresponding strain field to each dislocation core of Figs. 1(c) and 1(d) is shown in Figs. 2(a) and 2(b), respectively. Variation of color from blue to red in the strain map indicates strain changes of negative value to positive value. Regions showing convergence of color in Fig. 2 (a) and 2(b) were very consistent with location of white arrows indicating extra half-plane in Figs. 1 (c) and 1(d).

3. Conclusions

Microstructural characterization study for nodular ZrO_2 layer after the transition was carried out by HRTEM analysis and GPA method. It is assumed that great deformation of ZrO_2 during transition in oxidation kinetics occurred by stress increase in the oxide layer which is caused by Pilling and Bedworth ratio (1.56) of the Zr/ZrO_2 system. As a result, the dislocation density increases with plastic deformation in the ZrO_2 layer. This behavior was clearly seen in geometric phase image. Thus it would seem that the abrupt rise in the oxidation rate at the critical stress is caused by mechanical failure of a protective oxide. In this process, microscopic change such as formation of a number of dislocations was closely related to transition in the oxidation kinetics of Zr based alloy.

REFERENCES

[1] D. H. Bradhurst and P. M. Heuer, “The Influence of Oxide Stress on the Breakaway Oxidation of Zircaloy-2”, J. Nucl. Mater., Vol. 37, p. 35-47, 1970.
[2] B. Cox, J. Nucl. Mat. Vol. 29, p. 55, 1969.
[3] T. Arima, T. Masuzumi, H. Furuya, K. Idemitsu, Y. Inagaki, “The oxidation kinetics and the structure of the oxide film on Zircaloy before and after the kinetics transition” J. Nucl. Mater. Vol. 294, p. 148-153, 2001.
[4] Hy¨tch MJ, Snoeck E, Kilaas R., “Quantitative measurement of displacement and strain fields from HREM micrographs", Ultramicroscopy Vol. 74, p.131, 1998.
[5] Hy¨tch MJ, Putaux J-L, Pe´nisson J-M. Nature, Vol. 423, p. 270, 2003.