CORROSION SCIENCE AND TECHNOLOGY, Vol.7, No.3(2008), pp.187~191

SCC Mechanism of Ni Base Alloys in Lead Contaminated Water

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Transgranular stress corrosion cracking of nickel base alloys was reported by Copson and Dean in 1965. Study to establish this cracking mechanism needs to be carried out. Laboratory stress corrosion tests were performed for mill annealed(MA) or thermally treated(TT) steam generator tubing materials in a high temperature water containing lead. An electrochemical interaction of lead with the alloying elements of SG tubings was also investigated. Alloy 690 TT showed a transgranular stress corrosion cracking in a 40% NaOH solution with 5000 ppm of lead, while intergranular stress corrosion racking was observed in a 10% NaOH solution with 100 ppm lead. Lead seems to enhance the disruption of passive film and anodic dissolution of alloy 600 and alloy 690. Crack tip blunting at grain boundary carbides plays a role for the transgranular stress corrosion cracking.

Keywords *: Ni base alloys, alloy 600, alloy 690, Lead, Stress corrosion cracking, SCC mode*

1. Introduction

Nickel base alloy 600 and alloy 690 have been used for steam generator tubing materials in nuclear power plants. These alloys exhibit susceptibility to stress corrosion cracking (SCC) in high temperature aqueous environments with impurities. Stress corrosion cracking occurs in different modes; intergranular (IG) and transgranular (TG). Mill-annealed (MA) Alloy 600 generally showed the IG mode of SCC in alkaline water at high temperatures. However, thermally treated (TT) alloy showed the TG or IG modes, depending on the environmental conditions. Alloy 690 TT developed TGSCC in high-temperature water with a small amount of lead.[1),2)]

Many researchers have demonstrated a deleterious effect of lead on SCC by laboratory tests.[3)-5)] Transgranular stress corrosion cracking of nickel base alloys was reported by Copson and Dean in 1965.[6)] A lead-induced SCC (PbSCC) was indeed discovered in an operating nuclear power plant in 1990 (Fig. 1).[7)] Since a SCC involves the processes of passive film breakdown and dissolution of the underlying alloy matrix, it is important to understand the effect of lead on the characteristics of the passive film. The role of lead on the anodic polarization behavior of alloying elements such as Ni, Cr, and Fe needs to be clarified. Studies on the reaction of lead with alloy 600 and alloy 690 have been reported.[2)-5)] Grain boundaries and grain boundary precipitates play an important role for the SCC. It is thus necessary to understand the interplay of lead and grain boundary carbides of thermally treated materials.

The present paper addresses on the failure modes and the mechanisms of SCC for the thermally treated nickel base steam generator tubing materials in a high temperature water containing lead.

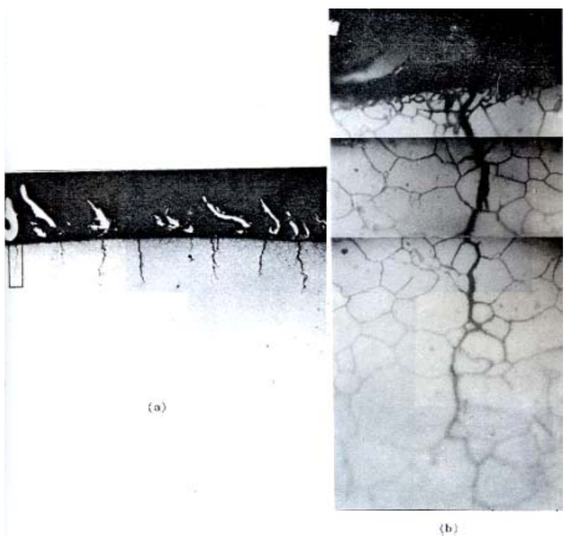

Fig. 1. Transgranualr SCC observed in an operating nuclear power plant.

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2. Experimental procedures

The test materials were alloy 600 MA, 600 TT, and 690 TT. The MA was at 960℃ for 10 minutes. The TT was at 715℃ for 12 hours for the alloy 600, and 725℃ for 10 hours for the alloy 690, respectively. Intergranular carbides were precipitated in the TT alloys. C-ring test specimens were fabricated from the materials in accordance with the ASTM G38 standard. The specimens were stressed to the value equivalent to 150% of the room temperature yield stress on the apex by using alloy 600 bolts and nuts. The apex of the outer surface of the C-ring specimens was ground by no. 600 emery paper before applying the stress. A distilled and demineralized high-purity (18 MΩcm) water used to prepare 10 % and 40 % of NaOH solutions. Lead oxide (PbO) was added to the solution to create concentration of 100 ppm and 5000 ppm of lead. The specimens were exposed to the deaerated test solutions at 315℃ and 1500 psi for 10 to 21 days. To accelerate SCC, the specimens were held at the potential +150 mV above the open circuit potential (OCP). A pure Ni wire and a plate were used as the reference and the counter electrode, respectively.

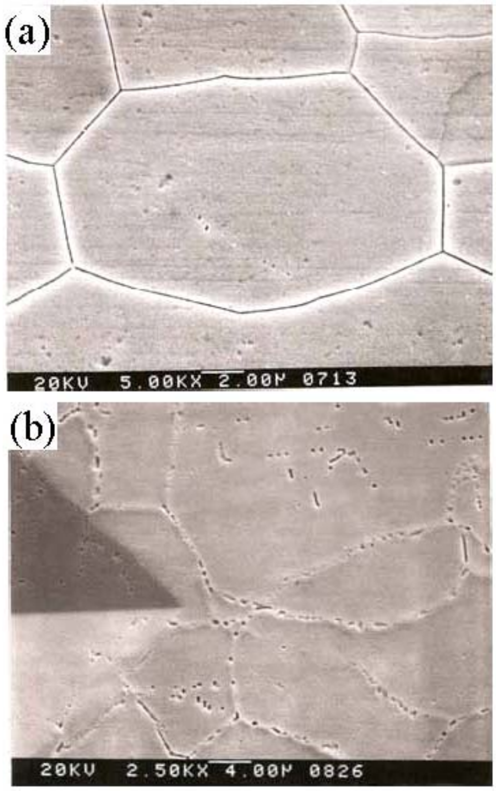


Fig. 2. Grain boundary microstructures etched in phosphoric acid: (a) alloy 600 MA and (b) 600 TT.

3. Results and discussion

3.1 SCC mode of the Ni alloys

Microstructures of the alloy 600 MA and TT are shown in Fig. 2. The specimens were etched in a phosphoric acid solution. Alloy 600 MA did not show any precipitates at grain boundaries. The carbides were fully dissolved. Alloy 600 TT, on the other hand, showed well developed grain boundary carbides.

Our high temperature tests showed that IG SCC occurred in the alloy 600 MA specimens in the 10% NaOH solution with 100 ppm lead, whereas TGSCC in the alloy 600 TT specimens in the 10 % NaOH solution with 5000 ppm lead (Fig. 3). Fig. 4 shows an example of TGSCC of an alloy 690 TT specimen which was tested in the 40% NaOH solution with 5000 ppm lead. The SCC is mostly in the TG mode, except the IG mode in small areas. A transition of crack path from IG into TG observed in the alloy 690 TT test specimens when the crack meets a grain boundary carbide, as shown in Fig. 5.

An intergranular cracking mode of alloy 600 TT and alloy 690 TT in high caustic solutions has also been reported by other investigators.[8),9)] A combination effect of the strain rate, carbon content and lead concentration on the TGSCC has been reported.[10)] According to M. Helie,[11),12)] a cracking process tends to be the TG mode when the test is conducted with SSRT even in MA alloys.

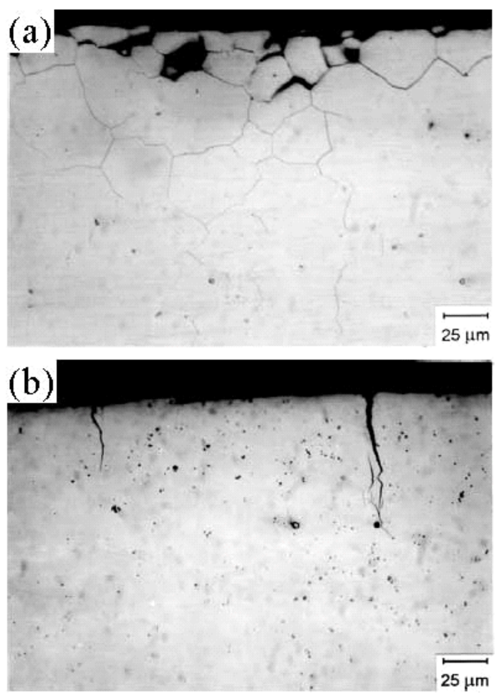


Fig. 3. Different cracking modes in 10 % NaOH test solution with 100 ppm lead at 315℃: (a) intergranular in alloy 600 MA and (b) transgranular in alloy 600 TT.

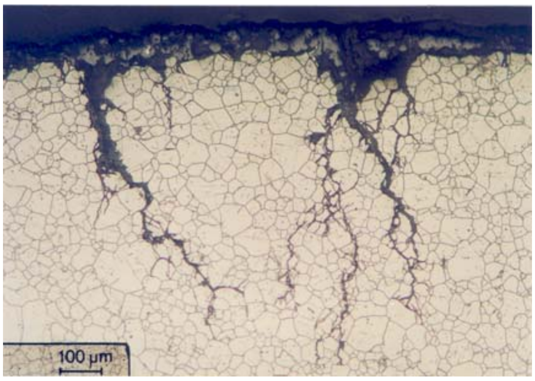


Fig. 4. TGSCC observed in alloy 690 TT tested in 40 % NaOH with 5000 ppm of lead at 315℃ for 21 days.

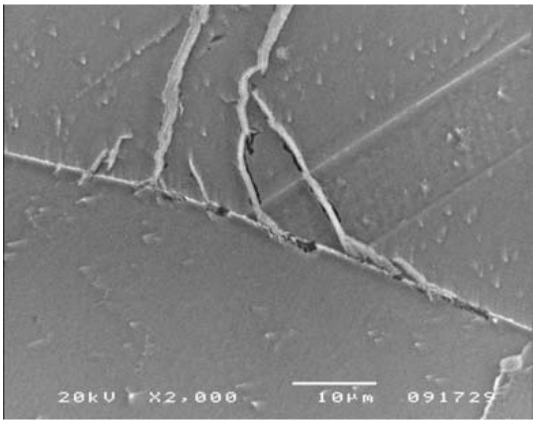


Fig. 5. Transition of crack path from IG into TG in the alloy 690 TT tested in 40 % NaOH solution with 5000 ppm lead at 315℃.

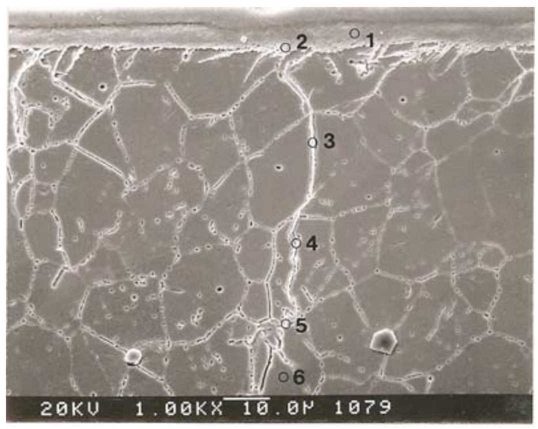
Thermally treated alloys were surveyed for a tendency of TGSCC in terms of microstructure, loading method and carbon content by R. Staehle.[13] The survey noted that a general cracking mode for a lead induced SCC was an IGSCC for alloy 600 MA and a TGSCC for sensitized (SN), stress relieved (SR) or thermally treated alloy 600 and 690, with some exceptions. A static loading, as with the C-ring or U-bend specimens, caused an IG mode and a TG mode SCC for MA and SR/SN/TT materials respectively.[12] It seems that high carbon content also enhances a TG cracking morphology.

3.2 Role of a grain boundary carbide on a TGSCC

According to Bruemmer, grain boundary carbides increase SCC resistance of thermally treated alloys.[14] He proposed a mechanism that grain boundary carbides would act as a dislocation source and blunt an IG crack at the crack tip near the carbide. Rice and Thompson proposed an energy balance theory for dislocation emission from cracks versus crack propagation in 1974.[15] In 600 and 690TT alloys, the dislocations would preferentially emitted from the grain boundary carbides, and thereby, reducing the stress concentration around them, and improve IGSCC resistance of TT alloys. On the other hand, a tangled dislocation structure appears in alloy 600 MA with a few grain boundary carbides.[10] While the grain boundary region attains an increased SCC resistance due to the grain boundary carbide, the applied stress can be relaxed by finding another crack path of the transgranular mode.

3.3 Effect of lead

Increased concentrations of oxygen and lead were found at the crack tip as presented in Fig. 6. Byers et al. and Sakai et al. also published that lead penetrated into a crack tip.[16),17] Soluble lead species played a role in a cracking, and a film dissolution by lead occurred inside a sharp crack. A selective dissolution of Ni has been demonstrated from alloy 600 and alloy 690 in an acidic water environment containing lead.[18-20] Lead increases the critical current density and the passive current density of alloy 600 and 690 in caustic solutions containing lead at elevated temperature as shown in Fig. 7.[10,21,22] In the SCC tests, the tendency of cracking mode shifted to the TG in the



W/O

Element	O	Pb	Ni	Cr	Fe
Location					
1. Near Crack	3.80	0.49	89.03	3.42	3.26
2. Crack mouth	2.47	0.27	91.36	2.84	3.06
3. Middle crack	1.97	0.11	86.09	6.98	4.84
4. Middle crack	5.85	0.17	74.11	12.47	7.39
5. Crack tip	2.81	0.00	72.39	16.01	8.78
6. Matrix	0.00	0.00	74.20	16.50	9.30

Fig. 6. TG cracking morphology and element profile along the crack formed on alloy 600 TT tested in 10% NaOH with 500 ppm Pb.

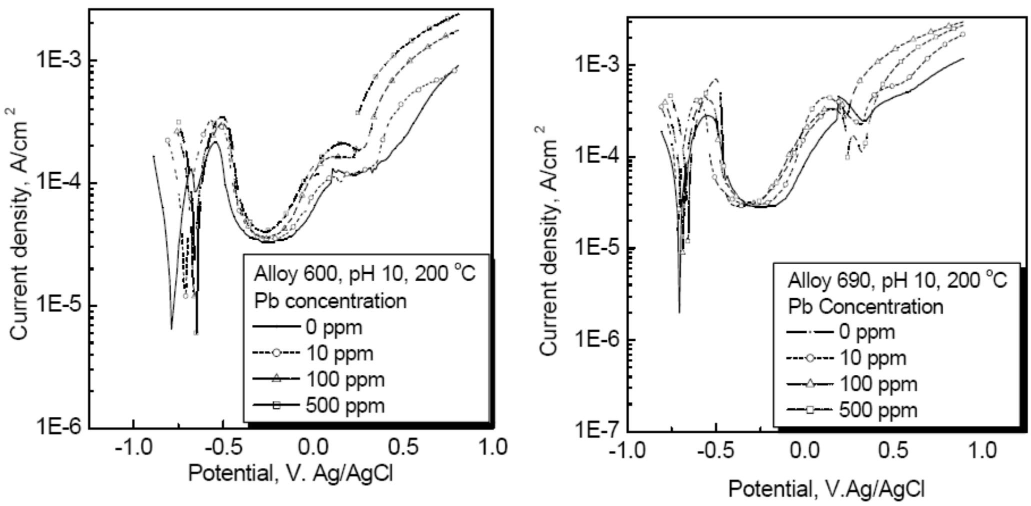


Fig. 7. Effect of the lead contents on the anodic polarization of alloy 600 and 690 at 200℃.[10]

thermally treated alloy 600 and 690 with increase of lead concentration.

4. Conclusions

Processes for TGSCC of thermally treated alloys in lead contaminated water are proposed; (a) Breakdown of the film by a tensile stress (b) Dissolution of Ni and Cr from the passive film by lead (c) Dissemination of a dislocation at the grain boundary carbide of thermally treated alloys and (d) Increase of resistance to cracking at the grain boundaries and facilitation of TG crack paths. It can be said that the transgranular SCC in thermally treated alloys is related to the grain boundary carbide decoration and the passive film damage by lead for the both alloy 600 and 690. Our investigation may be concluded:

• Thermally treated alloy 600 and 690 showed a TGSCC in a lead contaminated water at high temperatures.

• Grain boundary carbides and stress relaxation due to dislocation emission at carbides play a role for the TGSCC.

Acknowledgement

This work was carried out as a part of the nuclear R&D program sponsored by the Ministry of Science and Technology (MOST) of the Republic of Korea.

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