

니켈-알루미늄 합금의 부식성 연구

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Aqueous Corrosion Characteristics of Nickel Aluminides

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ABSTRACT

The aqueous corrosion characteristics of three nickel aluminides were studied by using (a) immersion corrosion test and (b) cyclic anodic polarization measurements.

The immersion tests were conducted in 15 different solutions at 25°C and 95°C. The nickel aluminides were found to have good corrosion resistance in inorganic acids, organic acids and basic solutions 25°C except at a higher concentration of hydrochloric acid in ferric chloride solution at the temperature. All three nickel aluminides were suitably resistant to corrosion in the organic acids (oxalic acid, acetic acid), sodium chloride solution, and bases (sodium hydroxide, ammonium hydroxide) at 95°C. The cyclic anodic polarization curves were developed in N₂-deaerated solution at 25°C and 95°C. In addition, open-circuit corrosion potentials were determined for the solutions in the aerated condition at 25°C to compare with the anodic curves. At 25°C, although all materials exhibited active-passive behavior in all solutions except the hydrofluoric acid, at $E_{corr}(aerated)$, passive corrosion was only indicated for the acetic acid, sodium hydroxide, and sodium chloride solutions. Nevertheless, in all cases, the predicted dissolution rates were consistent with immersion test results. Hysteresis loops indicating susceptibility to localized corrosion were observed in 0.6M sodium chloride(pH=7) solution. At 95°C, active-passive behavior was demonstrated in the acetic acid, sodium chloride, and to a limited extent in the nitric acid; but only active behavior was shown in the sulfuric and hydrofluoric acids.

From the above results, it was noted that anodic dissolution of nickel aluminides significantly increased with increasing temperature and that the Cr-containing compositions had better corrosion resistance in several solutions than the Cr-free composition. Prior manufacturing procedures, i.e., casting and powder metallurgy processes did not appear to influence the corrosion behavior of the nickel aluminides.

1. INTRODUCTION

A new class of nickel-based alloys which are based on the Ni₃Al stoichiometry has been developed at the Oak Ridge National Laboratory. It is believed that the nickel aluminides will compete with the superalloys because of several benefits. These include low density, simple composition, excellent oxidation resistance, and high yield strength with increasing temperature. However, until recently, a major problem restricting their uses was inherent brittleness. Recently, the ductility of nickel aluminide has been obtained through small additions of boron and control of aluminum content.^{1,2)} The nickel aluminides are usually resistant to oxidation and can be expected to have good corrosion resistance because of their ability to form compact adherent oxide surface films and strong binding of atoms. Nickel aluminides have a wide range of potential uses, e. g., turbine applications, fasteners, drill bits, forging dies, molds for aluminum and glass casting, bearings, components for corrosive environments, and heating elements but the use of nickel aluminides in corrosive environments has been limited because of lack of data.^{3,4,5)}

The major purpose of the research was to investigate the aqueous corrosion characteristics of three different compositions of nickel aluminides in various solutions at 25°C and 95°C. Immersion corrosion tests were used to evaluate general corrosion resistance in organic acids, inorganic acids, bases and salt solutions. Cyclic potentiodynamic polarization techniques were used to study the passive film behavior, to provide information on the corrosion rate and to determine the pitting resistance of nickel aluminides.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

Table 1 lists the chemical compositions of the three nickel aluminides investigated which are designated as IC-50, IC-218, IC-221. IC-50 and IC-218 were fabricated by casting into sheet form. IC-221 was fabricated by powder metallurgy processing into a rod form. Both processes were conducted at the Oak Ridge National Laboratory. Before annealing, IC-50, IC-218 were sectioned by 2.5 cm × 2.5 cm × 0.06 cm and IC-221 was sectioned by 3.2 cm diameter × 0.15 cm. After sectioning, the specimens were mechanically polished with 600 grit silicon carbide paper. Subsequently, the samples were vacuum annealed (8.2×10^{-6} - 1.2×10^{-5} torr.) for an hour at 1100°C followed by furnace cooling.

2.2. Immersion Tests

Immersion tests⁶⁾ were conducted in 11 different electrolytes each of which has 15 different concentrations at 25°C and 95°C. Test solutions were prepared with reagent-grade chemicals and distilled water. In conducting these experiments, a 0.48 cm diameter hole was drilled near the edge of each sample. The specimens were ground with 120 grit silicon carbide paper and finally finished with 600 grit paper. Three different compositions of nickel aluminides which were hung on a glass rack were exposed to the solution in each flask. The solutions

Table 1. Nominal compositions of nickel aluminides

Alloy	Element: Weight % (Atomic %)				
	Ni	Al	Cr	B	Zr
IC- 50	88.1(77.9)	11.3(21.7)	-	0.02(0.10)	0.6(0.3)
IC-218	82.9(74.8)	8.5(16.7)	7.8(7.9)	0.02(0.10)	0.8(0.46)
IC-221	82.0(74.2)	8.5(16.7)	7.8(8.0)	0.02(0.10)	1.7(0.99)

were aerated under ambient conditions. The tests at 25°C were conducted at ambient laboratory temperature. For the tests at 95°C, the flasks were placed in an isothermal water bath at 95°C and Allihn reflux condensers were used to avoid concentration changes in the test solutions. Boiling chips were used at this temperature to avoid excessive turbulence and bubble impingement. The solution was maintained at constant level throughout the test. When the colour of a given solution changed to a dark green, the solution was replaced with a fresh one. After each test period, the specimens were rinsed with distilled water, degreased with acetone and scrubbed with a nylon brush to remove corrosion products. Then, the specimens were dried in the oven at 80°C for about 1 hour and weighed to 0.001g.

2.3. Polarization Tests

Brass screw was soldered to each specimen for electrical contact with polarization cell. After soldering, the soldered specimen was cleaned by rinsing with acetone. Each specimen was mounted in Maraglas 655 epoxy (ACME Chemicals and Insulation Co.) which was cured in the oven at 80°C during 24 hours. The specimen was finished by grinding on 600 grit silicon carbide paper. To avoid the initiation of crevice corrosion between epoxy and specimen, the specimen was painted with Glyptal 1201 Red Enamel (General Electric Co.) leaving an exposed area of 1 sq.cm. Then the exposed surface was polished again to remove the air-formed oxide film just before being introduced into a polarization cell.

The EG&G Model 273 potentiostat was connected to the polarization cell which was a modified two-liter vessel. A salt bridge assembly, working electrode, Pt-counter electrode, gas inlet and

outlet, and thermometer were introduced into polarization cell through compression fittings in the cell lid. Before polarization measurement, the corrosion sample was allowed to stabilize in deaerated electrolyte (nitrogen gas purged) until the potential changed was less than one millivolt per minute, at which condition the measured potential was then taken as the open-circuit corrosion potential (E_{corr}). The open-circuit corrosion potential in aerated condition was also measured separately. The sample was then potentiodynamically scanned at a rate of 600mV/h to a potential corresponding to a reversing current density of 10^{-3} A/sq.cm. At this point, the scan direction was reversed.⁷⁾ The downscan was continued until either the protection potential was identified or it was demonstrated that no hysteresis loop was being developed. The tests at 25°C were conducted at ambient laboratory temperature and the solution heating was conducted by using a flexible electric heating tape and Staco EJ901 variable power source. All potentials were converted to the standard hydrogen electrode (SHE) scale.

3. RESULTS AND DISCUSSION

3.1. Immersion Tests

Calculations for average penetration rate in rails per year were performed based on Faraday's law. The conversion for the three nickel aluminide compositions is:

$$PR(\text{mpy}) = 4.21 \times 10^3 M/t$$

where M is the mass-loss per unit area (g/cm^2) and t is time (hour).

The cumulative 200h mass-loss per unit area (g/cm^2) and average penetration rates (mpy) obtained

Table 2. 200-hour mass loss and average penetration rate, discontinuous exposure, 25°C

Solution (25°C)	Concentration Molar Wt. %		IC-50		IC-218		IC-221	
			Mass Loss in 200-h (g/cm ²)	Average Penetration Rate (mpy)	Mass Loss in 200-h (g/cm ²)	Average Penetration Rate (mpy)	Mass Loss in 200-h (g/cm ²)	Average Penetration Rate (mpy)
Sulfuric Acid	1	9	1.58×10^{-3}	3	2.67×10^{-3}	6	1.93×10^{-3}	4
	18	96	1.34×10^{-2}	28	1.55×10^{-2}	33	1.21×10^{-2}	25
Hydrochloric Acid	1	4	2.18×10^{-3}	5	3.87×10^{-3}	8	1.90×10^{-3}	4
	12	37	1.29×10^{-1}	271	1.21×10^{-1}	254	5.49×10^{-1}	1150
Nitric Acid	1	6	8.18×10^{-2}	172	1.30×10^{-1}	273	3.89×10^{-1}	817
	8	40	2.22×10^{-1} (a)	>3894(a)	4.23×10^{-4}	1	4.47×10^{-3}	9
	16	70	4.48×10^{-2}	94	1.24×10^{-3}	3	1.59×10^{-3}	3
Hydrofluoric Acid	1	2	1.92×10^{-3}	4	2.14×10^{-3}	4	1.91×10^{-3}	4
Phosphoric Acid	1	10	1.12×10^{-3}	2	1.42×10^{-3}	3	1.97×10^{-3}	4
Oxalic Acid	1	10	2.26×10^{-4}	0.5	6.23×10^{-4}	1	4.17×10^{-4}	1
Acetic Acid	1	6	8.66×10^{-4}	2	3.11×10^{-4}	0.5	-1.16×10^{-4} (b)	(b)
Sodium Chloride	0.6	3.5	9.28×10^{-4}	2	1.43×10^{-3}	3	9.95×10^{-4}	2
Sodium Hydroxide	10	30	-1.50×10^{-4} (b)	(b)	-2.28×10^{-4} (b)	(b)	-1.79×10^{-4} (b)	(b)
Ammonium Hydroxide	10	18	1.03×10^{-3}	2	-8.60×10^{-5} (b)	(b)	-3.99×10^{-3} (b)	(b)
Ferric Chloride	1.2	20	2.41×10^{-1} (c)	>2114(c)	2.62×10^{-1} (a)	>4596(a)	5.20×10^{-1}	1090

(a) Total dissolution in < 24h

(b) Very small mass gain

(c) Total dissolution between 24-48h

* Removed from solution, scrubbed and rinsed with distilled water, dried, and weighed every 24 hours

by discontinuous exposure at 25°C and 95°C are presented in Tables 2 and 3. For the continuous exposure at 25°C and 95°C, the results in terms of the same corrosion parameters are given in Tables 4 and 5. The discontinuous exposure behavior was evaluated by measuring weight loss at an interval of 24 hours whereas in the continuous exposure the sample was not disturbed until 200 hours. Table 6 shows the average penetration rates of the continuous and discontinuous exposures at 25°C. In order to provide a frame of reference for comparing the corrosion behavior of the three nickel

aluminide compositions with other commercial alloys, Table 7 has been constructed.⁸⁾

Sulfuric acid is a non-oxidizing acid up to a concentration of about 50 to 60 percent by weight but beyond that concentration it is considered to be oxidizing. The corrosion rate of nickel aluminides increased with acid concentration for the 25°C tests, but the higher concentrations of sulfuric acid were less corrosive than its lower concentrations at 95°C. Surface examination showed that the surfaces of all the specimens in higher concentrations at 95°C were shiny and were not corroded severe-

Table 3. 200-hour mass loss and average penetration rate, discontinuous exposure, 95°C

Solution (25°C)	Concentration Molar Wt. %		IC-50		IC-218		IC-221	
			Mass Loss in 200-h (g/cm ²)	Average Penetration Rate (mpy)	Mass Loss in 200-h (g/cm ²)	Average Penetration Rate (mpy)	Mass Loss in 200-h (g/cm ²)	Average Penetration Rate (mpy)
Sulfuric Acid	1	9	5.18×10^{-2}	122	4.25×10^{-2}	89	4.49×10^{-1}	945
	18	96	6.67×10^{-2}	140	4.12×10^{-2}	87	3.84×10^{-2}	81
Hydrochloric Acid	1	4	2.09×10^{-1}	438	2.15×10^{-1}	452	5.61×10^{-1}	1180
	12	37	$>2.41 \times 10^{-1}(a)$	$>4230(a)$	$>2.43 \times 10^{-1}(a)$	$>4260(a)$	$6.35 \times 10^{-1}(a)$	$>11139(a)$
Nitric Acid	1	6	$>2.52 \times 10^{-1}(a)$	$>4420(a)$	$>2.31 \times 10^{-1}(a)$	$>4050(a)$	1.26×10^{-1}	265
	8	40	$>2.52 \times 10^{-1}(a)$	$>4420(a)$	1.76×10^{-2}	37	2.84×10^{-2}	60
	16	70	$>1.86 \times 10^{-1}(a)$	$>3260(a)$	3.03×10^{-2}	64	1.23×10^{-1}	258
Hydrofluoric Acid	1	2	7.73×10^{-3}	17	1.40×10^{-2}	29	7.82×10^{-2}	164
Phosphoric Acid	1	10	1.02×10^{-1}	214	$>2.28 \times 10^{-1}(c)$	$>2000(c)$	3.92×10^{-1}	825
Oxalic Acid	1	10	2.28×10^{-3}	5	1.63×10^{-3}	3	6.68×10^{-3}	14
Acetic Acid	1	6	3.35×10^{-3}	7	3.76×10^{-3}	8	5.72×10^{-3}	12
Sodium Chloride	0.6	3.5	1.51×10^{-4}	0.3	1.48×10^{-4}	0.3	1.79×10^{-4}	0.4
Sodium Hydroxide	10	30	0	0	7.51×10^{-5}	0.16	5.96×10^{-5}	0.13
Ammonium Hydroxide	10	18	-7.94×10^{-5}	(b)	0	0	$-5.89 \times 10^{-5}(b)$	(b)
Ferric Chloride	1.2	20	$>2.27 \times 10^{-1}(c)$	$>3980(a)$	$>2.48 \times 10^{-1}(a)$	$>4350(a)$	$>6.50 \times 10^{-1}(a)$	$>11400(a)$

(a) Total dissolution in <24h

(b) Very small mass gain

(c) Total dissolution between 24-48h

* Removed from solution, scrubbed and rinsed with distilled water, dried, and weighed every 24 hours

ly, as compared to those in the lower concentration. Chromium-containing compositions of the nickel aluminides, IC-218, and IC-221, showed a higher resistance to the 18M sulfuric acid at 95°C than chromium-free IC-50. All the specimens exhibited good corrosion resistance at low acid concentrations at 25°C compared to other commercial alloy, i. e., 304 SS, Inconel in Table 7.

Hydrochloric acid is, on the whole, more corrosive than sulfuric acid because of the high solubility of the chlorides, the lesser tendency to form insoluble films, and the high mobility of the chloride

ions.⁹⁾ The temperature effect of hydrochloric acid was greater than that of sulfuric acid. All the specimens showed poor corrosion resistance at high concentration of hydrochloric acid at 25°C.

Aqueous solutions of nitric acid are highly oxidizing in nature and the nickel aluminides were subject to rapid attack in these acids. Chromium is an essential alloying element for corrosion resistance because it readily forms a passive film in nitric acid. From the immersion test data, chromium-containing compositions showed increased resistance. Corrosion rates in more dilute acid

Table 4. 200-hour mass loss and average penetration rate, continuous exposure, 25°C

Solution (25°C)	Concentration Molar Wt. %		IC-50		IC-218		IC-221	
			Mass Loss in 200-h (g/cm ²)	Average Penetration Rate (mpy)	Mass Loss in 200-h (g/cm ²)	Average Penetration Rate (mpy)	Mass Loss in 200-h (g/cm ²)	Average Penetration Rate (mpy)
Sulfuric Acid	1	9	8.63×10^{-4}	2	1.18×10^{-3}	2	1.20×10^{-3}	3
	18	96	3.41×10^{-3}	7	3.02×10^{-3}	6	3.05×10^{-3}	6
Hydrochloric Acid	1	4	2.50×10^{-3}	5	1.51×10^{-3}	3	1.49×10^{-3}	3
	12	37	5.79×10^{-2}	121	9.14×10^{-2}	192	1.79×10^{-1}	376
Nitric Acid	1	6	2.06×10^{-1}	433	2.47×10^{-1} (a)	>1600(a)	2.50×10^{-1}	525
	8	40	2.31×10^{-1}	>12156(b)	2.41×10^{-4}	1	1.54×10^{-3}	3
	16	70	3.02×10^{-2}	63	4.68×10^{-4}	1	1.26×10^{-3}	3
Hydrofluoric Acid	1	2	1.55×10^{-3}	3	1.66×10^{-3}	3	1.55×10^{-3}	3
Phosphoric Acid	1	10	1.03×10^{-3}	2	9.58×10^{-4}	2	1.11×10^{-3}	2
Oxalic Acid	1	10	4.33×10^{-4}	1	5.49×10^{-4}	1	5.74×10^{-4}	1
Acetic Acid	1	6	1.47×10^{-3}	3	8.11×10^{-5}	0.2	0	0
Sodium Chloride	0.6	3.5	8.57×10^{-5}	0.2	7.97×10^{-5}	0.2	5.72×10^{-5}	0.1
Sodium Hydroxide	10	30	1.79×10^{-4}	0.4	8.05×10^{-5}	0.2	5.68×10^{-5}	0.1
Ammonium Hydroxide	10	18	2.71×10^{-3}	6	1.54×10^{-4}	0.3	1.14×10^{-4}	0.2
Ferric Chloride	1.2	20	2.37×10^{-1} (c)	> 5869(a)	2.61×10^{-1} (d)	>4578(d)	4.25×10^{-1}	893

(a) Total dissolution in <65h

(a) Total dissolution in < 8h

(a) Total dissolution in <17h

(a) Total dissolution in <24h

were very high at both temperatures. This indicated that the nickel aluminides tended to undergo passivation with increasing concentration. As the temperature increased, the corrosion rates were enhanced. From the discontinuous exposure data, the Cr-free IC-50 dissolved completely within 24 hours while the others were more slowly dissolved.

All the nickel aluminides had good corrosion resistance in hydrofluoric acid at 25°C compared to 304 SS. In the test at 95°C, the corrosion rates of continuous exposure were higher than those of

discontinuous exposure. Many pits were observed on the specimen tested only at the high temperature.

Phosphoric acid was not corrosive for nickel aluminides at 25°C; however, nickel aluminides suffered considerable attack by such a solution at 95°C. From the discontinuous exposure data at 95°C, IC-218 dissolved completely within 72 hours while IC-50 dissolved more slowly. Comparing to the other commercial alloy, the nickel aluminides had higher corrosion rates at high temperature.

Table 5. 200-hour mass loss and average penetration rate, continuous exposure, 95°C

Solution (25°C)	Concentration Molar Wt. %		IC-50		IC-218		IC-221	
			Mass Loss in 200-h (g/cm ²)	Average Penetration Rate (mpy)	Mass Loss in 200-h (g/cm ²)	Average Penetration Rate (mpy)	Mass Loss in 200-h (g/cm ²)	Average Penetration Rate (mpy)
Sulfuric Acid	1	9	>2.33 × 10 ⁻¹ (a)	>490(a)	1.44 × 10 ⁻¹	302	>4.12 × 10 ⁻¹ (a)	> 867(a)
	18	96	3.20 × 10 ⁻²	67	8.39 × 10 ⁻³	18	9.36 × 10 ⁻³	20
Hydrochloric Acid	1	4	2.43 × 10 ⁻¹	510	>2.50 × 10 ⁻¹ (a)	>526(a)	5.25 × 10 ⁻¹	1101
	12	37	>2.40 × 10 ⁻¹ (a)	>505(a)	>2.42 × 10 ⁻¹ (a)	>509(a)	>6.35 × 10 ⁻¹ (a)	>1337(a)
Nitric Acid	1	6	>2.43 × 10 ⁻¹ (a)	>511(a)	>2.52 × 10 ⁻¹ (a)	>530(a)	1.47 × 10 ⁻¹	308
	8	40	>2.27 × 10 ⁻¹ (a)	>477(a)	2.12 × 10 ⁻²	45	2.68 × 10 ⁻²	56
	16	70	>2.45 × 10 ⁻¹ (a)	>514(a)	2.83 × 10 ⁻²	59	9.42 × 10 ⁻²	198
Hydrofluoric Acid	1	2	>2.55 × 10 ⁻¹ (a)	>534(a)	>2.34 × 10 ⁻¹ (a)	>492	1.91 × 10 ⁻¹	402
Phosphoric Acid	1	10	>2.26 × 10 ⁻¹ (a)	>475(a)	>2.46 × 10 ⁻¹ (a)	>517(a)	3.58 × 10 ⁻¹	752
Oxalic Acid	1	10	-7.63 × 10 ⁻³ (b)	(b)	1.25 × 10 ⁻³	3	1.70 × 10 ⁻³	4
Acetic Acid	1	6	1.94 × 10 ⁻³	4	1.93 × 10 ⁻³	4	1.97 × 10 ⁻³	4
Sodium Chloride	0.6	3.5	7.56 × 10 ⁻⁵	0.2	-7.82 × 10 ⁻⁵ (b)	(b)	-9.68 × 10 ⁻⁵ (b)	(b)
Sodium Hydroxide	10	30	-8.15 × 10 ⁻⁵ (b)	(b)	-1.60 × 10 ⁻⁴ (b)	(b)	-9.47 × 10 ⁻⁵ (b)	(b)
Ammonium Hydroxide	10	18	-1.40 × 10 ⁻⁴ (b)	(b)	-1.60 × 10 ⁻⁴ (b)	(b)	-1.88 × 10 ⁻⁴ (b)	(b)
Ferric Chloride	1.2	20	>2.49 × 10 ⁻¹ (a)	>524(a)	>2.30 × 10 ⁻¹ (a)	>484(a)	>5.38 × 10 ⁻¹ (a)	>1132(a)

(a) Total dissolution in < 20h

(b) Very small mass gain

Oxalic acid is less corrosive than inorganic acids because of its lower acidity. Corrosion rates of all the nickel aluminides were quite low on oxalic acid at both temperatures.

All nickel aluminides were suitably resistant to corrosion in acid at both temperatures. The penetration rate at 95°C was slightly higher than that at 25°C

All three specimens underwent pitting corrosion with 200 hour exposures to a 0.6M sodium chloride solution. It was observed that the pit growth increased at high temperature. However, the average corrosion penetration rates were very low

at both temperatures.

All specimens exhibited excellent corrosion resistance to a caustic, alkaline, sodium hydroxide solution. There was no pitting susceptibility to this solution at higher temperature. Surfaces of the specimens were shiny after testing.

The nickel aluminides had a high degree of resistance to corrosion by ammonium hydroxide at 25°C and 95°C. Corrosion rates of nickel aluminides in ammonium hydroxide were on the same order or less than those of commercial alloys such as 304 SS, Inconel, and Hastelloy-C. As shown in Table 7, nickel is attacked by ammonium

Table. 6. Average penetration rate, continuous and discontinuous exposure, 25°C

Solution	Concentration		Avg. of 200-h continuous and discontinuous exposures		
	Molar	Wt. %	IC-50	IC-218	IC-221
Sulfuric Acid	1	9	2	4	3
	18	96	17	19	15
Hydrochloric Acid	1	4	5	5	3
	12	37	196	223	765
Nitric Acid	1	6	302	273(>1600)	671
	8	40	>8025	1	6
	16	70	78	2	3
Hydrofluoric Acid	1	2	3	3	3
Phosphoric Acid	1	10	2	2	3
Oxalic Acid	1	10	1	1	1
Acetic Acid	1	6	2	<1	<1
Sodium Chloride	0.6	3.5	1	1	1
Sodium Hydroxide	10	30	<1	<1	<1
Ammonium Hydroxide	10	18	4	<1	<1
Ferric Chloride	1.2	20	>3990	>4587	993

hydroxide, but aluminum is more resistant.

Ferric chloride, a strong oxidizing agent, was very corrosive to all nickel aluminides at both temperatures. All three specimens were dissolved within 24 hours at 95°C.

3.2. Cyclic Potentiodynamic Polarization Test

The cyclic anodic polarization¹⁰⁾ results for the three nickel aluminide compositions at 25°C and 95°C are presented in Figures 1-7. These data were generated in N₂ deaerated solutions. In addition, the open-circuit corrosion potentials at 25°C were later evaluated in O₂-aerated solution in order to estimate the penetration rate and compare

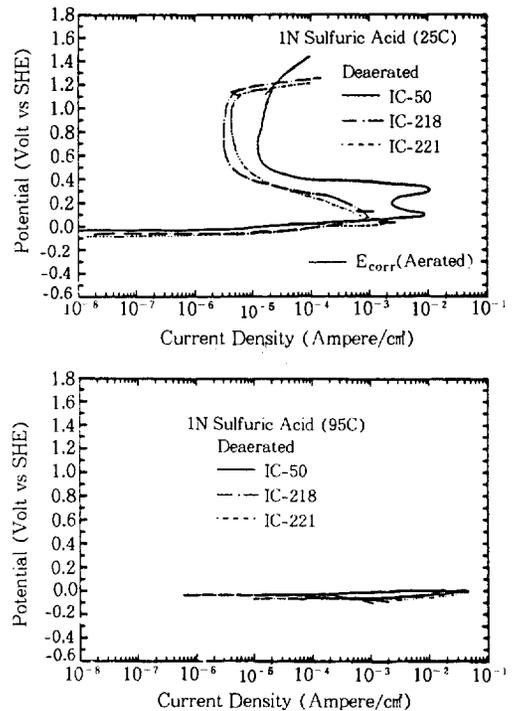


Fig. 1. Anodic polarization in 1N sulfuric acid, 25°C and 95°C

with immersion test data. The estimation was performed by application of Faraday's law for the nickel aluminides:

$$PR(\text{mpy}) = 3.9 \times 10^6 i_{\text{corr}}(\text{aerated})$$

A reasonably good estimate of $i_{\text{corr}}(\text{aerated})$ corresponds to the current density intersection of the anodic curve at $E_{\text{corr}}(\text{aerated})$, provided that $E_{\text{corr}}(\text{aerated})$ is above $E_{\text{corr}}(\text{deaerated})$ by more than about 0.050V.

Cyclic potentiodynamic polarization curves for the three nickel aluminides in the deaerated 1N H₂SO₄ solution at both 25 and 95°C are shown in Figure 1. At 25°C all three nickel aluminides showed typical active-passive behavior. The chromium-containing IC-218 and IC-221, as compared to the

Table 7. Comparison of corrosion rates for several alloys in various solutions used for the testing of Ni₃Al in this study.⁵

Solution	wt. %	mpy(25°C)/mpy(95°C)				
		Nickel	Aluminum	304SS	Inconel	Hastelloy-C
Sulfuric Acid	10	<50/>50	>50/>50	<50/>50	>50/>50	< 2/<2
	95	>50/>50	> 50/>50	<20/-	>50/>50	< 2/<20
Hydrochloric Acid	dilute	<20/>-	>50/>50	>50/>50	<20/-	< 2/>50
	35	>50/>50	>50/>50	>50/>50	>50/>50	< 2/<50
Nitric Acid	5	>50/>50	>50/>50	< 2/< 2	<20/>50	< 2/<20
	40	>50/>50	>50/>50	< 2/< 2	>20/>50	< 2/>50
	70	>50/>50	>50/>50	< 2/<50	>50/>50	< 2/>50
Hydrofluoric Acid	dilute	<20/>50	>50/>50	>50/>50	< 2/>50	< 2/<2
Phosphoric Acid	10	<20/>50	<50/-	< 2/< 2	<20/<20	< 2/<20
Oxalic Acid	10	<50/-	<20/>50	>50/<50	<20/<20	<20/<20
Acetic Acid	10	<20/-	<20/>50	< 2/< 2	<20/-	< 2/<2
Sodium Chloride	-	< 2/<20	>50/>50	<20/<20	< 2/<20	<20/<20
Sodium Hydroxide	30	< 2/< 2	>50/>50	< 2/<20	2/<20	<20/<20
Ammonium Hydroxide	35	>50/>50	<20/<20	< 2/<20	<20/-	<20/<20
Ferric Chloride	50% in water	>50/>50	>50/>50	>50/>50	<50/>50	<50/>50

chromium-free IC-50, appeared to have lower critical anodic current densities and lower passive current densities. Further, all three nickel aluminides had almost identical apparent-breakdown potential at about 1.1V. The rapid increase in current density at about 1.1V was due to passive-film breakdown and/or anodic current associated with oxygen evolution. In any event, none of the cyclic curves had hysteresis loops, i. e., the apparent breakdown potentials were identical to the protection potentials, which indicates that these alloys were not susceptible to localized corrosion in 1N H₂SO₄ at room temperature.

The corrosion potential measured in the aerated 1N sulfuric acid for all three compositions were in the active regions. The estimated penetration rates were in the 200 mpy range. These values were considerably higher than the values calculated from immersion test data, 2 mpy for 1M(or 2N) H₂SO₄ given in Table 6. A possible explanation may

be that passivation was easier in the somewhat higher sulfuric acid concentration employed for the immersion tests. When the test temperature was increased to 95°C, the polarization curves showed only active corrosion behavior with no tendency for passivation.

The above results for the behavior of the three nickel aluminides in 1N sulfuric acid revealed that the corrosion behavior was strongly influenced by the chemical composition of samples and solution temperature. However, the different manufacturing condition (i.e. casting and powder metallurgy) for the similar chemical compositions (IC-218 vs IC-221) did not appear to significantly influence the corrosion behavior. Further, no effect of chemical composition was found at the high testing temperature of 95°C; all three nickel aluminides had essentially identical behavior.

In this study, in order to investigate which element(s) was responsible for the passivation of the

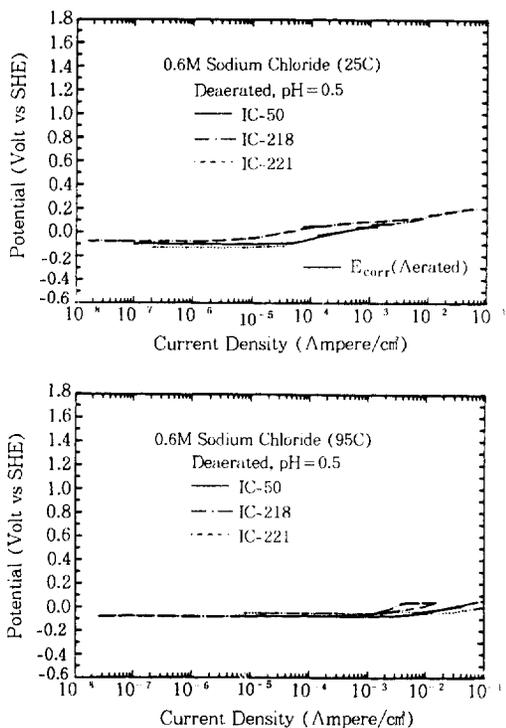


Fig. 2. Anodic polarization in 0.6M sodium chloride(3.5wt.%) , pH=0.5(sulfuric acid), 25°C and 95°C.

nickel aluminides in the sulfuric acid, three pure Ni, Al and Cr samples were also tested in deaerated 1N sulfuric acid at room temperature. The anodic polarization behavior of pure elements together with IC-218 are shown in Figure 8. Figure 8 clearly shows that the passive behavior of Cr-containing nickel aluminide is similar to those of the pure Ni and Cr. Therefore, the Al in nickel aluminide does not seem to influence the passivation of nickel aluminide as compared to Cr and Ni.

The effect of pH, at a given Cl^- ion concentration, on the anodic polarization behavior of the three nickel aluminides is given in Figures 2 and 3. The pH value was adjusted by sulfuric acid. For a pH=0.5, it is seen that there is no active-passive transition behavior at both 25 and 95°C. The

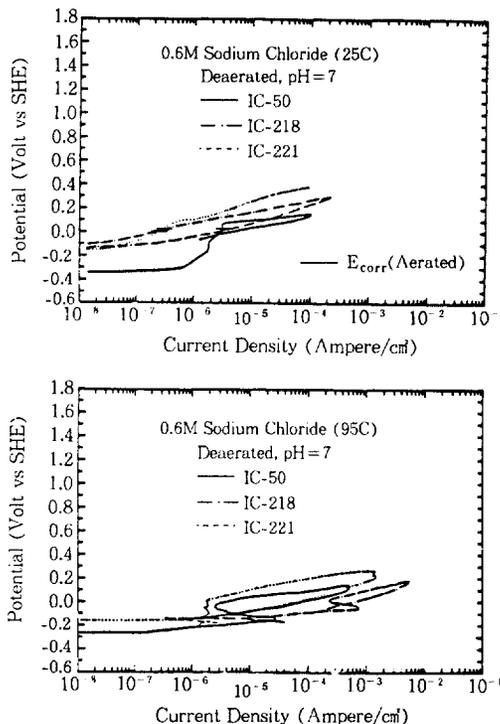


Fig. 3. Anodic polarization in 0.6M sodium chloride(3.5wt.%) , pH=7(sulfuric acid), 25°C and 95°C.

aluminides only exhibited severely active corrosion behavior. The values of pH=0.5 was attained by approximately 1N sulfuric acid. With small increment of potential, the anodic current density increased by an order of 10^6 , which revealed severe anodic dissolution.

Comparing the polarization curves in the chloride ion-free 1N sulfuric acid to those in the 0.6M sodium chloride plus 1N sulfuric acid, it is obvious that the chloride ions have a detrimental effect on the corrosion properties of nickel aluminides. At the higher temperature (95°C), as may be expected, an addition of Cl^- in 1N sulfuric acid did not significantly affect the anodic polarization behavior of all three alloys. However, at room temperature, the Cl^- influence is clear such that the passivation behavior completely disappeared. This

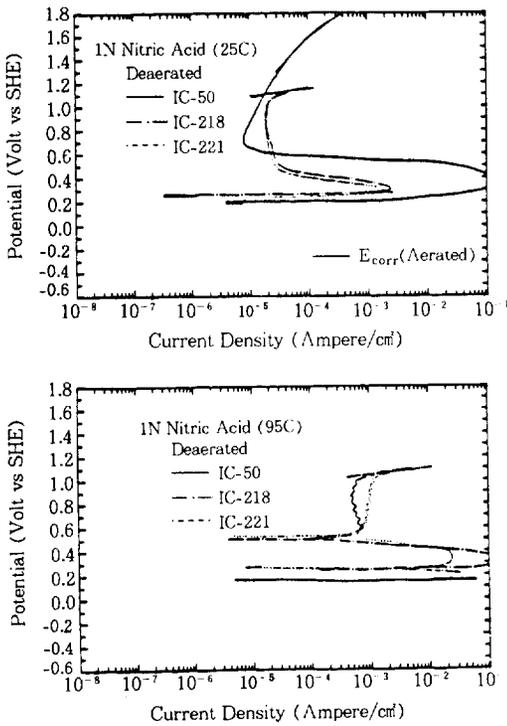


Fig. 4. Anodic polarization in 1N nitric acid, 25°C and 95°C.

effect indicated that the Cl^- ion seemed to destroy the passive film as soon as it attempted to form at $\text{pH}=0.5$.

When the pH was increased to 7 in Figure 3, while maintaining the Cl^- concentration at 0.6M, all the nickel aluminides in the test at 25°C showed active-passive behavior. Pitting was found on all the specimens at both temperatures after the polarization tests. The estimated penetration rates in the aerated condition at 25°C from these polarization results were in the range of 0.1-1.0 mpy which was more or less consistent with the immersion test results, 0.2 mpy. At the 95°C temperature the pitting and protection potentials of IC-50 were -0.04 and -0.1 V(SHE) which were lower values than 0.06, -0.04 V(SHE) at 25°C. This means that both the pitting and protection potentials are de-

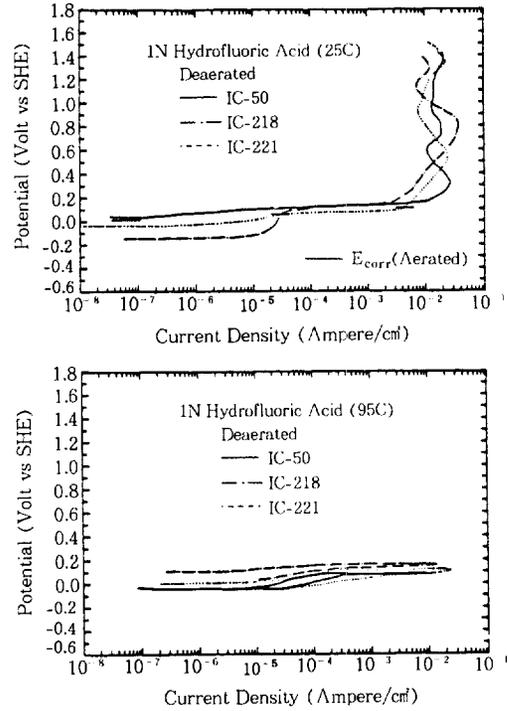


Fig. 5. Anodic polarization in 1N hydrofluoric acid, 25°C and 95°C.

creased with increasing temperature.

The above test results, with regard to the effects of Cl^- and pH on the anodic behavior of aluminides, clearly indicated that the Cl^- ion exerts a detrimental influence on the passivation behavior of aluminides. For a given Cl^- concentration, the increase in acidity resulted in a decrease in the breakdown potential regardless of the chemical composition of the alloy and the prior manufacturing procedures. Further, the higher temperature appeared to accelerate the detrimental influence of Cl^- on the initiation of pits.

From the cyclic polarization curves in 1N nitric acid in Figure 4, every specimen showed passive regions in the tests at 25°C. The Cr-free IC-50 exhibited the highest critical anodic current density compared to the chromium-containing composi-

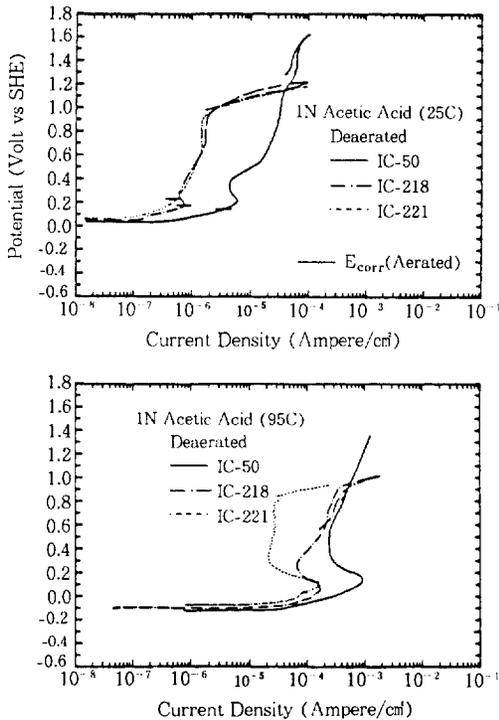


Fig. 6. Anodic polarization in 1N acetic acid, 25°C and 95°C.

tion, IC-218 and IC-221. At this concentration under aerated conditions, active behavior was predicted with estimated penetration rates on the order of 400 mpy or greater. These results were consistent with immersion test results of Table 6. In the 95°C tests, the critical anodic current densities and the passive current densities were higher than those for the 25°C tests. This meant that as the temperature increased, passivation became more difficult. While chromium-containing IC-218 and IC-221 underwent passivation, IC-50 showed only active corrosion behavior in the 95°C tests. At 95°C, IC-218 and IC-221 showed two corrosion potentials. These cases exist when the cathodic reduction curve intersects the anodic curve at two different potentials. Figure 9 represents schematic drawings of the anodic and cathodic reaction

curves when the cathodic curve intersects the anodic curve at two different potentials. The intersection (a) is in the active region and gives a higher corrosion rate, whereas intersection (b) is at the active-passive transition point with a low corrosion rate. There was no hysteresis trace at either temperature, i. e., the breakdown potential was virtually identical to the protection potential revealing a relatively good localized corrosion resistance of the nickel aluminides in the solution regardless of the composition. However, all alloys had significantly high critical anodic current densities as compared to those in 1N sulfuric acid behavior. This fact indicated that aluminides in nitric acid may be susceptible to high uniform corrosion rates. The tested sample in this solution showed dark color at either temperature. Temperature and the presence of Cr play a significant role in the corrosion behavior in nitric acid.

Figure 5 shows anodic polarization curves in 1N hydrofluoric acid at 25°C and 95°C. For the 25°C tests, only active behavior was exhibited by all three nickel aluminides. The observed active behavior indicated the aggressive effects of fluoride ions in preventing the formation of passive films. For the nickel aluminides at 25°C, the apparent passivation at high current densities, 10^{-2} A/cm², was likely not passivation but diffusion limited current densities. Some types of fluoride layers may limit diffusion of metal ions. For the 95°C tests, all the specimens exhibited active corrosion. The surfaces of the specimens were corroded uniformly.

For both the 25°C and the 95°C temperatures in 1N acetic acid as shown in Figure 6, all specimens showed passivation. By comparing both temperature tests, the passive current densities are shown to be increased by increasing temperature. The

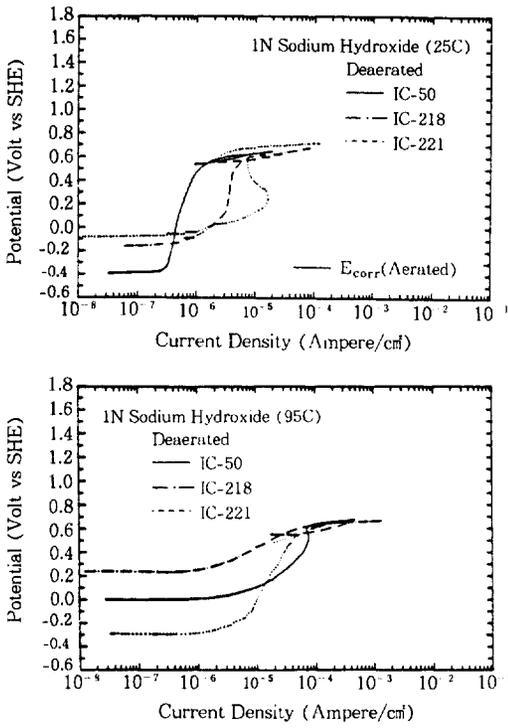


Fig. 7. Anodic polarization in 1N sodium hydroxide, 25°C and 95°C.

passive current densities increased in order of IC-221, IC-218, IC-50. Microscopic examination did not show any evidence of pit formation and there was no trend for hysteresis behavior. The rapid increase of current is not a result of localized corrosion but of uniform corrosion in the transpassive region, or oxygen evolution. The breakdown potentials of IC-221 and IC-218 at 25°C were the same at 1.0 V(SHE) and 0.9 V(SHE) at 95°C. The active peaks were distinct in the 95°C tests, but not clear in the 25°C tests. The estimated penetration rates at 25°C were approximately 0.2 mpy for IC-218 and IC-221, and 1.0 mpy for IC-50. These values were consistent with the immersion test results as shown in Table 6. As far as the passive current density is concerned, the aluminides seemed to have the best corrosion resistance in the

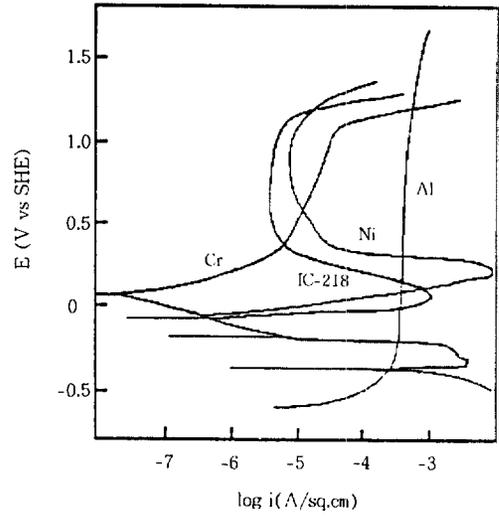


Fig. 8. Anodic polarization curves in deaerated 1N sulfuric acid, 25°C.

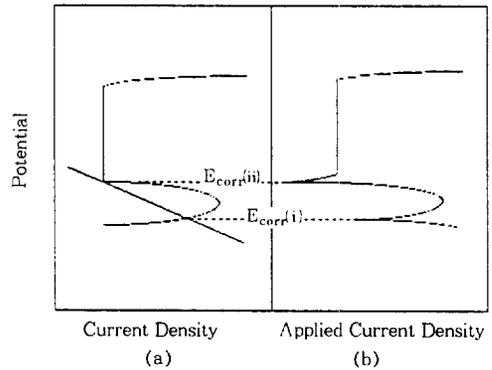


Fig. 9. Schematic polarization curves (a) actual (b) measured curves.

acetic acid solution at room temperature as compared to the other solutions.

In the 1N sodium hydroxide solution, Figure 7 shows that all three nickel aluminides were passivated at both temperature. In this highly basic solution, the IC-50 exhibited the lowest passive current density at 25°C. The penetration rates were on the order of 0.3 mpy which were consistent with the immersion test results as presented in Table 6. The effect of the temperature was to

narrow the passive regions for all the specimens except IC-221. No hysteresis was exhibited at either temperature.

4. CONCLUSIONS

1. The nickel aluminides are suitable for uses in organic acids and basic solutions and in limited categories of inorganic acids at 25°C and 95°C.
2. Pitting susceptibility was observed in halide ion media, i. e., Cl⁻ and F⁻.
3. Chromium was found to be an important alloying element for the corrosion resistance of nickel aluminides although aluminum played an important role in the formation of passive films in neutral chloride solution.
4. The differences in manufacturing procedures, i.e., casting and powder metallurgy processes did not seem to affect the corrosion behavior.

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