Oxidation Behavior and Cracking Susceptibility of Ni-Cr Alloys in Dry Steam and Inert Gas under Extremely-Low Oxygen Partial Pressure*

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Abstract

In order to investigate oxidation behavior and cracking susceptibility of the Ni-Cr alloys under extremely-low oxygen partial pressure, three Ni-Cr alloys (Ni-14Cr, Ni-22Cr and Ni-30Cr) were used as plate specimen and reverse U-bend specimen for oxidation experiments for 750 hours at 400 °C in two kinds of gas system (inert gas and dry steam) under various oxygen potential (Ni stable, Ni/NiO equilibrium and NiO stable). The Ni-Cr alloys cracked along grain boundary both in inert gas system (with trace O₂, without H₂O) and in hydrogenated steam. In the inert gas system, the cracking susceptibility was confirmed in near NiO stable condition. On the other hand, no crack was found in near Ni stable condition. In the dry steam system, the cracking susceptibility was confirmed in near Ni/NiO equilibrium. In contrast, no crack was found in near NiO stable condition. The cracking susceptibility was confirmed in near Ni/NiO equilibrium in hydrogenated steam as contrasted with higher oxygen potential in inert gas system. This result shows that potential range for the cracking susceptibility seemed to be different between the two kinds of gas system. Cracking severity was highest for Ni-14Cr and lowest for Ni-30Cr both in inert gas and steam; however, even Ni-30Cr was not immune to intergranular cracking in steam near Ni/NiO equilibrium.

Key words: Ni-Cr Alloy, Grain Boundary, Oxygen Partial Pressure, Superheated Steam, Oxidation

1. Introduction

Stress corrosion cracking (SCC) of structural alloys in a light-water reactor is one of the most considerable issues for the safe plant management. Since SCC thought to be a complex phenomenon which relates material, environment and mechanics factors, the mechanism of SCC is not fully understood. In the recent findings, the inward oxidation with selective oxidation of specific alloying elements was observed near the crack tip of L-grade stainless steels in boiling water reactor (BWR) environment and of Ni-base alloys in pressurized water reactor (PWR) primary water environment by using analytical transmission electron microscope (ATEM)^(1,2), and selective internal oxidation (SIO) is proposed as a root mechanism of intergranular stress corrosion cracking (IGSCC) of alloy600 in a primary water environment⁽³⁾. Hydrogenated steam is widely accepted in cracking tests as a substitute environment for a primary water environment⁽³⁻⁶⁾. However, cracking susceptibility of Ni-Cr alloys in the simple oxidation system (inert gas with trace oxygen) and particular correlation between cracking susceptibility and oxide characteristics

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have not been known well.

In this study, assuming that solid state-oxidation is fundamental mechanism of IGSCC, oxidation behavior and cracking susceptibility of Ni-Cr alloys with different Cr content under extremely-low oxygen partial pressure have been investigated by oxidation experiments using plate specimens and Reverse U-bend (RUB) specimens in two kinds of gas system under various oxygen potential range.

2. Experimental details

2.1 Materials

Three kinds of Ni-Cr alloys with different Cr content (Ni-14Cr, Ni-22Cr, and Ni-30Cr) were made for this study. The alloys were solution heat-treated at 1180 °C for 30 minutes after homogenizing heat-treatment at 1230 °C for 10 hours and hot-rolling. Chemical compositions and mechanical properties of the alloys are shown in Tables 1 and 2. Plate specimens and RUB specimens were fabricated from the alloys. Plate specimens of approximately 10×10×2 mm dimensions were mechanically polished to 2400 grid surface finish using SiC paper. RUB specimens were polished with 320 grid SiC paper before bending. All specimens were ultrasonically cleaned in acetone before use for the oxidation experiments.

Table 1 Chemical compositions of Ni-Cr alloys used [wt %]

	Ni	Cr	Fe	Mn	Mg	Si	P	S	C
Ni-14Cr	Bal.	13.89	0.014	0.049	0.008	<0.001	0.002	<0.001	0.008
Ni-22Cr	Bal.	21.87	0.019	0.046	0.003	0.007	0.001	<0.001	0.004
Ni-30Cr	Bal.	29.67	0.029	0.044	0.002	0.012	<0.001	<0.001	0.003

Table 2 Mechanical properties of Ni-Cr alloys used

	0.2% proof stress	tensile strength	Elongation	Young's modulus	Poisson's ratio	Hardness, HBW
	N / mm ²	N / mm ²	%	GPa	-	-
Ni-14Cr	115	458	51.0	210	0.260	110.2
Ni-22Cr	151	531	63.0	209	0.274	132.4
Ni-30Cr	208	567	57.3	202	0.255	113.2

2.2 Oxidation Experiments

Oxidation experiments were performed for 750 hours at 400 °C in two kinds of gas system, one is “inert gas system” which consists of inert gas and trace oxygen, and the other is “dry steam system (hydrogenated superheated steam)” under various oxygen potentials. The reason that the two types of gas systems were adopted for environment of the experiments is to evaluate water molecule effect on characteristics of oxide ⁽⁷⁾ and cracking susceptibility of Ni-Cr alloys. Figure 1 shows target oxygen partial pressure (P_{O_2}) in the experiments. The target P_{O_2} of the experiments was determined based on alloying elements (Ni, Cr)/oxide equilibrium. Since it is possible that the actual P_{O_2} might be different from the target P_{O_2} , pure metal (Cu, Fe, Ni, and Co) specimens were also set with specimens in the test section to evaluate the actual P_{O_2} range from the basis of presence or absence of oxide films on the pure metal specimens after the oxidation experiments.

The schematic of test loop of inert gas system is shown in Fig. 2. Though high purity Ar gas (99.9999%) was supplied to test loop, it contains much amount of oxygen compared with the target P_{O_2} range and impurity of water molecules. First, water molecules were removed using by cold trap, after that amount of oxygen molecules were reduced to the target P_{O_2} by oxidation of the pure metal wool in the getter section. The P_{O_2} level of testing gas was determined to the dissociation pressure of getter metal (ex. Ti, Fe, Ni, or Cu) /

oxide at any temperature condition.

The schematic of test loop of dry steam system has been shown in Fig. 3. The target P_{O_2} was achieved by an adjustment of hydrogen-to-water vapor partial pressure ratio. High-purity water was evaporated at steam generator, and then it was mixed with a predetermined volume of hydrogen gases at the upper stream of the test section.

Figure 1 Target potential of oxidation experiments

Figure 2 Schematic of test loop: Inert Gas + Trace Oxygen

Figure 3 Schematic of test loop: Hydrogenated Superheated Steam

3. Results and discussion

3.1 Validation result of the actual oxygen potential

Figure 4 shows target P_{O_2} and actual P_{O_2} ranges which was determined by presence or absence of oxide films on the pure metal specimens after the oxidation experiments, and it suggests that the actual P_{O_2} is lower than target P_{O_2} in all the experiments. While there were a certain level of gap between the target P_{O_2} and actual P_{O_2} , the oxidation experiments in extremely-low oxygen partial pressure were achieved in this study.

Figure 4 Validation result of the actual oxygen potential

3.2 Inert gas system (with trace O_2 , without H_2O)

The surface oxide and cracking morphologies of RUB specimen in NiO stable condition ($\log P_{O_2} = -19$ to -15) are shown in Fig. 5. Cracks have been observed in all the specimens, and surface morphology and cracking susceptibility seems to be totally different between the Ni-14Cr and the others. The ragged surface morphology and a number of millimeter-scale IG cracks have been observed in the Ni-14Cr; on the other hand, relatively smooth surface morphology and only one small crack have been observed in the Ni-22Cr and Ni-30Cr, respectively. The difference in cracking susceptibility is considered to be caused by protective oxide film formed or not. It has been also suggested that the threshold level of Cr content required for the protective oxide film to form in the P_{O_2} range locates somewhere in between 14 wt% and 22 wt%. However, even Ni-30Cr was not immune to IG cracking in the NiO stable condition.

Figure 5 NiO stable-inert gas: appearance and cross-sectional view of RUB specimen

The surface morphologies of RUB specimen in Ni stable condition ($\log P_{O_2} = -35$ to -29) are shown in Fig. 6. No crack has been found in all Ni-Cr alloys, but the surface morphology of Ni-22Cr seems more ragged compared with that of the others.

Figure 6 Ni stable-inert gas: appearance of RUB specimen

3.2 Dry steam system (hydrogenated superheated steam)

The surface oxide and cracking morphologies of RUB specimen in near Ni/NiO equilibrium ($\log P_{O_2} = -29$ to -28) are shown in Fig. 7. Cracks have been observed in all the specimens tested near Ni/NiO equilibrium, and cracking severity was highest for Ni-14Cr and lowest for Ni-30Cr same as in the case in NiO stable condition-inert gas system. Figure 8 shows the surface morphology of RUB specimen in near NiO stable condition ($\log P_{O_2} = -25$ to -19). Smooth surface and no crack were found in all the specimens at NiO stable condition.

Figure 7 Ni/NiO equilibrium-dry steam: appearance and cross-sectional view of RUB specimen

Figure 8 NiO stable-dry steam: appearance of RUB specimen

3.3 Summary of cracking susceptibility

The cracking susceptibility in all the experiments is summarized in Table 3. It is suggested that potential range for the cracking susceptibility seems to be different between the two environments; near Ni/NiO equilibrium in hydrogenated steam, while higher P_{O_2} for the inert gas system. Further characterizations focused on the oxide film characteristics are needed to reveal the reason for the cracking susceptibility in the certain potential range described above.

Table 3 Summary of cracking susceptibility

	Environment	Materials		
		Ni-14Cr	Ni-22Cr	Ni-30Cr
Inert Gas (Ar + O ₂)	Inert Gas Ni stable (log P_{O_2} = -35 ~ -29)	No Crack	No Crack	No Crack
	Inert Gas NiO stable (log P_{O_2} = -19 ~ -15)	Cracked	> Cracked	= Cracked
Steam	Dry Steam Ni/NiO equilibrium (log P_{O_2} = -29 ~ -28)	Cracked	> Cracked	> Cracked
	Dry Steam NiO stable (log P_{O_2} = -25 ~ -19)	No Crack	No Crack	No Crack

4. Conclusion

Oxidation behavior and cracking susceptibility of Ni-Cr alloys with different Cr content under extremely-low oxygen partial pressure have been investigated by oxidation experiments using plate specimens and RUB specimens in two kinds of gas system under various oxygen potential range. The main conclusions can be summarized as follows;

- (1) The Ni-Cr alloys have cracked along grain boundary both in inert gas system (with trace O₂, without H₂O) and in hydrogenated steam.
- (2) Potential range for the cracking susceptibility seems to be different between the two environments; near Ni/NiO equilibrium in hydrogenated steam, while higher P_{O_2} for the inert gas system.
- (3) Cracking severity has been highest for Ni-14Cr and lowest for Ni-30Cr both in inert gas and steam; however, even Ni-30Cr has been not immune to IG cracking in steam near Ni/NiO equilibrium.

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