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Detection of intergranular cracking susceptibility due to hydrogen in irradiated austenitic stainless steel with a superconducting quantum interference device (SQUID) sensor

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Abstract

To investigate the detection method of intergranular (IG) cracking susceptibility by hydrogen in irradiated austenitic stainless steel (SS), magnetic and mechanical properties were examined after two repeats of hydrogen charging and discharging (hydrogen treatment) in Type 304 SS which had been irradiated during use in different reactor cores. The residual magnetic flux density (Br) was measured with a superconducting quantum interference device sensor and Br increased with increased neutron fluence and repeated hydrogen treatments. Elongation decreased with an increase of Br and IG cracking appeared above Br of 2×10^{-5} T for this measuring method after repeated hydrogen treatments. These phenomena would be caused by hydrogen-induced martensite phase being formed on grain boundaries. It was thought the appearance of IG cracking susceptibility due to hydrogen in irradiated SS could be predicted by measuring the Br of the steel. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The irradiation assisted stress corrosion cracking (IASCC) mechanism is not fully understood, but Cr depletion is one dominant factor in an environment with high dissolved oxygen concentration [1–3]. Intergranular (IG) cracking appears due to the hydrogen charging and discharging process (hydrogen treatment) in highly irradiated Type 304 stainless steel (SS), in which a Cr depleted zone along grain boundaries is observed [4]. It is known that radiation-induced segregation (RIS) appears at grain boundaries in irradiated Type 304 SS when the neutron fluence is higher than about 5×10^{23} n/m^2 [5] and that RIS by neutron irradiation induces a phase transformation, which is the ferrite phase in austenitic steels [6]. The magnetic properties of irradiated Type 304 SS would be expected to be changed by the phase transformation. These changes have been studied with a superconducting quantum interference

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device (SQUID) sensor. A SQUID sensor is an extremely sensitive magnetic sensor that uses Josephson junctions. It can detect magnetic fields as small as 10^{-14} T (Tesla). In recent years, the use of SQUID for non-destructive inspection of metals has been studied, particularly for thermal degradation and fatigue damage evaluations [7–10]. To investigate the correlation between IG cracking susceptibility due to hydrogen and magnetic properties, irradiated Type 304 SS specimens, both as-irradiated and with two repeats of hydrogen treatment, were subjected to SQUID measurements. Measured magnetic properties and tensile test results [4] were compared and the correlations were discussed.

2. Experimental procedure

2.1. Materials

Type 304 SS tubes were irradiated in the core of boiling water reactors at 561 K. Chemical composition, mechanical properties and neutron fluence and neutron flux are listed in Table 1. The tubes were 16 and 17.3 mm in diameter with 1 and 2.3 mm thicknesses, respectively. Archives Type 304 SS tubes (16 mm diameter with 1 mm thickness) were used for reference materials. Specimens were cut from the tubes and were a quarter section wide and 20 mm long to ensure the magnetic flux density in the space during measurements was uniform. Surfaces of specimens hardened by cutting were removed by immersing in 35% hydrochloric acid for 20 min at room temperature.

2.2. Hydrogen treatment

Cathodic hydrogen charging of specimens was employed as a safer method for treating irradiated materials in the hot laboratory than using high temperature and high pressurized hydrogen gases.

The solution used was 1 N H_2SO_4 with $NaAsO_2$ as the surface activator and it was kept at 323 K by using a mantle heater. An intermediate current density [11] of 42 A/m^2, which did not cause hydrogen-induced cracking, was used for hydrogen charging. Hydrogen discharging was done on a hot plate at 373 K. Hydrogen charging was continued for 24 h, followed by hydrogen discharging for 24 h. One cycle of hydrogen charging and discharging is referred to as the hydrogen treatment. The hydrogen treatment was done twice.

2.3. Measurement of magnetic properties

This apparatus (Fig. 1) was composed of a liquid helium cryostat, readout electronics, an *X–Y* recorder and a SQUID sensor, which is made up of a SQUID, a gradiometer and a superconducting magnet. The SQUID was a radio frequency type. The present gradiometer configuration has been commonly used in SQUID applications and is well known as a first-order pick-up coil for the perpendicular axis (z). Therefore, the gradiometer is sensitive to changes in the field gradient $\partial^2 B/\partial z^2$. The SQUID sensor and superconducting magnet were placed in the liquid helium cryostat. The cryostat was made of non-magnetic fiber reinforced plastic. The stand off distance between the gradiometer and the specimen was 60 mm.

Table 1
Chemical composition, mechanical properties, neutron fluence and neutron flux

Material	Dimensions (mm)	Chemical composition (wt%)[a]							Mechanical properties[a]		Radiation conditions	
		C	Si	Mn	P	S	Cr	Ni	Tensile strength (Mpa)	Elongation (%)	Neutron fluence (n/m^2)/ $E > 1$ MeV	Neutron flux ($n/m^2/s$)
Type 304	$\phi 16 \times 1^t$	0.06	0.49	1.74	0.034	0.013	18.50	9.35	596	63.4	0	0
											1.0×10^{24}	3.6×10^{16}
											5.0×10^{24}	4.9×10^{16}
											1.1×10^{25}	1.0×10^{17}
	$\phi 17.3 \times 2.3^t$	0.05	0.37	1.75	0.03	0.014	18.14	9.03	608	57.0	1.4×10^{26}	7.4×10^{17}
	$\phi 16 \times 1^t$	0.06	0.49	1.74	0.034	0.013	18.50	9.35	596	63.4	2.0×10^{24}	3.1×10^{16}
												4.5×10^{16}
												7.5×10^{16}
											5.0×10^{24}	4.9×10^{16}
												6.7×10^{16}
												9.2×10^{16}

[a] Mill sheet value.

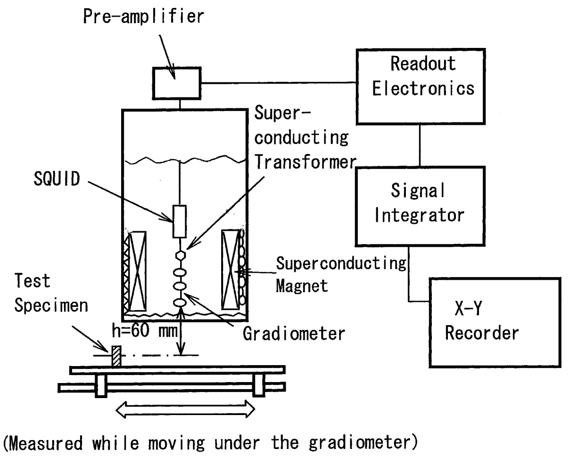

Fig. 1. System diagram of apparatus for measuring magnetic properties.

The measurement system was set up in the hot cell and the control unit was placed in the control room of the hot laboratory. An irradiated specimen was placed on the moving table by using a manipulator. This specimen was magnetized to 43 kA/m by the superconducting magnet. This was the maximum magnetic field strength (*H*) in this measuring system. The measuring method was the same as in previous reports [9,10,12–14] and the magnetic flux density (*B*)–*H* curves for irradiated Type 304 SSs were observed.

3. Test results and discussion

3.1. Magnetic properties of as-irradiated Type 304 SSs

Typical *B*–*H* curves of the specimens are shown in Fig. 2. The Br and magnetic coercive force (H_c) of unirradiated specimens were zero, but hysteresis loops appeared for the irradiated Type 304 SSs. The effects of neutron fluence on Br of irradiated specimens are shown in Fig. 3. Numerals for each point show the neutron flux. Br increased with increasing neutron fluence. But there was a little scattering of the data. One reason for this seemed to be that the data with several neutron fluxes were plotted on this same figure. Br seemed to increase with decreasing neutron flux.

It is known that RIS occurs with neutron irradiation, and it increases with increasing neutron fluence [5]. The RIS in the austenite phase induces a partial phase transformation from the austenite phase to the ferrite phase in austenitic steels [6]. RIS would be expected to increase the magnetic properties and the RIS in Type 304 SS at 561 K was thought to induce a phase transformation from the austenite phase to the ferrite phase, although the test temperature and the tested materials

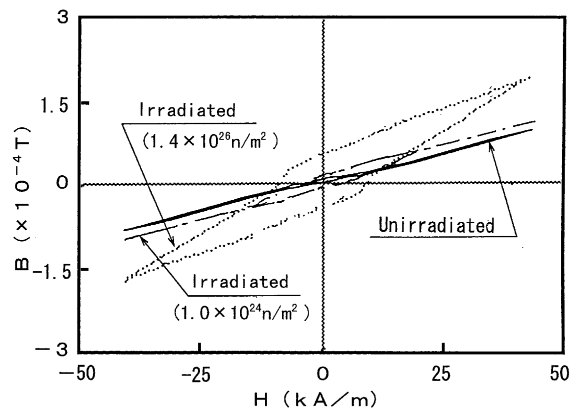

Fig. 2. Typical hysteresis loops (*B*–*H* curves of unirradiated and irradiated Type 304 SSs).

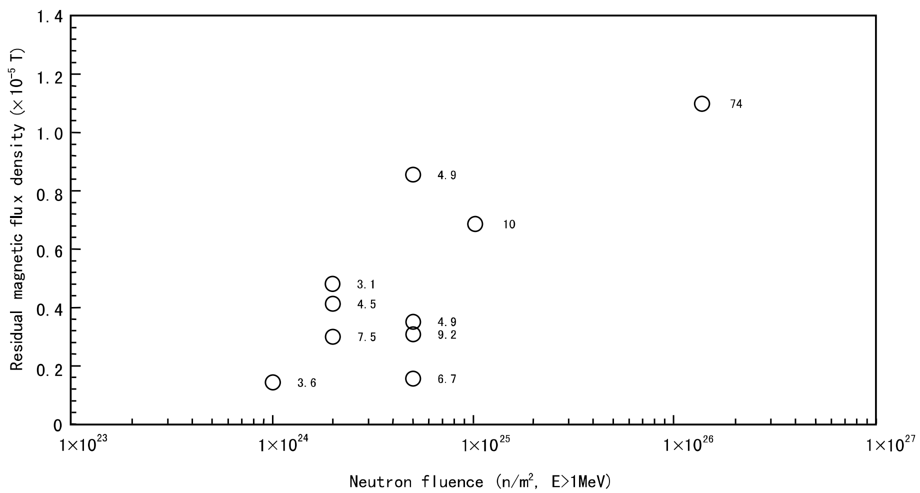

Fig. 3. Effect of neutron fluence on residual magnetic flux density (no hydrogen treatment).

are different between this study and the reference [6] (638 K, Fe–10Cr–15Mn). The RIS and the mass of the phase transformation by RIS would increase with increasing neutron fluence. So Br in irradiated Type 304 SSs would increase with increasing neutron fluence. This would be one of the reasons Br increased with increasing neutron fluence.

On the other hand, in the present study Br seemed to increase with decreasing neutron flux. It reported that RIS increased with decreasing neutron flux at 561 K [15]. The flux dependence of Br and RIS shows the same tendency. The present results would indicate that the decreasing neutron flux brought on the increase of the mass of the phase transformation by RIS.

3.2. Magnetic properties of irradiated and hydrogen treated Type 304 SSs

The effect of neutron fluence on Br for two repeats of hydrogen treatment is shown in Fig. 4 which plots results for both as-irradiated (no hydrogen treatment) and with hydrogen treatment. The Br was increased by both hydrogen treatment and the increase of the neutron fluence. It was reported that the hydrogen-induced martensite phase was induced by the hydrogen treatment [4], and that RIS increased with increasing neutron fluence [5] and the phase transformation would be expected to be induced through RIS by the neutron fluence as mentioned in Section 3.1 though the materials used and the test temperature were different from this study. The mass of the phase transformation seemed to increase with increasing neutron fluence. So the Br after the hydrogen treatment was larger than that of as-irradiated SS at the same neutron fluence and increased with increasing neutron fluence.

3.3. Relationship between Br and appearance of IG cracking susceptibility

To investigate the effect of Br on elongation and average depth of IG cracking of irradiated SS, measured Br and tensile test results [4] were compared with as-irradiated and hydrogen treated Type 304 SSs. The heat numbers of the materials used for this study and these tensile tests were the same and the hydrogen treatment conditions for both studies were the same also. Tensile tests were done at room temperature in air and the cross head speed was 0.55 mm/min, which corresponded to a strain rate of 4.2×10^{-5} s^{-1} for the specimen. The fracture surface was observed by scanning electron microscopy (SEM) after the tensile tests. For the intergranularly fractured specimens, at first the area ratio of IG fracture was measured, then the average depth of IG cracking was calculated. The effect of Br on elongation and average depth of IG cracking in both as-irradiated and hydrogen treated specimens is shown in Fig. 5.

The elongation decreased with an increase of Br in both irradiated and hydrogen treated SSs. IG cracking was not observed when the value of Br was $<2 \times 10^{-5}$ T. But when the value of Br was over 2×10^{-5} T, the elongation decreased to 10% and IG cracking appeared. According to these results, the appearance of the IG cracking susceptibility by hydrogen treatment in irradiated Type 304 SSs would be predictable by measuring Br after the hydrogen treatment. These results seemed to be due to the mass of the phase transformation by RIS and

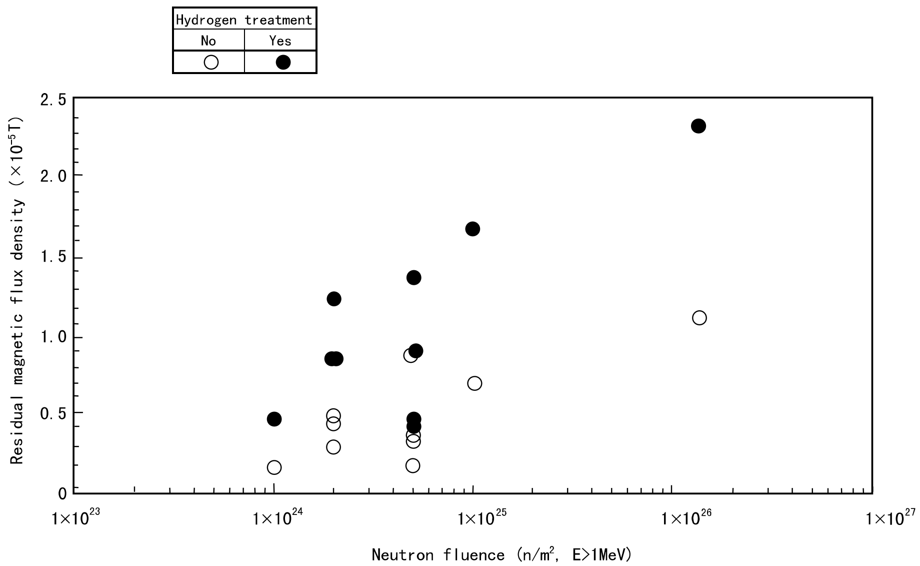

Fig. 4. Effect of neutron fluence on residual magnetic flux density (no hydrogen treatment and with it).

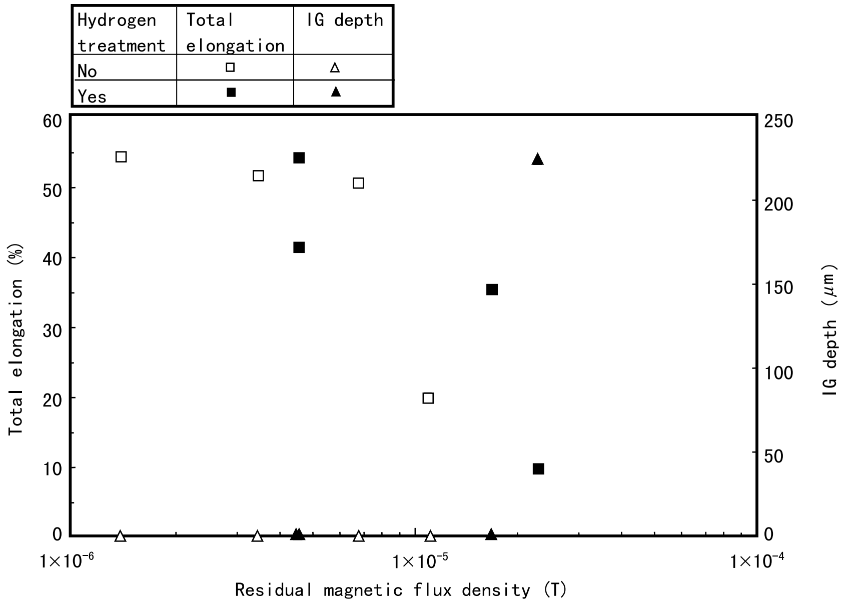

Fig. 5. Effect of residual magnetic flux density on elongation or average depth of IG cracking (average depth of IG cracking: IG depth).

the hydrogen-induced martensite phase. The reason for the detection of the IG cracking appearance over Br of 2×10^{-5} T after hydrogen treatment was explained as follows. The Cr content at grain boundaries in Type 304 SS has been reported to decrease with increasing neutron fluence [5]. As the Cr depleted zone at the grain boundaries existed in SS neutron irradiated to 1.4×10^{26} n/m^2, hydrogen-induced martensite phase was able to be formed at the grain boundaries after the hydrogen treatment [4]. So IG cracking appeared over Br of 2×10^{-5} T for this measuring method.

3.4. Evaluation for appearance of IG cracking susceptibility due to hydrogen

To evaluate the relationship between Br and the appearance of IG cracking susceptibility after the hydrogen treatment in irradiated SS, tensile test results of unirradiated SSs were collected from the authors' other literature [16] and Br was measured from the hysteresis loops for unirradiated sensitized (no hydrogen treatment) and hydrogen treated Type 304 SSs [16]. These materials were the same as archives Type 304 tubes (1.6 mm diameter with 1 mm thickness) used for reference materials in this study. The tensile test and the hydrogen treatment conditions were the same as in references [4,16]. The relationship between Br and elongation or average depth of IG cracking is shown in Fig. 6. The elongation decreased with an increase of Br. Though IG cracking was not observed at lower Br, it appeared and increased in hydrogen treated SS as Br increased. The ε-martensite phase and α′-martensite phase were observed after the hydrogen treatment and these phases were designated as the hydrogen-induced martensite phase [16]. The martensite phase seemed to be formed at the grain boundaries, where the Cr depleted zone existed [16]. In general, martensite phase is brittle and hydrogen has a tendency to accumulate in the boundaries of martensite and austenite phases [17]. The grain boundaries became brittle and IG cracking occurred in the tensile tests after the hydrogen treatment. The increase of the Br would be caused by the increase of the mass of martensite phase on the grain boundaries. So average depth of IG cracking increased with an increase of Br.

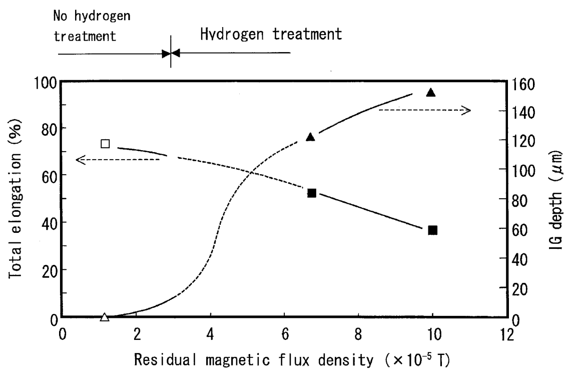

Fig. 6. Effect of residual magnetic flux density on elongation or average depth of IG cracking in Type 304 SSs unirradiated and sensitized with 923 K × 3 h [16].

The same reason would explain the relationship between the appearance of IG cracking susceptibility of irradiated SS and Br. IG cracking appeared when Br was larger than 2×10^{-5} T for this measuring method in irradiated SSs, namely when the neutron fluence was larger than 1×10^{25} n/m^2 from the results of Fig. 4 for hydrogen treated materials. And then the Cr depleted zone would be expected to exist at the grain boundaries [5] and hydrogen-induced martensite phases would be formed on the grain boundaries after the hydrogen treatment. Considering these results, the appearance of IG cracking after the hydrogen treatment could be predicted by measuring the Br after hydrogen treatment. On the other hand, the Br of as-irradiated SS was about 7×10^{-6} T when the neutron fluence was 1×10^{25} n/m^2. When the neutron fluence became larger than 1×10^{25} n/m^2, Br became larger and the IG cracking appeared after the hydrogen treatment. When the Br of as-irradiated SS became larger than about 7×10^{-6} T, IG cracking appeared after this hydrogen treatment. So the appearance of IG cracking susceptibility due to hydrogen under this condition of hydrogen treatment in irradiated SSs could be predicted by measuring the Br of the steel. Namely, after the following database was built up, the appearance of IG cracking susceptibility due to hydrogen under various conditions of hydrogen treatment would be able to be predicted by measuring the Br of irradiated SSs. The database contains relationships for neutron fluence and Br for both as-irradiated SSs and hydrogen treated SSs, and for IG depth and Br for both as-irradiated SSs and hydrogen treated SSs.

4. Conclusion

The detection of IG cracking susceptibility by hydrogen in Type 304 SS irradiated with neutrons at 561 K was investigated and the following conclusions were obtained.

1. Br for irradiated Type 304 SS increased with increasing neutron fluence. One reason for this would be the increasing mass of RIS and the phase transformation by RIS.
2. Br increased due to the hydrogen treatment and was more than Br of as-irradiated SS. Also Br increased with increasing neutron fluence. These results were attributed to formation of hydrogen-induced martensite phase by the hydrogen treatment.
3. Elongation decreased with an increase of Br and IG cracking appeared when Br was over 2×10^{-5} T for this measuring method after the hydrogen treatment. These phenomena would be caused by hydrogen-induced martensite phases being formed on grain boundaries.
4. The appearance of IG cracking susceptibility due to hydrogen in irradiated austenitic SS would be able to be predicted by measuring the Br of irradiated SS after building up the database of the relationships between IG depth and Br for both as-irradiated and hydrogen treatment specimens.

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