Surface Analysis on Pulled Steam Generator Tubes from Kori 1 Nuclear Power Plant

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1. Introduction

It was found in 1994 that the steam generator tubes in Kori 1 nuclear power plant (NPP) had underwent extensive outer diameter stress corrosion cracking (ODSCC). For the plant, hideout returns were analyzed during shutdown and the fracture surfaces of pulled tubes were analyzed. The analysis results showed that the molar ratio index, defined as $(Na^+ + K^+)/(Cl^- + SO_4^{--}{}_{excess})$ was higher than 1 and Cr in outer layer of the oxide on fracture surface was depleted compared with that of the matrix. This indicated that the ODSCC might have occurred in a caustic environment. To mitigate this degradation phenomenon, TiO_2 was injected to the secondary side water of the steam generator in Kori unit 1. Titanium has been identified to effectively mitigate the ODSCC in caustic solution in laboratories [1, 2]. Also, TiO2 has been injected to several NPPs in other countries [3]. However, it is unclear whether Ti or Ti compound can penetrate into the expansion transition region that was covered with sludge. The expansion transition region is known to be most susceptible to ODSCC because of the high residual stress and the high concentration of impurities within sludge file.

This study focuses on clarifying the penetration of Ti or Ti compound into the expansion transition region of the tubes covered with sludge file. The analysis results of the pulled tubes and a sample prepared in the laboratory will be discussed from the standpoint of the effectiveness of the TiO_2 addition.

2. Methods and Results

2.1 Pulled tubes

The steam generator tubes pulled out from Kori 1 were analyzed by an EDS (Energy Dispersive Spectroscopy) in the semi-hot laboratory in KAERI. The tubes were low-temperature annealed Alloy 600. The analysis was performed on the two tubes. One was R14062 which outer surface was identified to be damaged and the other was R15C58 not damaged.

Table 1 shows the analyzed chemical compositions of the pulled tube surfaces. TiO_2 was injected to the secondary side water in Kori 1 unit in 1995. Therefore, it was expected that more amount of Ti than that in Alloy 600 would be detected. As shown in the table, however, the detected content of Ti was very small, 0.16 to 0.29, implying that Ti might not have been able to penetrate through the sludge deposited between the tubes and tube sheets. These results can be compared with the analysis results of the pulled tubes from Ringhals 3 [3]. They reported that titanium was detected only on the tubing free span locations where no sludge was deposited.

2.2 Immersion test

In order to confirm whether or not TiO2 was soluble in the secondary side water and to examine how much Ti was deposited to Alloy 600, an immersion test was performed. A sample, 10 x 5 x 1 mm, machined from an Alloy 600 archived tube was exposed to simulated secondary side water for 5 days. Test temperature was 315°C and the pH_{RT} of the solution was adjusted to 9.8 by adding ammonia (NH_3). After the exposure, the sample surface was analyzed using the EDS and AES (Auger Electron Spectroscopy). Table 2 shows the atomic percents of some selected elements determined in the EDS analysis. The detected atomic percent of Ti was 0.46 that was a little higher than that of Ti in the pulled tubes. However, based on this, it cannot be determined whether titanium ions in the solution were deposited to the surface of the sample or not.

Figure 1 shows the depth profile of the surface oxide by the AES. In the AES analysis, Ti more than 2% was detected. Since this amount of Ti is much more than the nominal content of Ti in Alloy 600 it can be speculated that TiO_2 is soluble in the simulated secondary side water and the Ti ions in the solution is deposited to the surface of Alloy 600 tubes.

The analysis results by the EDS and AES are not consistent each other (Table 2 and Figure 1). This is due to the relatively thin surface oxide of the alloy and the large electron beam size in the EDS analysis. Thus, the analysis result by the EDS was judged to include the compositions of the base alloy as well as those of the surface oxide, which underestimated the actual content of Ti in the surface oxide.

2.2 Effectiveness of TiO_2

As above mentioned, the effectiveness of TiO2 has been confirmed in laboratories, but it is debatable

Table 1 EDS analysis results for the pulled tubes

Tube No.	Sample	Location	O	Mg	Al	Si	S	Cl	Ti	Cr	Mn	Fe	Ni
R14062	SB22-x100-7	Adjacent to TTS	21.59	-	0.26	0.48	-	0.14	0.16	11.22	0.83	17.84	47.49
(OD damaged)	SB22-x50-9	10 mm above TTS	20.96	-	0.56	1.18	0.49	0.15	0.22	17.63	0.56	9.68	47.91
R15C58	B1-2-x30-1	Adjacent to TTS	25.26	0.55	0.87	4.59	1.3	0.34	0.18	13.68	0.88	9.19	40.62
(Not damaged)	B1-2-x30-7	10 mm above TTS	21.83	1.32	1.72	3.82	0.78	-	0.29	11.93	1.95	7.36	41.92

whether or not it can penetrate through the sludge and it can inhibit the corrosion related phenomena on Alloy 600 tubes in operating NPPs. It was reported that the plant application of Ti compounds was very limited due to the insolubility of Ti compounds and their difficulty to penetrate into packed crevices [3, 4].

In this study, no increase in the Ti content in the pulled tubes was observed. However, the results for the Alloy 600 sample prepared in the laboratory indicated that the surface oxide should be analyzed using the AES to examine the effect of the Ti addition on the corrosion of the alloy more accurately. The final conclusion about the penetration of Ti or Ti compound into the expansion transition region will be drawn after further examination.

3. Conclusion

The pulled steam generator tubes from Kori 1 were analyzed by an EDS. Only small amount of Ti was detected, implying that Ti might not be able to penetrate into the sludge packed crevices. However, the analysis results for the laboratory prepared sample suggested that the surface oxide should be analyzed by more accurate devices such as an AES.

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REFERENCES

[1] U.C. Kim et al., in Proceedings of the 10th International Symposium on Environmental Degradation of Materials in Nuclear Power Systems, 2001.

[2] J. Daret, J.P. N. Paine, M. J. Partridge, in Proceedings of the 10th International Symposium on Environmental Degradation of Materials in Nuclear Power Systems, p. 177, 1995.

[3] A.M. Lancha et al., in Proceedings of the 8th International Symposium on Environmental Degradation of Materials in Nuclear Power Systems, p. 27, 1997.

[4] J. Daret, T. Cassagne, Y. Lefevre, in Proceedings of the 8th International Symposium on Environmental Degradation of Materials in Nuclear Power Systems, p. 100, 1997.

Table 2 EDS analysis results for the laboratory prepared sample

Tube No.	O	Al	Si	Ti	Cr	Fe	Ni
Reference (Alloy 600)	20.15	0.55	0.46	0.46	13.77	7.52	57.09

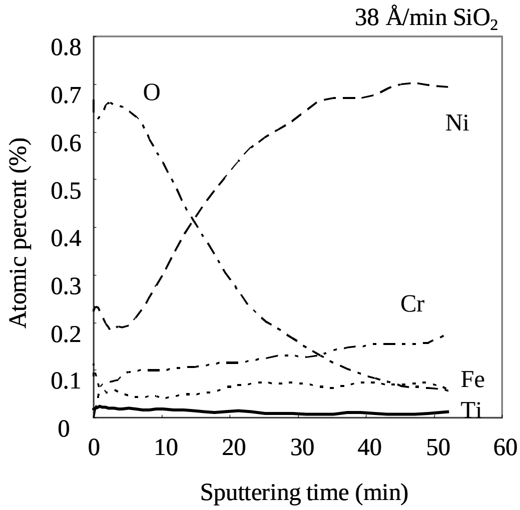

Fig. 1 AES depth profiles of main elements in the surface oxide on Alloy 600 formed in an ammonia solution (pH_{RT} = 9.8) at 315°C for 5days.