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The effects of Pb on the passive film of Ni-base alloy in high temperature water

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Abstract

The effects of Pb on the passive film of Alloy 600 were investigated using polarization and immersion tests. The anodic dissolution behavior was observed using anodic polarization tests in water with up to 500 ppm of PbO at pH 4 and pH 10 at 90°C. The immersion tests were conducted at 250°C with lead concentrations of 0, 25, and 250 ppm. The chemical composition of the surface films formed after 5–10 days of immersion was analyzed by AES (Auger electron spectroscopy) and XPS (X-ray photoelectron spectroscopy). The metal ions dissolved from Alloy 600 during the immersion tests were analyzed by ICPS (ion coupled plasma spectroscopy). The results indicate that, as Pb concentration increased, the critical current densities of Alloy 600 increased at both pH 4 and pH 10. At pH 10, the outermost surface films were enriched in Cr and depleted in Ni with increased levels of Pb, but the inner layer showed the opposite trend. In solution analysis, higher concentrations of Ni were observed with increased levels of Pb, which indicates that Pb facilitates Ni dissolution. This is consistent with the analysis results of outer films by XPS. These results show that a Ni-depleted/Cr-enriched outer film and a Cr-depleted/Ni-enriched inner layer may be formed on Alloy 600 in mildly caustic water containing Pb. © 1997 Elsevier Science B.V.

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1. Introduction

Recently, Alloy 600 steam generator tubing has been found to suffer from stress corrosion cracking in high temperature water contaminated with lead [1,2]. When an alloy is exposed to water, a thin film is formed on the alloy surface. Since the film is formed by an interaction between an aqueous environment and metal, it is important to evaluate the characteristics of the film to understand the corrosion mechanism.

Ni-depletion in the film of Alloy 600 by the addition of lead in acidic condition was reported [3]. Other researchers demonstrated that while there is almost no effect of lead on Alloy 690 in acidic solution, lead enhances Ni composition in film in caustic environment [4].

It is necessary to review these results and elucidate the interaction mechanism between lead and Alloy 600.

The objectives of this work are: evaluate the film formation behavior by anodic polarization test, analyze surface film by AES/XPS, and analyze dissolved metal ions in test solution.

2. Experimental procedure

The samples used in the study were cut from Alloy 600 tubing manufactured by Mitsubishi Heavy Industry. The chemical composition and a brief description of the alloy are given in Table 1.

For the anodic polarization tests, the tubing was cut in three pieces in longitudinal direction and flattened by a press. The degree of coldwork from this process was estimated at less than 2% [5] and was assumed to have a negligible effect. The 10 mm × 10 mm specimens were abraded by #600 emery paper and spot welded to Alloy 600 wire coated with heat-shrink Teflon tubing. The tests were conducted at 90°C and a SCE (saturated calomel electrode) and a carbon rod were used as reference and

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Table 1
Chemical composition (wt%) and description of Alloy 600

C	Si	Mn	P	Si	Cr	Ni	Cu	Al	Fe
0.01	0.1	0.3	—	< 0.001	15.4	75.1	0.2	0.22	8.0

Mill annealed at 960°C, 10 min., 22.23 mmOD, 1.27 mm thick (Tubing).

counter electrodes, respectively. The reference electrode was cooled by a glass cooling jacket. The test solution was prepared from distilled and deionized water with the conductivity of 1 MΩ cm. Prior to each anodic scan, the solution was deaerated using high purity nitrogen gas for 30 min. Also, each specimen was cathodically polarized at 0.2 V below Ecorr to remove any pre-existing oxide film and was held at Ecorr for one minute prior to anodic scan at the rate of 1 mV/s. For these tests, an EG&G Model 273 potentiostat with the 352 corrosion software running on an IBM-PC was used. The test was performed under the condition of IR compensation by the current interruption method and the data was plotted as potential versus current density.

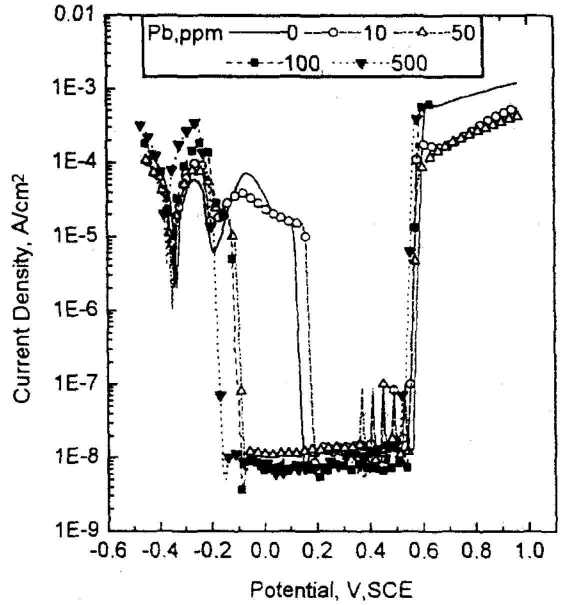

Fig. 1. Anodic polarization curves of Alloy 600 in 90°C water containing Pb at pH 4.

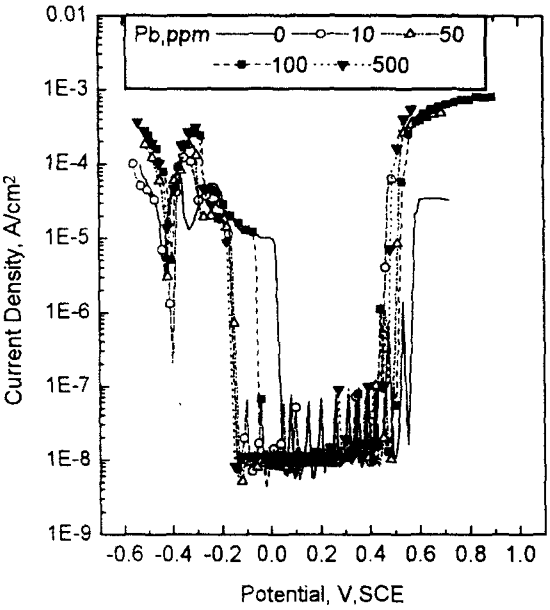

Fig. 2. Anodic polarization curves of Alloy 600 in 90°C water containing Pb at pH 10.

For the immersion tests, 50 mm long tubing samples were polished using #600 emery paper and ultrasonically cleaned in acetone and distilled water. Each sample was inserted into a Teflon-lined stainless steel canister filled with air-saturated water. The pH was adjusted to 4 and 10 (measured at room temperature) using H_2SO_4 and NaOH, respectively. Lead concentrations were adjusted to 0, 25, 250 ppm by adding PbO. The specimens for surface film analysis were inserted into the same canister. The test conditions are summarized in Table 2.

After the immersion tests, the oxidized samples were rinsed with distilled water and stored in a desiccator. AES analyses were performed with the VG Scientific Microlab 310D. The sputtering rate of argon ion was 1.6 A/s calibrated for SiO_2. Three major alloying elements (Ni, Cr, Fe) were normalized to 100% and the thickness of oxide was related to the sputtering time when matrix alloying compositions were detected.

XPS analyses were performed with a VG ESCALAB 200R equipped with a Mg–K X-ray source (1253 eV). All samples were sputtered by argon ion for 1 min (~ 20 Å depth) to remove any air-contaminated layer.

Table 2
Test conditions of polarization and immersion tests

Test	Material	pH [a]	Temperature	Pb concentration (as PbO), ppm	Analysis
Anodic polarization	Alloy 600	4, 10	90°C	0, 5, 10, 50, 100, 500	Critical current density
Immersion test	Alloy 600	4, 10	250°C	0, 25, 250	Surface film, dissolved metal ion

[a] pH: adjusted with H_2SO_4 or NaOH.

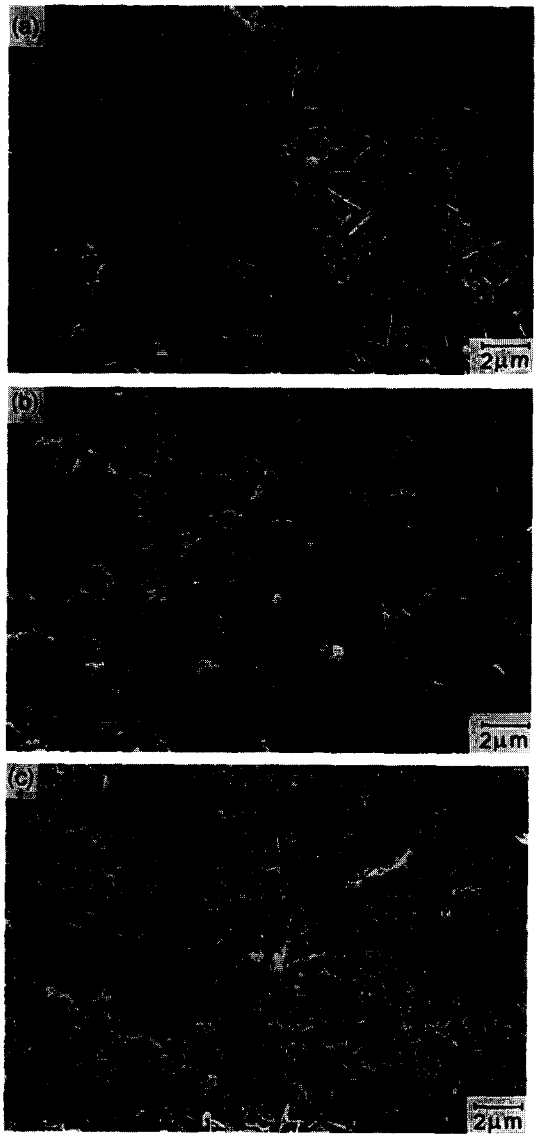

Fig. 3. Surface of Alloy 600 immersed in water containing Pb at 250°C, pH 4 for 10 days. (a) 0 ppm Pb, (b) 25 ppm Pb, (c) 250 ppm Pb.

SEM image and X-ray map were obtained by an Akashi Beam Technology DS 130S and Microspec WDX 3PC system, respectively.

Dissolved metal ions were measured by the means of ICPS using a Jobin Yvon JY50P system.

3. Results and discussions

3.1. Anodic polarization test

Fig. 1 shows that lead increases the lower peak current densities and decreases the upper peak current densities of Alloy 600. It is thought that there may be two active peaks due to Ni and Cr in Alloy 600; the lower peak represents the active dissolution of Ni and the upper peak is for the transpassive dissolution of Cr [6]. Lead may play a role in enhancing Ni dissolution and suppressing Cr dissolution.

Fig. 2 is for the case of pH 10; a behavior similar to the case of pH 4 is observed.

3.2. Surface morphology

Fig. 3 shows the surface morphology of oxide film formed in 250°C water for 10 days. At 250 ppm of lead, the whole surface was covered with bulky, needle-like precipitates. As shown in Fig. 4, lead-rich precipitates were formed on the surface. Considering that the PbO additives were granular, the precipitates were considered metallic lead. This means that PbO is a strong oxidizer for Alloy 600. M.D. Wright proposed the possibility of the presence of metallic lead by the following reaction [7]:

$$PbO + Ni \rightarrow Pb + NiO. \qquad (1)$$

3.3. XPS analysis

Fig. 5(a) shows the XPS spectra obtained from a bare Alloy 600 sample. The binding energies of $Ni_{2p3/2}$ and

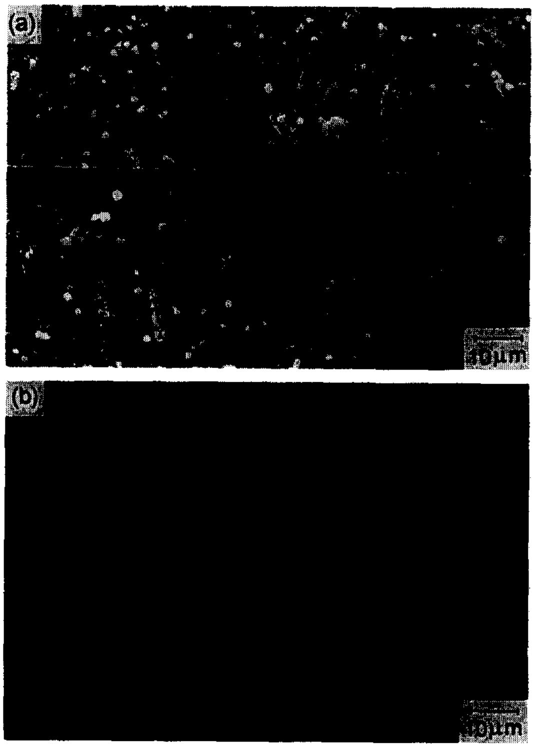

Fig. 4. Precipitate formed on Alloy 600 in water containing Pb at 250°C, pH 4 for 10 days. (a) Image and line profile of Pb (b) Pb image mapping.

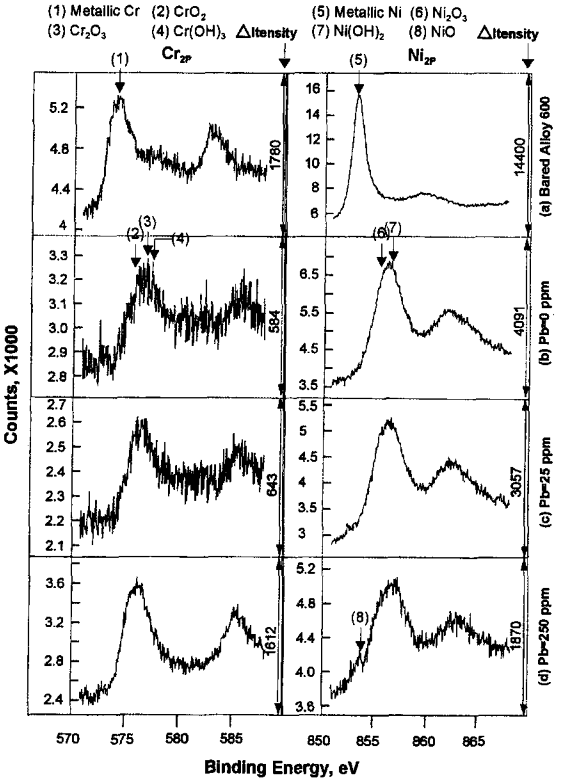

Fig. 5. XPS spectra obtained on the surface of Alloy 600 immersed in water containing Pb at 250°C, pH 4 for 10 days.

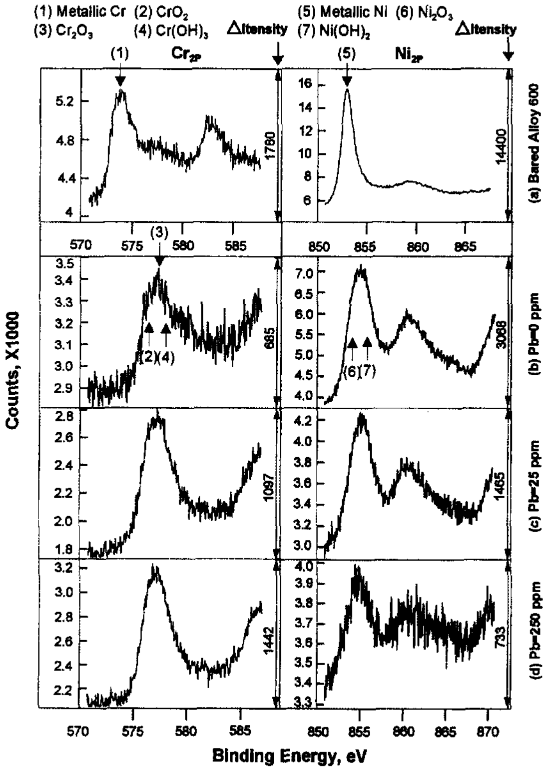

Fig. 6. XPS spectra obtained on the surface of Alloy 600 immersed in water containing Pb at 250°C, pH 10 for 10 days.

$Cr_{2p3/2}$ were evaluated at 853.78 eV and 574.35 eV, respectively. The binding energy of an element may shift in accordance with the chemical states. The chemical forms of Ni and Cr can be differentiated by the means of the reference binding energy.

Fig. 5(b)–(d) show the shift of chemical binding energy of Cr_{2p}, Ni_{2p} at pH 4. The FWHM (full width half maximum) was enlarged, which means that oxides/hydroxides were formed on the surface. As lead concentration increased, the Cr_{2p} peak intensities increased which implies that Cr portion in outermost surface increased with lead. The chemical states of Cr were $Cr(OH)_3$, Cr_2O_3, and CrO_2 at low lead concentrations; they were Cr_2O_3 and $Cr(OH)_3$ at high lead concentrations. Ni_{2p} peak intensities decreased with the addition of lead, this means that outermost films were depleted in Ni. The chemical states of Ni were Ni_2O_3 and $Ni(OH)_2$ at low lead concentrations, and NiO state appeared at high lead concentrations.

Fig. 6 shows the XPS spectra obtained at pH 10; they are similar to the results obtained at pH 4.

The oxygen peaks are shown in Fig. 7. Ni_2O_3 was the main component at low lead concentrations while PbO, Cr_2O_3, and NiO appeared at high lead concentrations. These results are consistent with the analyses of Cr_{2p} and Ni_{2p} peaks.

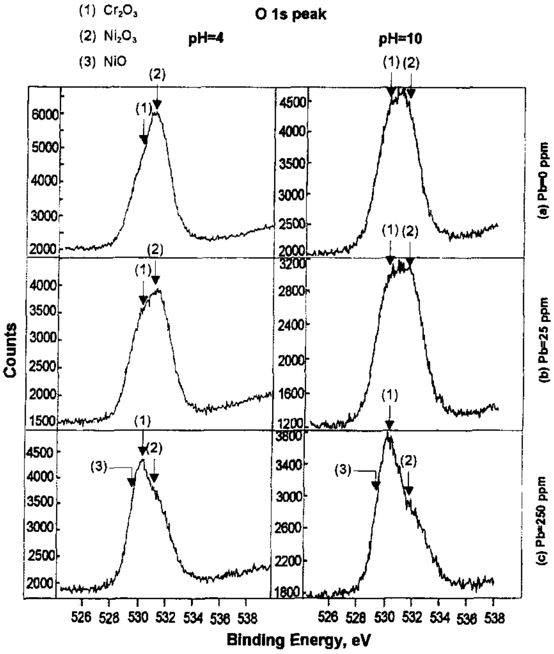

Fig. 7. XPS spectra obtained on the surface of Alloy 600 oxidized in water containing Pb at 250°C, for 10 days.

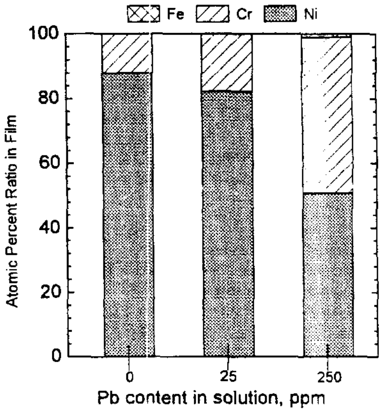

Fig. 8. The effect of Pb content on film composition formed on Alloy 600 at 250°C, pH = 4.

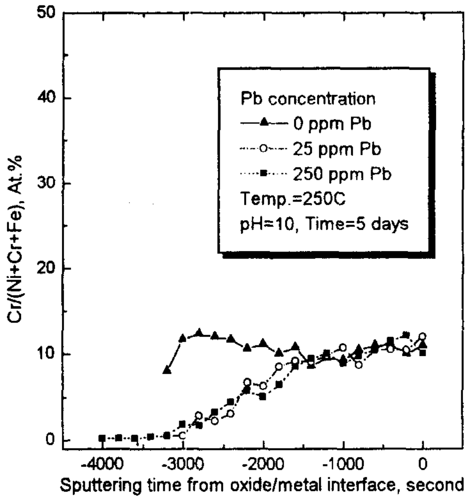

Fig. 9. The effect of Pb on the Cr ratio of surface film on Alloy 600. (250°C, pH = 10, 5 days).

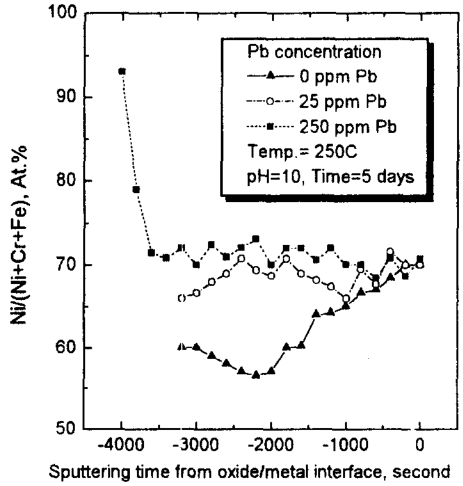

Fig. 10. The effect of Pb on the Ni ratio of surface film on Alloy 600. (250°C, pH = 10, 5 days).

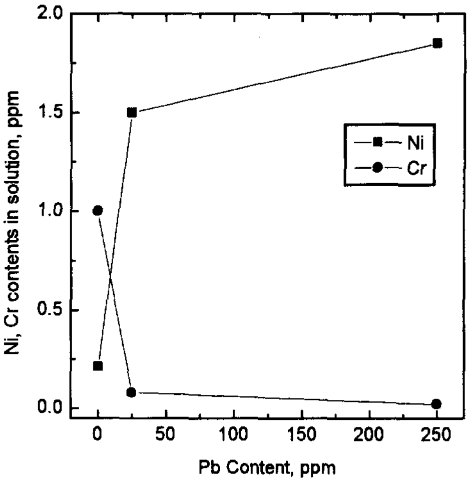

Fig. 11. The effect of Pb on dissolved ion contents at 250°C, pH = 4, for 10 days.

Fig. 8 shows the atomic ratio of Ni, Cr, Fe in XPS analyses. For the quantitative evaluation, the sensitivity factors of each element were obtained from a polished Alloy 600 sample. As Pb concentration increased, the quantitative analysis results also confirmed that the Cr portion increased and the Ni portion decreased. In other words, Pb enriched Cr and depleted Ni in the outermost film of Alloy 600 after immersion in pH 4 and pH 10 solutions.

3.4. AES analysis

AES depth profiles on the surface of Alloy 600 immersed for 5 days in 250°C water containing lead at pH 10 are given in Figs. 9 and 10. The relative atomic ratio of Cr

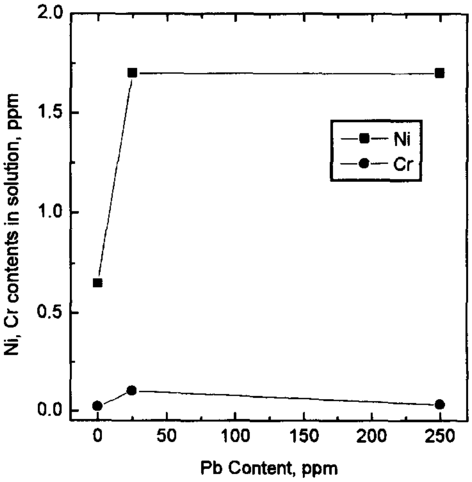

Fig. 12. The effect of Pb on dissolved ion contents at 250°C, pH = 10, for 10 days.

Table 3
Summary of the effect of Pb on surface film of various alloys

Material	pH	Outer film (XPS)	Depth profile (AES)	Author
Alloy 600	acidic	–	Ni↓, Cr↑	Sakai et al. [3]
	caustic	–	Ni↑, Cr↓	Lancha et al. [11]
Alloy 690	acidic	–	no effect	Garcia et al. [4]
	caustic	–	Ni↑, Cr↓	
Alloy 800	acidic	–	Ni↓, Cr↑	Garcia et al. [4]
	caustic	–	no effect	
Alloy 600	acidic	Ni↓, Cr↑	not analyzed	this work
	caustic	Ni↓, Cr↑	Ni↑, Cr↓	

decreased compared with the values obtained from no lead conditions. According to the AES analyses, Cr-enriched and Ni-depleted oxides were formed on Alloy 600 in high temperature acidic water containing lead [3] and Cr-depleted and Ni-enriched oxides were detected on Alloy 600/690 [4]. The latter results are consistent with the results from this study.

Table 3 summarizes the effect of lead on surface film composition which shows a pH dependence on the composition.

The analyzed depth of AES is different from that of XPS; it was thought to be about 1 mm in AES whereas a few tens angstrom in XPS. The XPS analysis results showed that the Ni-depleted zone was located in the outermost part of film regardless of pH. The composition of the inner part depends on the solution pH, and lead accelerates the tendency.

The protective properties of the passive layer on Ni–Cr–Fe alloys are governed by the characteristics of inner layer, and the layer composed of high Cr is more protective due to less defects compared with Ni oxides [8]. Many researchers reported that lead induced cracking was dominant in caustic environments [9–11]. Consequently, it may be proposed that the depletion of Cr in inner layer in caustic solution is related to the SCC susceptibility of Ni-base alloys.

3.5. Dissolved metal ion

The possibility of film formation on Alloy 600 in caustic water containing lead can be supported by the

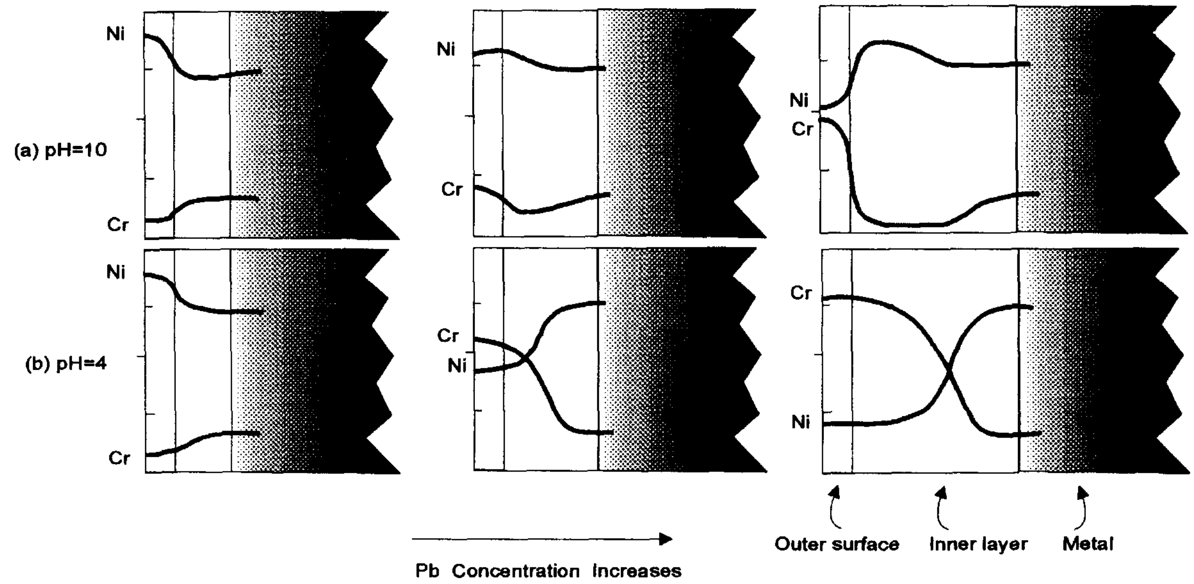

Fig. 13. The effect of Pb on passive film composition of Alloy 600 at different pH's.

results of solution analysis. Figs. 11 and 12 show the results of ICPS analyses of metal ion concentrations at pH 4 and pH 10, respectively. As lead concentration increased, dissolved Ni ions increased and dissolved Cr ions decreased. In relation with the XPS results, dissolved metal ions might have originated from the outer film.

3.6. Discussion on the film composition

It has been demonstrated by other authors that Ni is depleted at a low pH and Cr is depleted at a high pH using the AES technique [3,4,11]. The same results were obtained in this work. However, outermost film analyzed by XPS has a Ni-depleted and Cr-enriched composition regardless of pH in this work. From the results of film and solution analyses, the surface film formed on Alloy 600 in acidic or caustic conditions with lead is thought to have the characteristics shown in Fig. 13.

4. Conclusions

(1) Lead enhances Ni dissolution of Alloy 600 in anodic polarization tests.

(2) PbO is reduced to metallic lead while oxidizing Ni and Cr of Alloy 600.

(3) Bilayer structure with different compositions forms on Alloy 600 in mildly caustic water containing lead.

(4) The passive film on Alloy 600 is most governed by pH while lead accelerates the tendency.

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