The Most Susceptible Reason of Low Temperature Mill Annealed (LTMA) Alloy 600 to PWSCC

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1. Introduction

The structural components made of Alloy 600 and Weld 182 in PWR have suffered a PWSCC (primary water stress corrosion cracking) PWR for last several decades. This damage process is known to be a thermally activated process. This means that its initiation time is shorter when the temperature of component is higher. However, the nature of the thermally activated process is not explained properly.

The contradictions or limits of the previous explanation for PWSCC can be summarized as follows: (a) Alloy 600 is the most corrosion resistant material, whereas the primary water is the most mild solution in the aspect of corrosion; (b) The existence of residual stress is not pertinent to explaining the thermally activated nature of PWSCC; (c) although the level of residual stress is the highest in the early period in the reactor operation, it is recognized that PWSCC does not occur in an early stage; and (d) a sensitized Alloy 600 with Cr depletion at grain boundary is not most susceptible to PWSCC [1].

A PWSCC mechanism based on ordering reaction in Alloy 600 has been proposed in 2008. The model provides a proper explanation for the thermally activated process in PWSCC. The activation energy for the ordering reaction in Alloy 600, $Q_{ordering}$, is 190 kJ/mol [2-4]. This is very similar to the activation energy for the activation energy for the PWSCC initiation, $Q_{PWSCC\ initiation}$, 185 kJ/mol. Again, this means that the rate controlling step of PWSCC is the ordering reaction.

This fact suggests strongly that the origin of thermally activated process in PWSCC is closely related to the ordering reaction. According to this model based on ordering reaction, the driving force for the PWSCC is supplied by the additional stress formed by lattice contraction due to the ordering reaction [1]. Thus, the initiation of PWSCC in Alloy 600 is governed by the kinetics of lattice contraction.

In order to explain the most susceptible reason of LTMA (low temperature mill anneal) Alloy 600, a lattice variation with aging at 400℃ was systematically investigated using high resolution neutron diffraction (HRPD) in HTMA (high temperature mill anneal), LTMA, sensitization, AC (air cooled), and FC (furnace cooled) Alloy 600.

2. Experimental

Alloy 600 rod with 10 mm diameter was used. The chemical composition is shown in Table 1. Alloy 600 was variously treated; 1) water-quenched (WQ) from 1095°C-0.5H (HTMA), 2) water-quenched (WQ) from 965°C -1H (LTMA), 3) water-quenched (WQ) from 600 °C-24H (sensitization), 4) air-cooled (AC) from solution annealing (SA) treatment at 1095°C, 5) furnace-cooled (FC) from solution annealing (SA) treatment at 1095 °C.

These series were ordering-treated up to 5,500 hours at 400°C.The lattice variation of these specimens was examined by HRPD in Hanaro at KAERI. The schematic illustration of HRPD apparatus is shown in Fig. 1. The examined volume of Alloy 600 specimens is about 3cc. The specimen is rotated during neutron diffraction measurements. It is possible to measure the anisotropic lattice variation, since HRPD provides a focusing free characteristic of diffraction. The lattice variation is calculated by equation of $(d_{ordered} - d_{as\text{-}received})/d_{as\text{-}received}$.

Table 1. Chemical composition of Alloy 600 (wt.%).

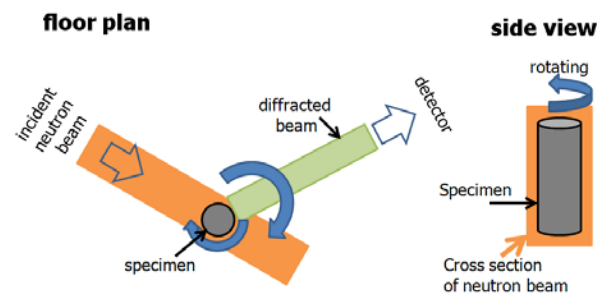| Elements	C	Cr	Fe	Ni	Mn	S
Alloy 600	0.009	16.25	8.15	74.55	0.32	0.002

Fig. 1. Schematic illustration of diffraction apparatus during measurement in high resolution neutron diffraction (HRPD).

3. Results and Discussions

Fig. 2 shows the lattice variation with ordering time at 400°C in HTMA specimen. The magnitude of lattice contraction in (111) and (200) appeared about 0.035% at 2,000 hours, whereas, that of (220) plane is 0.02%. The lattice contraction saturates after 2,000H at 400°C. It is understood that the lattice variation is anisotropic. This means that the difference in lattice contraction between high angle boundaries is larger than that of small angle boundaries. This large difference in lattice

contraction at high angle boundary would be a main reason that the PWSCC propagates generally along the high angle boundary [1].
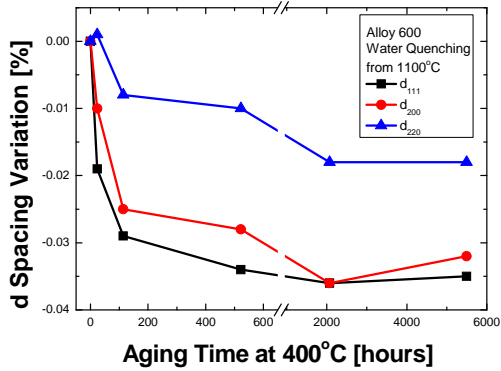

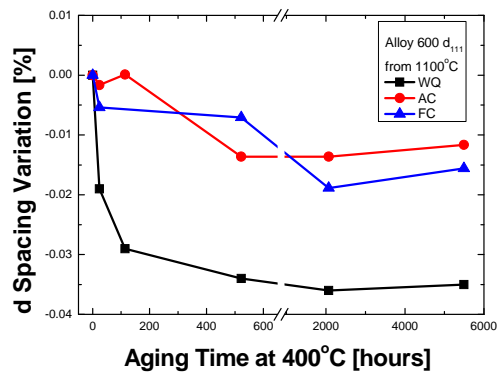Fig. 2. Comparisons of d spacing variation with aging time at 400°C in HTMA Alloy 600 [5].

Fig. 3. Comparisons of d_{111} spacing variation with aging time at 400°C in HTMA, AC, and FC Alloy 600 [5].

The lattice contraction in (111) plane in HTMA, AC, and FC conditions are compared in Fig. 3. The magnitude of the lattice contraction in HTMA is the largest compared to AC and FC. This means that the magnitude of the lattice contraction depends on the cooling rate in Alloy 600. The magnitude of lattice contraction in AC and FC specimens is lesser than 0.02% regardless of crystallographic planes.

Fig. 4 shows comparisons of d_{111} spacing variation of variously treated Alloy 600. The magnitude of lattice contraction of compared specimens is about 0.04% except FC specimen, whereas the FC specimen shows about 0.015%. The saturation times of lattice contraction are 4H, 522H, and 2068H in LTMA, Sensitization, and HTMA, respectively. This result explains the fact that the LTMA Alloy 600 is most susceptible to PWSCC.

According to the PWSCC mechanism based on the ordering reaction, the PWSCC is governed by the

ordering reaction. Therefore, the susceptibility of PWSCC initiation is governed by the kinetics of (111) lattice contraction. The lattice contraction of (111) plane in LTMA Alloy 600 is faster by 120 times than that of HTMA at least. It is thought that why the kinetics of LTMA Alloy 600 is fast can be explained by the content of carbon solution and/or the lesser degree of order in LTMA compared to the HTMA.
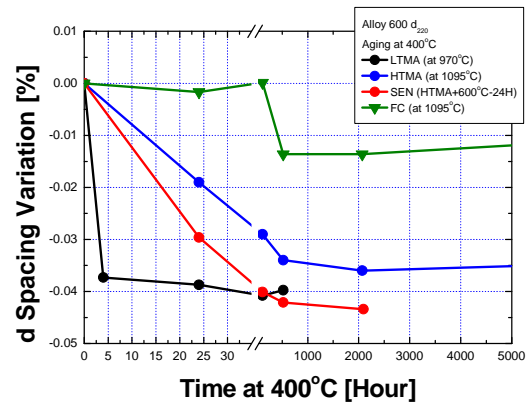

Fig. 4. Comparisons of d_{111} spacing variation with aging time at 400°C in HTMA, LTMA, Sensitization, FC Alloy 600.

Disordering occurs at above critical temperature (Tc, 520°C) in Alloy 600, whereas the ordering reaction occurs at below Tc. Therefore, disordering reaction and dissolution of carbide occur simultaneously during HTMA treatment at 1095°C [5]. The lattice contraction by ordering treatment at 400°C is natural, since the increase in the number of ordered bonds makes the atomic distance closer. The number of disordering bonds depends on the cooling rate. Thus, the number of disordering bonds will be a maximum by water quenching from 1095°C. Therefore, the magnitude of lattice contraction in HTMA specimen is the largest by the ordering reaction. The FC condition provides enough time to form the ordering bonds. It is understood that the magnitude of lattice contraction depended on both the cooling rate and the solution annealing temperature.

The ordering reaction is an unavoidable process in Ni base alloys (Alloy 600, Alloy 690, and Weld 182 etc.) and a spontaneous process in nuclear reactor environment. Therefore, the effect of lattice contraction due to ordering reaction should be considered in the assessment of integrity in the components made of Ni-based alloy

4. Conclusions

1. The saturated lattice contraction in (111) planes appeared about 0.04% in LTMA, Sensitization, and HTMA Alloy 600 for 4H, 522H, 2068H, respectively.

2. The kinetics of d_{111} lattice contraction LTMA 600 is most fast; the saturation time in lattice contraction in LTMA is 120 times shorter than that of HTMA. This can explain why the LTMA Alloy 600 is the most susceptible to PWSCC, since the PWSCC initiation process is governed by kinetics of lattice contraction due to ordering reaction, based on the based on ordering reaction mechanism.

3. The ordering treatment causes anisotropic lattice contraction according to the crystallographic planes. The ratio of minimum to maximum lattice contraction in HTMA Alloy 600 is about 2.

4. The effect of ordering reaction should be considered in the assessment of integrity of primary boundary materials made of Ni base alloys including Alloy 600, since the ordering reaction is an unavoidable phenomenon in nuclear reactor environment.

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