CORROSION SCIENCE AND TECHNOLOGY, Vol.5, No.3(2006), pp.85~89

Repassivation Behavior of Ni Base Alloys in a Mild Alkaline Water at 300 ℃

†Seong Sik Hwang, Dong Jin Kim, Joung Soo Kim, and Hong Pyo Kim

Korea Atomic Energy Research Institute
Yuseong-Gu, Deokjin-Dong 150, Daejeon, 305-353, Korea

KAERI(Korea Atomic Energy Research Institute) has developed a repassivation rate test system which can be operated at 300 ℃. It consists of an autoclave, three electrodes for an electrochemical test and a diamond scratch tip. All the electrodes are electrically insulated from the autoclave by using high temperature fittings. Reproducible repassivation curves of alloy 600 at 300 C were obtained. Repassivation rate of alloy 600 at pH 13 was slower than that of pH 10. Stress corrosion cracking test was carried as a function of the pH at a high temperature. At pH 10, alloy 600 showed a severe stress corrosion cracking(SCC), whereas it did not show a SCC at pH 7. From the viewpoint of a relationship between the current density and the charge density, a big difference was observed in the two solutions; the slope of pH 13 was steeper than that of pH 10. So the stress corrosion susceptibility at pH 13 seems to be higher than that of pH 10. The system would be a good tool to evaluate the SCC susceptibility of alloy 600 at a high temperature.

Keywords : *repassivation, scratch electrode, stress corrosion cracking, alloy 600, steam generator, nuclear power plant.*

1. Introduction

Though alloy 600 as the steam generator tubings of a pressurized water reactor is a high corrosion resistant material, it shows a stress corrosion cracking(SCC) in an alkaline water environment.[1] A lot of work to evaluate the SCC behavior of alloy 600 has been done. Since a high temperature stress corrosion test is difficult to perform and a time consuming task, some electrochemical techniques have been suggested. They are rapid straining techniques,[1)-4)] scratching electrode techniques,[5)-7)] continuous abrasion techniques,[8)-10)] 4-electrode in situ fracture techniques,[11)-12)] scraping electrode techniques,[13)-15)] and abrading electrode techniques,[16)-18)] etc.[19)-21)]

An economical SCC susceptibility evaluation method in terms of repassivation kinetics has been developed by using a scratching electrode technique.[22)] The scratching electrode technique was effective as a method to evaluate the SCC susceptibility of alloy 600. The technique, however, was for a room temperature environment, so it had a limitation in evaluating a high temperature SCC behavior.

This paper addresses the repassivation behavior of alloy 600 in a mild alkaline water at 300 ℃. The other objective of this article is to estimate a SCC susceptibility by using the repassivation data.

†Corresponding author: sshwang@kaeri.re.kr

2. Experimental

2.1 Repassivation test

KAERI(Korea Atomic Energy Research Institute) has developed a repassivation rate test system which can be operated at 300 ℃. It consists of an autoclave, three electrodes for an electrochemical test and a diamond scratch tip. All the electrodes are electrically insulated from the autoclave by using high temperature fittings as shown in Fig. 1.

A reference electrode for this system is an external silver/silver chloride electrode, a counter electrode is made of Ni plate for use in an alkaline water at a high temperature. A potentiostat of model 263A of EG&G was used for the electrochemical test.

A diamond tip coated with TEFLON is electrically insulated from the test system, and it is operated by compressed air. The working electrode of alloy 600 or alloy 690 was also insulated from the system with oxidized Zirconium plates and a TEFLON sheet. Platinum wire which was connected with the test coupon was wrapped

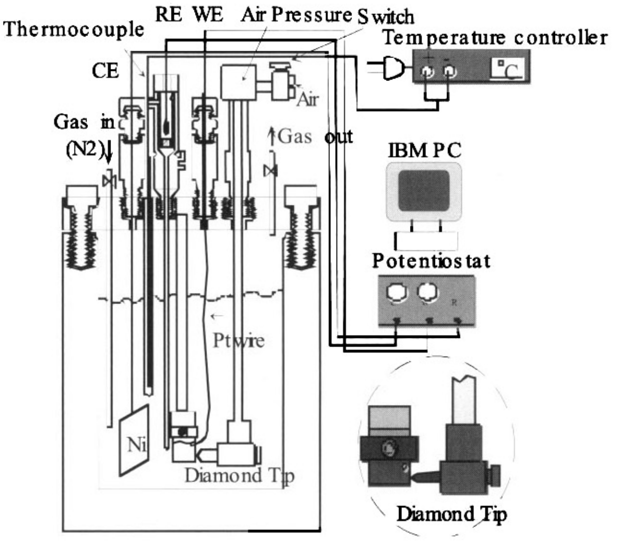

Fig. 1. Schematic of the repassivation rate testing system at a high temperature

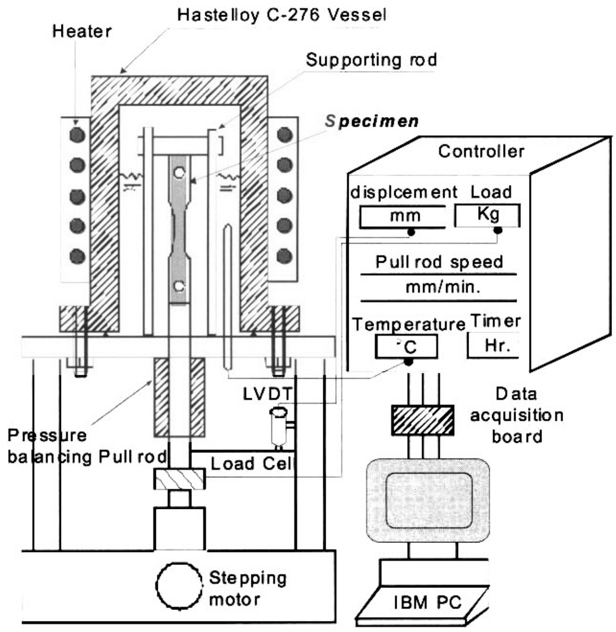

Fig. 2. Schematic of the stress corrosion test system(SSRT)

with a heat shrinkable TEFLON tube, and CONAX Glands were adapted for the wire installation to the autoclave lid.

The pH of the test solution was adjusted with NaOH. High purity nitrogen gas (99.99%) was purged into the solution for an hour to reduce the oxygen concentration of the test solution. After the nitrogen gas purging, +150 mV above the corrosion potential was applied to the working electrode for an hour in order to passivate the test specimen.

The repassivation current at the rate of one point per one micro second was acquired using the EG&G test system at +150 mV above the corrosion potential of the specimen.

An electrical charge density was calculated by an integration of the current on the graph of the current decay as a function of the time.

2.2 Stress corrosion cracking test

Slow strain rate test(SSRT) was conducted in a solution of a 10,000 ppm lead concentration as a form of PbO to accelerate the SCC by using the system shown in Fig. 2.

Alloy 600MA tube specimen was used for the SSRT. The tubes were split into two pieces longitudinally and machined to give a gauge section 25.4 mm long and 6.0 mm wide. The gauge section of the specimen was abraded by #600 emery paper. The specimen was degreased with acetone and cleaned with distilled water prior to the test. Initial pH of the solution was adjusted with NaOH. The SSRT was carried out at 340 ℃ and at a rate of $1x10^{-7}$/sec.

3. Results and discussion

3.1 Repassivation behaviors

Fig. 3-(a), (b) are the repassivation behaviors of alloy 600 at pH 10 and at pH 13 respectively at 300 ℃. Just after the moment of a scratch on the specimen, a stable current decay curve was obtained. The current decreased to a passive current range in about 0.02 seconds and it showed no more big change.

Fig. 4 is the current decay behavior of the alloy 600 in a water pH 10 and pH 13 at 300 ℃. They showed a similar tendency, but the repassivation rate at pH 13 was slower than that of pH 10. Repassivation rate of alloy 600 in a high pH is controlled by a stability of the Ni, Cr and Fe passivity. The slower repassivation of the pH 13 solution seems to come from an instability of the passivity.

Charge densities are obtained by an integration of the current densities. Yeom et. al showed a relationship between the SCC susceptibility and the slope of a plot of log(i) versus 1/charge density[23]; a SCC occurred at a specific range of the slope, that is, a SCC did not occur at a small slope or a general corrosion occurred at a higher range of the slope as shown in Fig. 5.

Alloy 600 showed a steeper slope at pH 13 than that at pH 10 as shown in Fig. 6. Hence the stress corrosion susceptibility of alloy 600 in a higher pH seems to be higher than that of a low pH.

Fig. 7 shows a comparison of the current decay of alloy 600 and alloy 690. The alloy 690 was repassivated easier

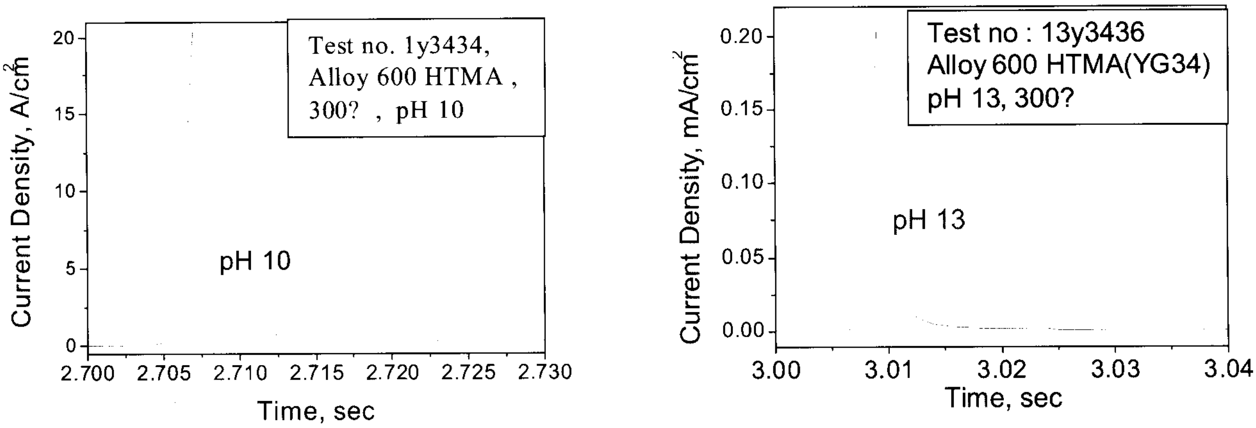

Fig. 3. Repassivation behavior of alloy 600 (a) at pH 10, (b) at pH 13 at 300 ℃.

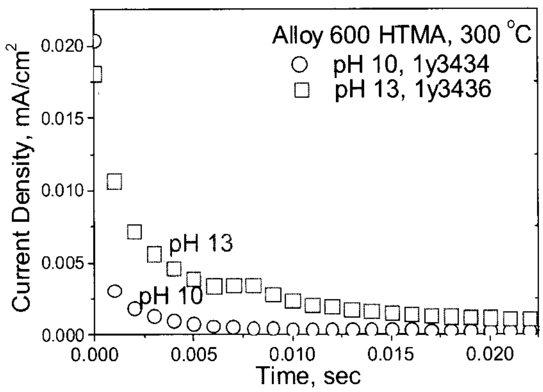

Fig. 4. Comparison of the repassivation behavior of alloy 600 in water at pH 10 and pH 13 at 300 ℃.

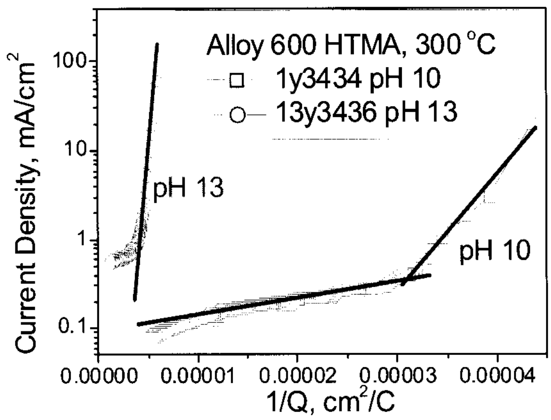

Fig. 6. Effect of the pH on the current transient of alloy 600 at 300.℃

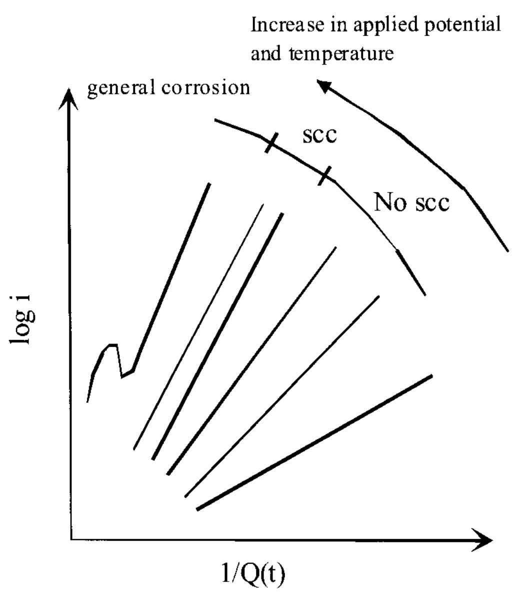

Fig. 5. Stress corrosion tendency for different conditions

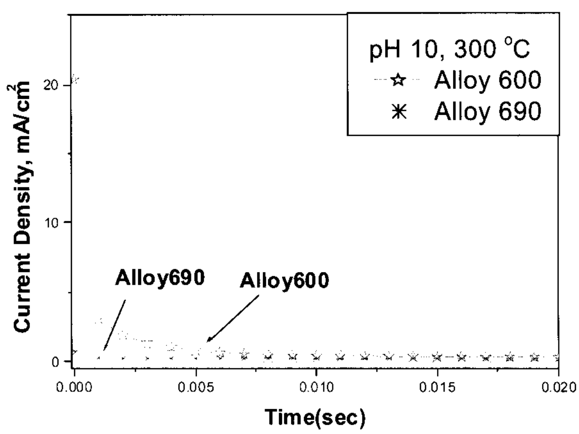

Fig. 7. Effect of the alloy composition on the current transient at 300 ℃.

than alloy 600 ; repassivation time of alloy 690 was 0.001 seconds, whereas the time of alloy 600 was 0.005 seconds. It seems that the passive film protectiveness of alloy 690

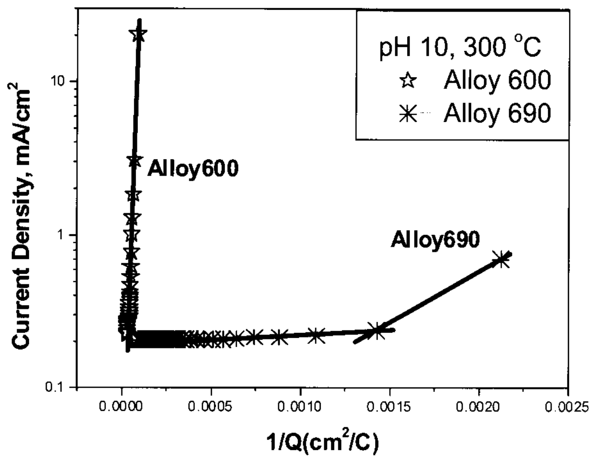

Fig. 8. Current density versus 1/Charge density of the alloys during a repassivation at 300 ℃

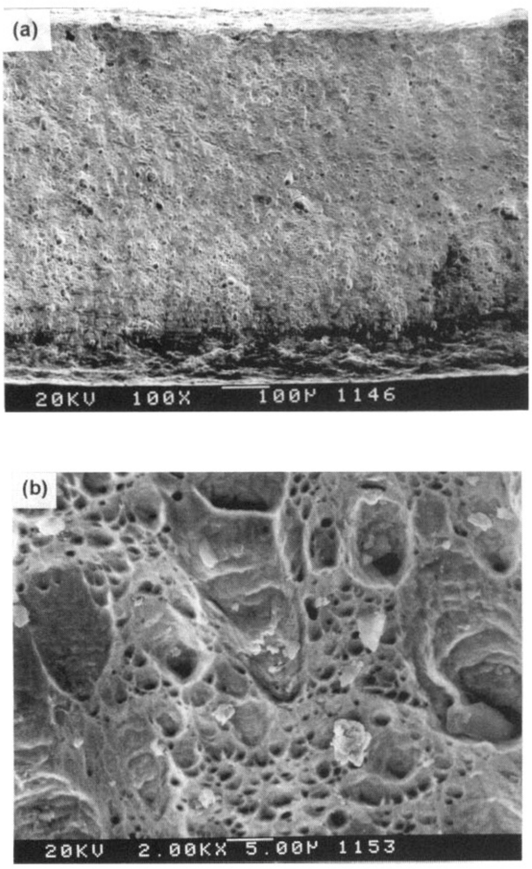

Fig. 9. No SCC at pH 7 of alloy 600MA at 340 ℃ in water containing 10,000 ppm Pb, strain rate is 1×10^{-7}/sec

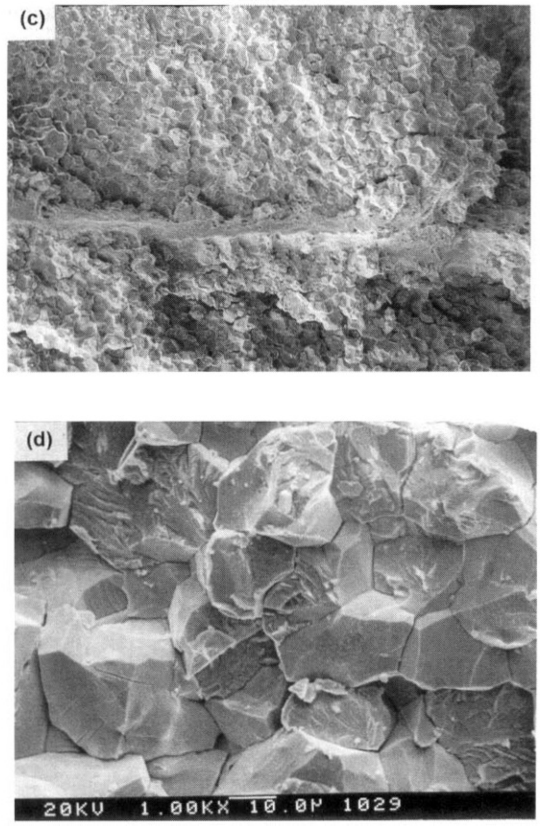

Fig. 10. Severe SCC at pH 10 of alloy 600MA at 340 ℃ in water containing 10,000 ppm Pb, strain rate is 1×10^{-7}/sec

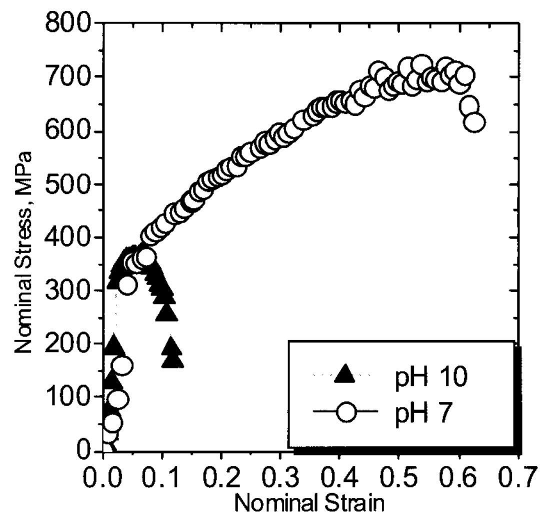

Fig. 11. SCC susceptibility of Alloy 600 MA at different pH conditions at 340 ℃ in water containing 10,000 ppm Pb, strain rate is 1×10^{-7}/sec.

is superior to alloy 600.

As deduced from Fig. 5, the steeper slope for alloy 600 than that of alloy 690 in the graph of Fig. 8 implies that alloy 600 is more susceptible than alloy 690.

3.2 Stress corrosion cracking test

pH dependency for a SCC of alloy 600 was evaluated for alloy 600MA. A SCC did not occur at pH 7 as shown in Fig. 9, while the whole area was fractured by an IGSCC at pH 10 as shown in Fig. 10. Elongations of the two conditions were 58% and 12% at pH 7 and at pH 10 respectively. Ultimate tensile stresses were 729 MPa and 366 MPa at pH 7 and at pH 10 respectively as shown in Fig. 11. So it can be said that a SCC of alloy 600 was more susceptible at a higher pH than at a lower pH. R.W. Staehle stated that a SCC in a lead contaminated environment was severer in an alkaline water than in a neutral solution.[24] These SCC test results agrees well with the repassivation analysis at different pHs.

As a summary, the repassivation technique of alloy 600 at a high temperature seems to be a good tool for an evaluation of the SCC susceptibility of the alloys in this study.

4. Conclusions

1) A high temperature operated scratch type repassivation test system has been developed.

2) Alloy 600 showed a steeper slope at pH 13 than that at pH 10.

3) Alloy 600 showed a steeper slope than that of alloy 690, and this means that alloy 600 is more susceptible to a SCC than alloy 690.

Acknowledgement

This work was carried out as a part of the nuclear R&D program sponsored by ministry of science and technology (MOST) in Korea.

References

1. T. P. Hoar and F. P. Ford, *J. Electrochem. Soc*, **120**, 1013 (1973).
2. T. Zakroczmski and R. N. Parkins, *Corros. Sci*, **20**, 723 (1980).
3. R. M. Carranza and J. R. Galvele, *Corros. Sci*, **28**, 233 (1988).
4. S. Fujimoto and T. Shibata, *Corros. Sci*, **31**, 643 (1990).
5. G. T. Burstein and D. H. Davies, *J. Electrochem. Soc*, **128**, 33 (1981).
6. G. T. Burstein and G. W. Ashley, *Corrosion*, **39**, 241 (1983).
7. H. C. Brookes, J. W. Bayles, and F. J. Graham, *J. Appl. Electrochem*, **20**, 223 (1990).
8. N. D. Tomashov and L. P. Vershinina, *Electrochim. Acta*, **15**, 501 (1970).
9. M. Keddam, R. Oltra, J. C. Colson, and A. Desestret, *Corros. Sci*, **23**, 441 (1983).
10. R. Oltra, C. Gabrielli, F. Huet, and M. Keddam, *Electrochim. Acta*, **31**, 1501 (1986).
11. A. Alavi, C. D. Miller, and R. P. Wei, *Corrosion*, **43**, 204 (1987).
12. R. P. Wei and A. Alavi, *Scripta Met.*, **22**, 969 (1988).
13. T. R. Beck, *Corrosion*, **30**, 408 (1974).
14. T. R. Beck, *Electrochim. Acta*, **30**, 725 (1985).
15. D. Boomer, R. Hermann, and A. Turnbull, *Corros. Sci*, **29**, 1087 (1989).
16. J. D. Kim and S. I. Pyun, *Electrochim. Acta*, **40**, 1863 (1995).
17. J. D. Kim and S. I. Pyun, *Corros. Sci*, **38**, 1093 (1996).
18. S. M. Moon and S. I. Pyun, *J. Solid state Electrochem*, **3**, 104 (1999).
19. J. W. Tester and H. S. Issacs, *J. Electrochem. Soc*, **122**, 1438 (1975).
20. J. C. Nelson, C. Kang, and A. Bronson, *J. Electrochem. Soc*, **136**, 2948 (1989).
21. U. Steinsmo and H. S. Isaacs, *J. Electrochem. Soc*, **140**, 643 (1993).
22. E. A. Cho and H. S. Kwon, *J. Corrosion Sci. Soc. of Korea*, **27**, 144 (1998).
23. K.A.Yeom E.W Cho, and H.S. Kwon, *J. Corrosion Sci. Soc. of Korea*, **26**, (1997).
24. R.W Staehle, Int'l steam generator conference hosted by Canadian Nuclear Soceity, Canada. August. (2002).