Corrosion of Alloy 600 in Reduced-Sulfur Containing Solutions at High Temperatures*

Takeshi Sakai**, Kazuhiko Aoki**, Toshinori Shigemitsu**
and Yasutada Kishi**

*** Engineering Service Div. Nuclear Fuel Industries, Ltd.*

It is well known that reduced sulfur species lead to intergranular attack (IGA) of sensitized Alloy 600 at low temperature, however the effect of these species on Alloy 600 at high temperature is not clear. Static autoclave tests were performed to investigate the effect of reduced sulfur (CaS_2O_3) on the high temperature aqueous corrosion of Alloy 600. The results show that reduced sulfur can cause severe corrosion on Alloy 600 in high temperature water.

Key words: corrosion, Alloy 600, sulfur, general corrosion, steam generator, oxide film

1. Introduction

Sulfur is one of the major impurities found in the secondary side water of several pressurized water reactor (PWR) nuclear power plants^{1),2)}. There are many possible sources of sulfur species ingress into nuclear steam systems, including make-up water, condenser leaks, improper regeneration of make-up demineralizers, condensate polishers, and so on. Corrosion damage, especially intergranular attack (IGA) and stress corrosion cracking (SCC), of steam generator (SG) tubes in several nuclear power plants is believed to be due to sulfur species^{3),4)}.

Based on laboratory studies and field data, sulfur induced corrosion mechanisms, agreed on at present, are categorized as follows:

(1) Reduced sulfur attack on sensitized Alloy 600 (600SR) at low temperature⁵⁾.

(2) Acid sulfate (SO_4) attack on mill-annealed Alloy 600 (600 MA) at high temperature⁶⁾.

Among these, the low temperature corrosion has been well investigated. However, there

still remains the unknown corrosion behavior of sulfur species at high temperature.

The commonly recognized sulfur species is sulfate, but many kinds of sulfur species at different valence states are known to exist. The complexity of this variety in chemical forms and their active chemical change makes corrosion research of sulfur species difficult, especially at high temperature. In general, sulfur species with lower valence numbers are considered to be more corrosive than sulfate, while the only recognized sulfur induced corrosion mechanism at high temperature is acid sulfate attack on Alloy 600 MA.

Recently, a laboratory study was conducted concerning the interaction between sulfate and hydrazine. According to Allmon et al.⁷⁾, several percent of available sulfate could be reduced by hydrazine (N_2H_4) at conditions that can exist during both plant operation and shutdown. At least, the production of sulfide (S^{2-}), sulfite (SO_3^{2-}) and thiosulfate ($\text{S}_2\text{O}_3^{2-}$) was confirmed. Because of hydrazine additions in actual steam generators, this data might suggest that various reduced sulfur species of different valence states are mixed in a steam generator in a reducing environment with hydrazine.

The objectives of the current study are to investigate the effects of reduced sulfur species on the corrosion behavior of Alloy 600 at high

* 4th International Symposium on Environmental Degradation of Materials in Nuclear Systems-Water Reactors. Jekyll Islands. GA. USA. (1989).

** 950, Ohaza-Noda, Kumatori-cho, Sennan-gun, Osaka, 590-04 Japan

temperature a solution with near neutral pH to focus on the PWR's secondary side normal operating conditions and to supplement the presently limited knowledge on sulfur induced corrosion.

Firstly, high temperature aqueous corrosion tests were conducted to investigate the severity and morphology of the corrosion which reduced sulfur species might induce.

Secondly, thin film analysis was performed to evaluate the behavior and effect of sulfur species on the corrosion of Alloy 600 at high temperature. In general, the thin film formed on metal reflects the interaction between the metal and the aqueous environment, so that information on characteristics of thin film is an useful tool to evaluate the effect of environment on the metal⁹⁾.

2. Experimental

Reduced Sulfur Corrosion Test

The calcium thiosulfate (CaS₂O₃) was selected as a reduced form of sulfur, since calcium is one of usual cations found in the deposits and sludge piles in a steam generator and thiosulfate is a common corrosive species at low temperature.

The specimens were cut from Alloy 600 steam generator tubing of 22.23 mm O.D.×1.27

Table 1 Chemical composition of tested materials (wt%).

	C	Si	Mn	P	S	Cu	Ni	Cr	Fe	Co
600MA *1	0.03	0.29	0.30	0.008	0.001	0.01	74.55	15.85	8.4	0.02
600TT	0.03	0.30	0.32	0.007	0.001	0.01	74.05	16.10	8.6	0.02
600SR *2	0.03	0.32	0.28	---	0.001	0.01	74.73	16.19	8.1	0.03

(MA = Mill Anneal, TT = Thermal Treatment, SR = Stress Relief)
*1 : MA condition 925°C×3min
*2 : SR Condition 621°C×18h
(Modified Huey Test : 1314mg/dm²/Day,EPR Test : 348 C/cm²)

mm in thickness. The chemical compositions and heat treatments of the test specimens are shown in Table 1. Three heats of tubings were involved in this study: mill annealed (600 MA), thermally treated (600 TT) and stress relieved (600 SR). These were machined to C-ring test specimens based on ASTM G-38-73, and their surfaces were polished with No. 600 grit paper to remove the pre-existing oxide film. Then they were ultrasonically cleaned in acetone. Two types of capsules (titanium capsules for the test above 300°C condition and SUS 304 capsules with inner Teflon (PTFE) coating for the test below 300°C) were utilized to contain

Table 2 Corrosion test matrix.

		CaS ₂ O ₃ · 2H ₂ O Concentration	Additives	pH *1 (Room Temp.)	DO ₂	Specimen	Stress*3 (% y.s.)	Test Temp. Test Time.	Note
I	1	1mol/l	N ₂ H ₄ 100ppb	6.0	<5ppb	600MA C-ring	90	350°C x 11h	Reducing Environment
	2			20					
	3			90					
	4			20					
II	1	0.5mol/l	N ₂ H ₄	6.0	<5ppb	600MA	140	280°C x 240h	Reducing Environment
	2		1000ppb	4.5		600TT	60		
	3		CuO (1g/l as Cu)	6.0		600SR C-ring	80		Oxidizing Environment
	4		—	6.0		80			
III	1	0.5mol/l	N ₂ H ₄ 100ppb	6.0	<5ppb	600MA C-ring	90	280°C x 168h 280°C x 336h	Reducing Environment
	2	0.1mol/l					90		
	3	0.05mol/l					90		
	4	0.005mol/l					90		
IV	1	—	H ₂ S gas bubble * ₂	—	<5ppb	600MA C-ring	0	280°C x 72h	—

*1.PH is adjusted by H₂SO₄.
*2.Bubbling for 5 min.
*3.% yeild strength

Table 3 Test matrix for the effect of sulfate species on surface film.

Test No.	CaSO ₄ Concentration	Additives	pH *1 (Room Temp.)	DO ₂	Specimen	Test Temp. Test Time.
I	0.5mol/l	—	6.0	<5ppb	600MA Ring	280°C × 168h
II	0.5mol/l	N ₂ H ₄ 1000ppm				280°C × 168h
III	0.5mol/l	N ₂ H ₄ 1000ppm				280°C × 168h (Slow heatup*2)
IV	—	CaSO ₃ 0.5mol/l N ₂ H ₄ 100ppb				280°C × 168h

*1. PH is adjusted by H₂SO₄.

*2. 60h for heat up to 280°C.

the Alloy 600 test specimens and test solutions.

The test solutions were made by adding the chemical additives shown in Table 2 into de-ionized and distilled water. High purity argon (>99.999% Ar) was used for degassing to attain low dissolved oxygen (DO₂) levels of less than 5 ppb. After the DO₂ levels of less than 5 ppb was confirmed, the capsules containing the specimens were sealed in a hood with an argon atmosphere.

These capsules were placed in a static autoclave. After the tests at high temperatures, the specimens were removed from the capsules, rinsed with pure water and examined metallographically.

Effect of Sulfur Species on Surface Films

Exposure tests of Alloy 600 in high temperature solution containing sulfate and reduced sulfur were conducted by using the same method of C-ring testing in capsules placed in a static autoclave as described in the previous section.

The test matrices are shown in Table 3. Since hydrazine thermally decomposes at temperatures higher than about 200°C, resulting in its loss of reducing ability, two different heating rates were selected to change the effective period for the reduction of sulfate by the hydrazine. The faster heating rate was 280°C in 2 hours, while the slower one was 280°C in 60 hours. As a reference, the exposure tests were performed by using sulfate

solution without hydrazine addition.

After one week of exposure at 280°C in the autoclave, the specimens were examined metallographically and surface films were analyzed by Auger electron spectroscopy (AES, JEOL model JAMP-30). In-depth profiles of main constituent elements of Alloy 600, oxygen and sulfur in surface films were analyzed using argon ion sputtering. The sputtering rate was 285 Å/min for a SiO₂ standard sample.

3. Results and discussion

Reduced Sulfur Corrosion Test

Corrosion tests were performed at 350°C

Fig. 1 Surface appearance and cross section of C-ring specimen of Alloy 600 MA.

Test condition: 1 mol/l CaSO₃·6H₂O + 100 ppb N₂H₄, pH 6, DO₂ < 5 ppb, 350°C × 11 h.

- (1) Severe general corrosion
- (2) Surface appearance under the thick deposit

Fig. 2 The relation between stress and corrosion loss of C-ring specimen.

Test condition: 1 mol/l $\text{CaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ + 100 ppb N_2H_4 , pH 6/pH 8.5, $\text{DO}_2 < 5$ ppb, $350^\circ\text{C} \times 11$ h.

Fig. 3 Cross section of C-ring specimen of Alloy 600 MA.

Test condition: 0.5 mol/l $\text{CaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ + 1000 ppb N_2H_4 , pH 6, $\text{DO}_2 < 5$ ppb, $280^\circ\text{C} \times 168$ h.

using a $\text{CaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ solution of 1 mol/l concentration with the addition of 100 ppb hydrazine, shown as Test No. I in Table 2.

The surface of the C-rings was covered with thick, black deposits, and also much precipitate, a mixture of white, grey and black in color, had accumulated in the bottom of the canister. XRD analysis showed that the deposit consisted mainly of nickel sulfide, while the main constituents of the precipitate were CaSO_4 and $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$. Ion Chromatography (I.C.) analysis of the test solution showed the exist-

Fig. 4 The relation between concentration of $\text{CaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ and corrosion loss of C-ring specimen.

Test condition: pH 6, $\text{DO}_2 < 5$ ppb, $280^\circ\text{C} \times 168 \sim 336$ h.

ence of SO_3^{2-} and SO_4^{2-} as well as $\text{S}_2\text{O}_3^{2-}$. Also the smell of H_2S was identified.

The metallography of the cross sections of specimens are shown in Fig. 1. It can be recognized that the morphology of corrosion damage by $\text{S}_2\text{O}_3^{2-}$ at high temperature is generally a severe general corrosion. As shown in Fig. 2, there is no significant stress dependency on the severity of corrosion based on the evaluation of the area reduction of various cross sections of the base metal after the corrosion test.

Because of the severity of the corrosion damage at 350°C , we performed subsequent corrosion tests at a lower temperature to investigate the effect of such parameters as pH, concentration of reduced sulfur, heat treatment and redox environment on the reduced sulfur induced corrosion. These tests are noted as Tests No. II and III in Table 2.

As shown in Fig. 3 typically, the same corrosion morphology observed at 350°C was observed on every specimen surface; that is, mainly general corrosion with pitting and minor intergranular penetration. There is no clear dependency of the severity of corrosion on any parameter, except for the concentration of reduced sulfur, as shown in Fig. 4. This might mean that the tested amounts of reduced sulfur were still too corrosive on Alloy 600 to

Table 4 Results of corrosion test.

Test No.	Surface Appearance	Morphology of Corrosion Damage	Deposit, Precipitate, Solution Analysis	Effect of experimental parameters
I	• The surface of C-ring was covered with thick and black deposit.	• General corrosion • Minor intergranular penetration under deposit layer. (Fig.1)	• Deposit Ni_3S_2 , Ni_7S_6 Ni_3S_4 , Fe_3S_4 • Precipitates CaSO_4 $\text{CaSO}_3 \cdot 0.5 \text{H}_2\text{O}$	• Severe corrosion damage in all specimens. • No significant dependence on • Stress • pH(around neutral)
II	• The surface of C-ring was covered with thick and black deposit.	• General corrosion /Pitting • Minor intergranular penetration under deposit layer. (Fig.3)	• Deposit Ni_3S_2 , Ni_7S_6 FeCr_2S_4 • Precipitates CaSO_4	• Severe corrosion damage in all specimens. • No significant dependence on • Stress • pH(around neutral) • Heat treatment • Oxidizing / Reducing environment
III	• The surface of C-ring was covered with thick and black deposit, which become thinner in lower $\text{S}_2\text{O}_3^{2-}$ concentration.	• General corrosion /Pitting • Minor intergranular penetration under deposit layer. • Larger corrosion loss for higher concentration of $\text{S}_2\text{O}_3^{2-}$. (Fig.4)	• Residual sulfur species $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} SO_4^{2-} Reduced sulfur species still remained even in the solution of lower $\text{S}_2\text{O}_3^{2-}$ concentration.	• Severe corrosion damage in all specimens except for the test of lower CaS_2O_3 concentration (less than 0.1mol/l). • Dependence on • Concentration
IV	• The surface of C-ring was covered with thick and black deposit.	• General corrosion /Pitting	—	—

Fig. 5 The depth profile of Alloy 600 MA surface film.
Test condition: 0.5 mol/l CaSO_4 , pH 6, $\text{DO}_2 < 5$ ppb, $280^\circ\text{C} \times 168$ h.

Fig. 6 The depth profile of Alloy 600 MA surface film.
Test condition: 0.5 mol/l $\text{CaSO}_4 + 1000$ ppm N_2H_4 , pH 6, $\text{DO}_2 < 5$ ppb, $280^\circ\text{C} \times 168$ h. (Slow heat up for 60 h).

allow determination of the effects of pH, stress, heat treatment and redox environment within the range investigated in the present study. The results of a corrosion test with H_2S solution indicated that H_2S also caused similar corrosion damage to Alloy 600 (Test No. IV in Table 2).

It might be difficult to evaluate the corrosion behavior of thiosulfate ($\text{S}_2\text{O}_3^{2-}$) because of the complexity of the mutual changes in valence

state of sulfur species. However, at least, thiosulfate ($\text{S}_2\text{O}_3^{2-}$) and H_2S were confirmed to cause corrosion damage to Alloy 600, when these reduced sulfur species are initially contained in the aqueous environment.

The test results are summarized in Table 4.
Effect of Sulfur Species on Surface Films

Figures 5 through 7 show the depth profiles of the elemental distribution of the main con-

Fig. 7 The depth profile of Alloy 600 MA surface film.

Test condition: 0.5 mol/l CaS_2O_8 + 100 ppb N_2H_4 , pH 6, $\text{DO}_2 < 5$ ppb, $280^\circ\text{C} \times 168$ h.

stituents of Alloy 600, oxygen and sulfur in each specimen described in Table 3.

As shown in Fig. 5, there was no significant contribution of sulfur to the surface film on the specimen in the 0.5 mol/l sulfate solution without N_2H_4 (Test No. I). When 1000 ppm hydrazine was added to the above sulfate solution, still no significant change was recognized in surface film characteristics (Test No. II).

In test No. III using the same solution as that of Test No. II, the heating rate was decreased so as to lengthen the effective period of the reducing ability of hydrazine below the critical temperature for the thermal decomposition. In this case, nickel and sulfur became enriched at the outer layer of the surface film (Fig. 6).

When a reduced sulfur species was used directly for the test solution, the tendency of nickel and sulfur enrichment in the outer oxide layer was greatly enhanced as shown in Fig. 7.

The enrichment of nickel and sulfur in the outer layer of the surface film indicated the formation of nickel sulfide. This is also supported by XRD analysis results of surface deposits. The nickel sulfide is considered to be non-protective, since it inhibits the formation of protective oxide film on Alloy 600⁹⁾.

Therefore, the film analysis study suggests the following:

(1) Reduced sulfur species have a high potential to enhance corrosion by the formation of non-protective nickel sulfide surface films at high temperature.

(2) Sulfate can be changed to reduced forms

of sulfur at some intermediate temperature in a strong reducing environment, as supported by other laboratory data.

4. Conclusions

The following conclusions are obtained in this study:

1. Reduced sulfur species can cause severe corrosion on not only Alloy 600 MA but also Alloy 600 TT and 600 SR in high temperature water. The morphology of the corrosion is general corrosion with pitting and minor intergranular penetration.

2. Nickel sulfide is formed at the outermost region of the Alloy 600 thin film in high temperature aqueous solution containing reduced sulfur species. Nickel sulfide is also formed on Alloy 600 in high temperature sulfate solution in a strong reducing environment.

(Received March 15, 1991)

References

- 1) V. W. Jones: Proceedings EPRI 1987 PWR Plant Chemists' Meeting (1987).
- 2) W. G. Flint & R. J. McIntosh: Proceedings 47th International Water Conference, p. 465 (1986).
- 3) G. O. Hayner, C. P. Frye, G. J. Theus, S. L. Harper, J. Moaba & J. P. N. Paine: Proceedings of The Third International Symposium on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, ed. by G. J. Theus & J. R. Weeks: The Metallurgical Society, p. 449 (1988).
- 4) S. L. Harper, B. P. Miglin, J. V. Monter & G. J. Theus, Proceedings of The Third International Symposium on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, ed. by G. J. Theus & J. R. Weeks: The Metallurgical Society, p. 457 (1988).
- 5) R. Bandy, R. Roberge & R. C. Newman: *Corros. Sci.*, **23**, 955 (1983).
- 6) J. F. Newman: EPRI NP-3043 (1983).
- 7) W. E. Allmon & S. P. Ulbricht: B&W Nuclear Chemistry Technology Update (Lynchburg, Virginia), (1985).
- 8) T. Sakai, K. Aoki, T. Shigemitsu & Y. Kishi: SFCA Int. Symposium Fontevraud II (Fontevraud, France) **1**, 2 (1990).
- 9) P. Combrade, O. Cayla, A. Gelpi & G. Slama: Proceedings of The Third International Symposium on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, ed. by G. J. Theus & J. R. Weeks: The Metallurgical Society p. 525 (1988).