

Oxidation Behavior of Proton-irradiated 316 SS Prepared by Inclined Grinding Method

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1. Introduction

Austenitic 316 stainless steel (SS) is a common structural material used in pressurized water reactor (PWR) components. The radiation environment in a reactor causes substantial degradation in the properties of 316 SS and can lead to premature failures. The failure mechanism of a core component manufactured by 316 SS in the PWR environment is still not well understood due to its intrinsic complexity; however, it appears that microstructural and microchemical alterations by neutron irradiation are the key variables responsible for the component failure. Proton irradiation is a useful experimental technique for simulating neutron radiation-induced phenomena in nuclear core materials despite some limitations [1]. A challenging issue associated with the irradiation using protons is that proton irradiation-induced defects accumulate near the surface within a narrow range of a few tens of micrometers with the level of radiation damage changing depending on the depth, resulting in a non-uniform and inhomogeneous distribution of defects within the irradiated layer.

In the present study, a newly developed inclined grinding method (IGM) is introduced. The purpose of the IGM is to overcome the difficulties in preparation of proton-irradiated test specimens from which the degree of radiation damage could be estimated precisely on the surface. Then, oxidation tests were conducted to obtain clear insight into the internal and intergranular oxidation behavior of proton-irradiated 316 SS when this material was exposed to PWR primary water.

2. Methods and Results

2.1 Material and Proton Irradiation

Table 1. Composition of the austenitic 316 SS (wt%)

Cr	Ni	C	Mo	Mn	Si	Cu	P	Fe
16.1	10.4	0.047	2.11	1.08	0.66	0.1	0.003	Bal.

Austenitic 316 SS was used in this study, and the chemical composition of the alloy is given in Tables 1. The test alloy was solution annealed at 1100 °C and finally water quenched. Before proton irradiation, the surfaces of the specimens were mechanically ground

and then electrochemically polished. The proton irradiation was performed with the General Ionex Tandatron accelerator at the Michigan Ion Beam Laboratory at the University of Michigan. The irradiation processes were conducted using 2 MeV protons at a current range of 40 μ A. The specimens were exposed at 360 °C to the level of irradiation of 2.7 displacements per atom (dpa) at a depth of 10 μ m from the surface. The radiation damage levels of the samples were calculated with the Stopping and Range of Ions in Matter (SRIM) program using a displacement energy of 40 eV in the 'quick calculation' mode [2].

2.2 Specimen Preparation by IGM

The specimens for oxidation test were prepared using the IGM. The basic idea of the IGM is that the change of the radiation damage depending on the depth is to project on the surface on an enlarged scale. Fig. 1 shows an example of the proton-irradiated 316 SS to prepare test specimens using the IGM. When 316 SS is irradiated by protons at an energy level of 2 MeV, the radiation damage reaches approximately 20 μ m in the depth direction. It can be confirmed from Fig. 1 that the range of radiation damage on the surface was enlarged to approximately 4.5 mm in the length direction. Therefore, one of the beneficial effects using the IGM is to be able to examine the large area with a variety of radiation damages on the surface.

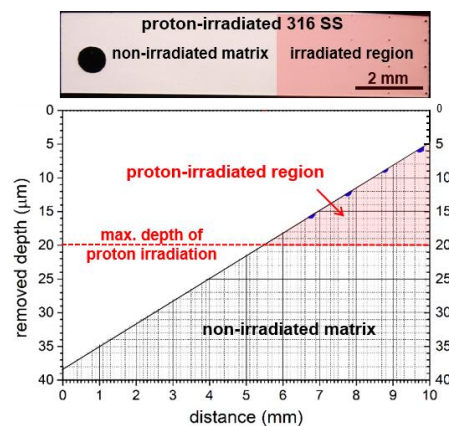


Fig. 1. Test specimen prepared by the IGM and the variation of removed depth depending on the distance on the surface.

2.3 Oxidation Test

Coupons ($10 \times 10 \times 2 \text{ mm}^3$) for the oxidation test of proton-irradiated type 316 SS were prepared by the IGM. The simulated PWR water was prepared prior to the test and held in a storage tank. In this study, 1200 ppm B (by weight) of H_3BO_3 and 2 ppm Li (by weight) of $\text{Li}(\text{OH})$ were added to pure water. The oxygen concentration was maintained at less than 5 ppb during the test. The test temperature was $325 \text{ }^\circ\text{C}$ with a dissolved hydrogen concentration of $30 \text{ cm}^3 \text{ H}_2/\text{kg H}_2\text{O}$. The oxidation coupons were exposed to the test solutions for a period of 5000 hrs.

2.3 Results

Fig. 2 presents a HAADF image and EELS composition maps of O, Cr, Fe, Mn and Ni around the surface oxidation layer and the grain boundary just beneath the surface of the proton-irradiated 316 SS test specimen prepared by the IGM. The FIB TEM specimen was taken from the location on which the radiation damage was estimated to be roughly 10 dpa.

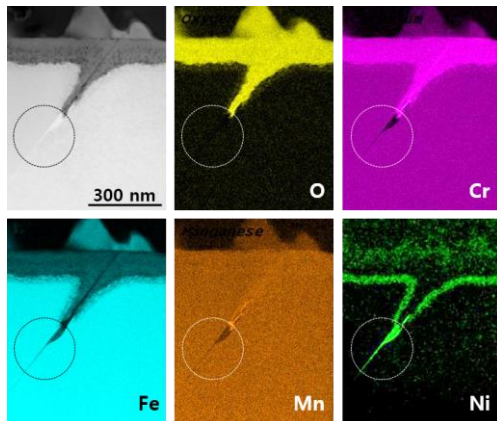


Fig. 2. HAADF image, and EELS spectrum images of O, Cr, Fe, Mn and Ni around the surface grain boundary of proton-irradiated 316 SS prepared by the IGM.

The grain boundary was oxidized due to the oxygen diffusion into the grain boundary. As confirmed from O and Cr composition maps, Cr-rich oxide formed inside the oxidized grain boundary (OGB). The remarkable feature in Fig. 2 is that Ni was enriched in the grain boundary just ahead of the oxidation front; however, the other metallic elements such as Cr, Fe, and Mn were depleted, as shown in the dotted circle in Fig. 2. A solution annealing treatment had been conducted, therefore, main metallic elements were not depleted in test alloy before the oxidation test. Ni enrichment was also found at the interfaces between the internal oxidation layer (IOL) and the adjacent 316 SS matrix.

When oxygen diffuses into Ni-base alloys, it reacts with metallic elements to form oxides. Cr and Fe always remain in an oxidized state, with more oxidation

reactivity of Cr than Fe. On the other hand, Ni ions are expelled to relieve the stress caused by the volumetric increase associated with the formation of the Cr oxide, as Ni should be in a metallic state under the present experimental conditions. Consequently, Ni ions expelled from the oxidized zone join the Ni-enriched area, as shown in Fig. 2.

Fig. 3 shows the results of a crystallographic examination conducted to identify the crystal structure of the IOL. The specimen was tilted so as to align the electron beam such that the zone axis of the right grain was $[110]$. From the analysis of the diffraction pattern inserted in the figure, it was found that the IOL had a spinel structure with the cube-cube orientation relationship with the 316 SS matrix [3].

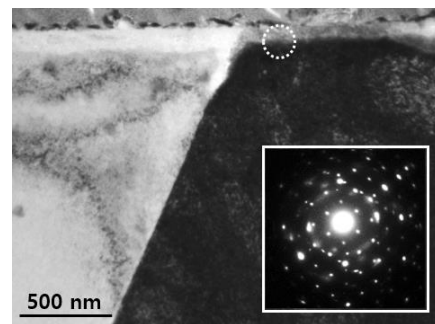


Fig. 3. TEM image and related diffraction pattern taken from the IOL denoted by the white dotted circle.

3. Conclusions

1. It was proved that the IGM could provide beneficial effects to prepare test specimens that had changing surface properties depending on the depth within a narrow range of a few tens of micrometers.
2. Intergranular oxidation occurred due to the oxygen diffusion into the grain boundary. Cr-rich oxide formed inside the OGB and Ni was enriched in the grain boundary just ahead of the oxidation front.
3. From the crystallographic examination, it was found that the IOL had a spinel structure with the cube-cube orientation relationship with the 316 SS matrix.

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