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EVALUATION OF THE ENVIRONMENTALLY INDUCED FRACTURE RESISTANCE OF DUCTILE NICKEL ALUMINIDE

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ABSTRACT

Slow-strain-rate tensile tests and electrochemical experiments were performed in different aqueous solutions on ductile nickel aluminide, $\text{Ni}_3\text{Al}+\text{B}$, in order to evaluate the possibility of environmentally induced fracture of this material in neutral pH solutions as a result of hydrogen absorption. Two different processes were postulated that could lead to hydrogen absorption and embrittlement: (1) local acidification due to hydrolysis of the corrosion reaction products and (2) hydrogen reduction during the potential transient that accompanies film rupture and repair. Experiments were designed to evaluate each of these possibilities. First, slow strain rate tests were conducted in solutions with varying concentrations of metal ions and pH to determine the critical metal ion concentration and pH that result in hydrogen absorption and embrittlement of this material. Second, the potential transient that follows the mechanical rupture of the protective surface film in different solutions was measured and the minimum potential during the transient was compared to the potential that results in a hydrogen fugacity large enough to cause cracking. The results indicate that hydrogen reduction, absorption, and embrittlement are not to be expected in neutral solutions as a result of local acidification during crevice corrosion or film rupture during crack propagation or cyclic loading.

INTRODUCTION

Nickel aluminide, Ni_3Al , is an intermetallic compound that forms as a result of ordering of the nickel and aluminum atoms on the FCC unit cell with the nickel atoms occupying the face center sites and the aluminum atoms occupying the corner sites (the L1_2 structure). This material has many desirable properties, such as a lower density than other nickel alloys and a yield strength that increases with temperature (1). Polycrystalline nickel aluminide is intrinsically brittle at ambient temperatures, but this material can be made ductile through microalloying additions of boron and by maintaining the aluminum concentration in the alloy slightly below the stoichiometric ratio (2,3). The resulting intermetallic alloy offers high strength and ductility, making it a promising structural material particularly for high temperature applications.

Although nickel aluminide was developed primarily for high-temperature applications, it is being considered for low-temperature applications because of the corrosion resistance, the lower density, and the excellent wear resistance of this material compared to other nickel alloys and stainless steels (4-9). Also, the low-temperature, aqueous corrosion behavior of this material is of concern because high-temperature components will not always be at operating temperatures, and corrosion damage or crack initiation during fabrication or maintenance could lead to catastrophic failures during service. As a result, the corrosion, stress-corrosion cracking, and hydrogen embrittlement susceptibility of this material at ambient temperatures has been the subject of several

studies (4,8-14).

Kuruvilla and Stoloff (12) demonstrated that the ductility of nickel aluminide is reduced by cathodic charging with hydrogen and that the fracture mode changed from transgranular to intergranular for simultaneous cathodic charging and straining. While Kuruvilla and Stoloff demonstrated that this material is susceptible to hydrogen embrittlement, the possibility that hydrogen absorption and embrittlement may occur as a result of corrosion during normal applications was not addressed by their study. Therefore, a series of studies into the corrosion and stress-corrosion cracking behavior of this material was initiated (8,13-14). The first objective of these studies was to determine if exposure to aggressive environments could result in environmentally induced crack propagation (13). When cracking was observed, the objective became identification of the mechanism of cracking and identification of environmental conditions that could lead to failure in service. Ultimately, the objective is to identify potential applications for nickel aluminide where environmentally induced fracture will not occur. In this paper, we will review our early work on the environmentally induced fracture behavior of this material and then present our recent work on understanding the processes that could lead to environmentally induced crack propagation in service.

BACKGROUND

As discussed above, the objective of the first study was to determine if nickel aluminide was susceptible to environmentally induced fracture. This question was addressed by conducting slow-strain-rate tensile tests in solutions of differing pH and chloride ion concentration; Figure 1 shows that the ductility and the strain-to-failure are essentially unaffected by the environment in the neutral and alkaline solutions, while in the acidic solutions the ductility was greatly reduced, and the fracture mode changed from transgranular to intergranular as shown in Figures 1 (c) and (d) (13,15).

During corrosion, the rate of the cathodic reactions, which remove the electrons generated by the anodic dissolution reactions, must be equal to the rate of the anodic reactions. The most common cathodic reactions are oxygen reduction according to the reaction

and hydrogen ion reduction according to the reaction

The adsorbed hydrogen created by this reaction can be removed from the surface of the corroding metal either by the formation of hydrogen gas according to the recombination reaction

by electrochemical desorption according to the reaction

or by being absorbed into the metal according to the reaction

At equilibrium, the fugacity of hydrogen gas, P_{H_2} , is related to the electrode potential by the Nernst

equation

$$E_{eq} = E^0 + \frac{RT}{\mathcal{F}} \ln \left\{ \frac{[H^+]}{P_{H_2}^{0.5}} \right\} \quad (3)$$

where E_{eq} is the equilibrium potential for the reaction, E^0 is the standard potential, R is the gas constant, $\mathcal{F}$ is Faraday's constant, T is the absolute temperature and brackets imply activities. Solving this for the equilibrium hydrogen fugacity, P_{H_2} , at 25°C yields

$$P_{H_2} = \exp \left[77.8(E^0 - E_{eq}) - 4.606 \text{pH} \right] \quad (4)$$

While hydrogen embrittlement experiments are not conducted under equilibrium conditions, it is common practice to consider P_{H_2} , obtained from the measured electrode potential and Equation (4), as an indication of the activity of the adsorbed hydrogen, which is the driving force for hydrogen absorption and diffusion into the metal. It should be kept in mind that, under non-equilibrium conditions, the hydrogen activity calculated from Equation (4) may differ greatly from its actual value because of local changes in pH and irreversible losses. Nevertheless, and in spite of the fact that hydrogen discharge and adsorption on a number of metals can occur at potentials positive to the equilibrium potential for a hydrogen fugacity of one atmosphere (10^5 Pa), this value, the so-called "hydrogen evolution potential," remains a reasonable choice for the critical potential below which hydrogen absorption and diffusion into the metal can be expected.

In Figure 1 (b), the free corrosion potentials of nickel aluminide in the solutions used for the slow-strain-rate tensile tests are plotted against the pH of the solutions, together with the hydrogen evolution potential E_{eq} calculated from (3) for fugacities of 10^3 , 10^5 , and 10^7 Pa. By comparing Figure 1 (a) with Figure 1 (b), it can be seen that the ductility and the ultimate tensile strength as percent of the value observed in air is essentially unchanged in the neutral and alkaline solutions where the hydrogen fugacity is extremely low, but that the ductility, the ultimate tensile strength, and the fracture mode change significantly when the corrosion potential exceeds the hydrogen evolution potential (13).

While this is strong evidence that hydrogen embrittlement is the mechanism of the observed environmentally induced fracture, it should be kept in mind that dissolution is occurring during exposure to these acidic solutions (4,8,11) and other processes such as film growth or dealloying may also occur in these solutions. As a result, these possibilities must be eliminated before it can be unambiguously concluded that hydrogen embrittlement is the responsible mechanism. To achieve this objective, two different types of experiments were performed. First, slow-strain-rate tensile tests were conducted in sulfuric acid with the potential of the samples with respect to a reference electrode controlled with a potentiostat (13). Three potentials, besides the open-circuit, free-corrosion potential, were used for these experiments as shown in Figure 2 (a): (1) a potential below the free corrosion potential, which will reduce the rate of anodic processes and may increase the hydrogen fugacity, (2) an active potential, which is above the free corrosion potential and will reduce the hydrogen fugacity, but increase the rate of anodic dissolution, and (3) a potential which is above the free-corrosion potential and the active-to-passive transition so that the hydrogen fugacity will be essentially zero and the surface of nickel aluminide will be passivated. It should be noted that steady-state current densities may differ significantly from those observed on a potentiodynamic polarization curve and the current density at the passive potential, potential number (3), decreased to less than $10^{-1} \text{ A}\cdot\text{m}^{-2}$ within 10 minutes.

Figure 2 (b) shows the results of these experiments and, in this figure, it can be seen that polarization to the potential below the free-corrosion potential did not significantly alter the fracture behavior, but that polarization to more positive potentials, which reduces the hydrogen fugacity, increases the tensile strength. At the active potential, $-200 \text{ mV}_{\text{SCE}}$, the rate of dissolution is significantly increased but intergranular fracture was not observed, and the tensile strength ratio increased though it was not as great as that observed in air. Since the tensile strength calculation is based on the cross section of the sample measured before initiation of the experiment, it is not surprising that the calculated tensile strength is lowered by the anodic attack because this attack will reduce the cross section of the sample. As a result, the true tensile strength ratio for these samples was estimated by (1) measuring the cross section after completion of the test, (2) estimating the cross section from current density measurements and (3) estimating a "reference" or air value for the ratio by corroding a sample in the solution for the same time as the test takes and then testing this sample in air. The open circle in Figure 2 represents the value of these estimates and it can be seen that the tensile strength, while considerably greater than that observed at open circuit, was not as great as that observed in air. This difference may be due to an environmental effect, or it may be due to our inability to account for the influence of surface roughening as a result of corrosion on the tensile properties. For the samples tested at the passive potential, $500 \text{ mV}_{\text{SCE}}$, fracture did not occur until the ultimate tensile strength was reached. It should be noted that the experiments at the potentials anodic to the free-corrosion potential were extremely difficult, and sections of the sample not in contact with the bulk 0.5 M sulfuric acid solution had to be thoroughly protected to prevent intergranular fracture, especially in the grip section above the solution (13,15).

The second type of experiment used to evaluate hydrogen embrittlement as the mechanism of the observed environmentally induced fracture in the acidic solutions was pre-exposure embrittlement experiments. The purpose of these experiments was to determine if charging hydrogen into the sample by pre-exposure to sulfuric acid results in reducing the mechanical properties in a subsequent slow-strain-rate tensile test conducted in air before the absorbed hydrogen can diffuse out of the sample (14). Figure 3, shows that pre-corrosion in sulfuric acid for 10 hours reduced the strain-to-failure of cold worked nickel aluminide to 57 % of the value normally exhibited in air, but not as much as testing in sulfuric acid. Since the reduced ductility could be the result of surface damage during the pre-exposure as well as hydrogen embrittlement, a sample was given an identical pre-exposure to sulfuric acid, but was placed in a vacuum for over 100 hours prior to testing in air, and all of the ductility was restored in this sample (97%). Since hydrogen embrittlement is the only mechanism of environmentally induced fracture which is consistent with these observations, it was concluded that this is the mechanism of environmentally induced fracture in the acidic solutions (14).

It is unlikely that the failure of the pre-corrosion treatment to reduce the ductility as much as simultaneous corrosion and straining is an indication of any special interaction. For example, one could postulate that dislocation motion accelerates hydrogen transport or promotes supersaturation of the plastic zone with hydrogen. Also, one could postulate that anodic dissolution contributes to crack propagation in the solution. However, the rate of hydrogen diffusion in nickel aluminide is not very rapid. Measurements indicate that the diffusion coefficient is between 1×10^{-14} and $3 \times 10^{-14} \text{ m}^2 \cdot \text{s}^{-1}$ at room temperature (16). Based on this range for the diffusion coefficient, less than 25% of the hydrogen which can be absorbed by this material has been absorbed in the 10 hours of the pre-exposure, and the central region of the sample is essentially hydrogen free (16,17). For simultaneous straining and exposure, the hydrogen must penetrate only a very short distance along the grain boundary ahead of the growing crack, and this requires only a very short time as compared to charging the entire sample with hydrogen. Therefore, no special significance should be attached to the observation that simultaneous straining and charging results in a lower ductility than precharging with hydrogen (12).

Since in many applications a nickel aluminide component may be galvanically coupled by an

electronic conductor to a less noble metal which will supply electrons for reaction (2), experiments were conducted to evaluate the possibility that polarizing currents could cause hydrogen absorption and embrittlement in different environments (14). Accordingly, slow-strain-rate tensile tests were conducted in different pH solutions at potentiostatically controlled potentials. The passivating film on nickel aluminide will be composed of oxides or hydroxides of nickel, aluminum, or both, which are not stable in low pH solutions, but they are stable in neutral and alkaline pH solutions. As a result, these experiments are a test of the ability of the naturally formed films on nickel aluminide to prevent hydrogen absorption on polarization to potentials negative to the hydrogen evolution potential. In these experiments, the strain-to-failure ratio was reduced, and intergranular fracture was observed in both neutral and alkaline solutions when the potential was in the range where hydrogen evolution is predicted. That is, it appears that the naturally formed oxides do not block hydrogen entry under these conditions (14). This is in contrast to the conclusion reached by Kuruvilla and Stoloff (12) who concluded that oxide films were an effective barrier to hydrogen absorption based on experiments conducted under different conditions.

THEORETICAL BASIS FOR EXPERIMENTS

Examination of Equation (4) for the fugacity of hydrogen on the surface of an electrode indicates that there are two variables that influence the hydrogen fugacity: pH and potential. The objective of this study was to evaluate the possibility that, during exposure to neutral solutions, local changes in these two variables could cause hydrogen absorption and embrittlement.

Local Acidification

The metal ions generated by anodic processes will diffuse away from the electrode surface and, at the same time, they will undergo step-wise hydrolytic reactions of the form

where M^{+n} represents the metal ions and the end product may be ions in the solution or insoluble hydroxides or oxides. Assuming that the rates of these reactions are reasonably fast, then the local pH will be determined by the hydrolytic equilibria. Therefore, as shown by Equation (5), the local hydrogen ion concentration will depend on the local concentration of metal ions with the pH going down as the metal ion concentration increases. The local pH will thus depend on the rate of production of metal ions, that is, the local corrosion rate and the concentration gradients necessary for charge transport. If something prevents the mixing of the metal ions generated by corrosion with the bulk solution, then the pH of this occluded region will decrease. Since pH is one of the two variables that affect hydrogen fugacity, it is conceivable that hydrogen embrittlement may result from this local acidification.

Table I is a listing of some of the hydrolysis reactions that may occur between aluminum or nickel and water. In this table, the equilibrium pH for ionic concentrations of unity, pH^0 , is given for different reactions and it can be seen that the hydrolysis reaction between water and the aluminum ion can decrease the pH to values close to those where intergranular fracture was observed in Figure 1. As a result, it was decided that slow-strain-rate tensile tests would be conducted in solutions of different concentrations of aluminum chloride in order to obtain a reasonable estimate of the critical pH as a function of aluminum ion concentration.

Film Rupture and Repassivation

When the passive film which protects the surface of a metal from attack is ruptured by strain, bare metal will be exposed to the solution as shown in Figure 4. By examining this figure, it can

be seen that when film rupture occurs, three phases come into contact: (1) the metal, (2) the passive film, and (3) water. The chemical reaction that occurs where the bare metal is exposed to the solution may be written as

and Equation (5) represents the reaction that is occurring at the solution to oxide or hydroxide interface. At the point where the three phases come into contact, the system will attempt to reach equilibrium for the reactions shown in Equations (5) and (6) simultaneously, which is equivalent to equilibrium for the reaction

This system will attempt to reach the equilibrium potential for this reaction which is given by the relationship

$$E_{eq} = E^0 + \left(\frac{2.303RT}{xn\mathcal{F}} \right) \log [M_xO_y(OH)_z \cdot wH_2O^{+nx-(2y+z)}] - \left[\frac{2.303(2y + z)RT}{xn\mathcal{F}} \right] pH \quad (8)$$

Table II gives the equilibrium potentials for the reactions represented by Equations (7) and (8) for nickel and aluminum species. By examining this table, it can be seen that the minimum potential predicted for nickel dissolution or repassivation does not correspond to significantly large hydrogen fugacities. On the other hand, the potentials predicted for aluminum dissolution or repassivation correspond to extremely large hydrogen fugacities. Therefore, if aluminum contributes significantly in shaping the transient of the electrode potential that accompanies film rupture and repassivation on nickel aluminide in neutral solutions, hydrogen absorption might occur where bare metal is exposed and, if the loading and environmental conditions are such that film rupture occurs repeatedly at the same spot, then hydrogen embrittlement may result. Therefore, experiments were designed to test the hypothesis that during the transient the potential would fall below the hydrogen evolution potential. These experiments consisted of artificially generating bare metal surface by scratching with a sapphire scribe and then recording the potential transient so produced.

EXPERIMENTAL

Samples of a ductile nickel aluminide alloy, IC-50, were obtained from Oak Ridge National Laboratory. The composition of this alloy is: 77.0 at. % Ni, 22.2 at. % Al, 0.42 at. % Hf, 0.11 at. % Fe, and 0.087 at. % B. The samples were annealed at 1100°C for 1 hr in a quartz tube which was evacuated, backfilled with Ar, and sealed.

The slow-strain-rate tests were conducted at two concentrations of $AlCl_3$ 0.17 M and 1.7 M, having a pH of 2.7 and 1.4, respectively. The test specimens were ≈ 0.75 mm thick with a gage length of 25.4 mm at a constant crosshead speed of $2.54 \times 10^{-8} \text{ m} \cdot \text{s}^{-1}$. The samples were coated with a lacquer outside of the gage section and the grips of the load frame were isolated from the solution. The fracture surfaces were examined in a scanning electron microscope (SEM).

For the second type of experiments, an apparatus as schematically shown in Figure 5 was used. A more detailed description of the apparatus and of the experimental methods can be found

in another publication (18). Samples of nickel, aluminum, and nickel aluminide were mounted in epoxy, polished, and then coated with lacquer in preparation for scratching. The scribe scratched through this lacquer coating and deep into the sample during the scratch process. Electrical contact was made to the sample with a wire, which was attached to the back of the sample and isolated from the solution. Three different solutions were used for these experiments: 0.5 M NaCl (pH≈6.3), 0.5 M Na₂SO₄ (pH≈6.5), and 0.5 M NiCl₂ (pH≈4.5). The first two were used to represent typical neutral solutions with and without halide ions, and the third solution was used to determine if conditions that might exist within an occluded region such as a crack tip might influence the transients.

RESULTS

Figure 6 shows the strain-to-failure and ultimate tensile strength ratio as a function of pH for the AlCl₃ experiments with the data for the same alloy from the earlier experiments. From this figure, it can be seen that the ductility of nickel aluminide was not significantly reduced for a AlCl₃ concentration of 0.17 M (pH=2.7), but that the strain-to-failure ratio was reduced in the 1.7 M (pH=1.4) solution. Figure 7 shows the fractographic features observed in these two solutions and it can be seen that in the 0.17 M solution the fracture was essentially 100 % transgranular while mixed intergranular and transgranular fracture was observed in the 1.7 M solution.

The repassivation transients recorded in the three solutions are shown in Figures 8, 9 and 10. The curves for nickel and nickel aluminide are very similar, and lie above the hydrogen evolution potential, especially in 0.5 M Na₂SO₄. Those recorded for aluminum had a more pronounced minimum, and moreover, lie well below the hydrogen evolution potential. Table III gives the average minimum in potential for each material in each of the solutions.

DISCUSSION

The results of the slow-strain-rate tensile tests in the AlCl₃ solutions indicate that the critical pH for hydrogen absorption in this solution is about 2, and relatively high concentrations of aluminum ions are required to generate this pH by hydrolysis. This concentration would not be expected during exposure to bulk solutions, but it might be reached during wet/dry cycling. However, nickel species will be present on the surface of nickel aluminide and reactions with these species may limit the pH shift during drying. The possibility of hydrogen embrittlement under these conditions should be evaluated by conducting alternate immersion tests on precracked samples of nickel aluminide. Also, it should be noted that the environment used for these tests was open to the air, and dissolved oxygen was present in the solutions. Removal of this oxygen will result in lowering the corrosion potential and, since electrode potential plays a role in hydrogen absorption, this could influence the value of the threshold pH for hydrogen absorption and embrittlement. The magnitude of this influence will be determined, in part, by the magnitude of the contribution that aluminum dissolution makes to the corrosion potential and, if the corrosion potential is relatively uninfluenced by aluminum, then the nickel reactions given in Table II and the transport conditions will determine the minimum corrosion potential and the maximum threshold pH.

The results of the scratch repassivation experiments indicate that the oxidation of aluminum during repassivation of nickel aluminide does not contribute significantly to shaping the potential transients, so that hydrogen embrittlement of nickel aluminide in neutral solutions should not be expected in spite of the presence of an element that is electronegative to hydrogen. If it is assumed that the reduction reaction occurs at the same rates at the same potentials on the surface of nickel and nickel aluminide (O₂ reduction is probably transport limited), since the minimum potentials

observed for transients on nickel aluminide were not significantly different from that observed for pure nickel, it must be concluded that the rate of oxidation of bare nickel aluminide is similar to that of bare nickel and significantly different from that of bare aluminum. This implies that the rate of oxidation on bare nickel aluminide is determined by the nickel removal rate. Since the aluminum atoms in nickel aluminide have only nickel atoms for nearest neighbors, dissolution of an aluminum atom exposes only nickel atoms to the solution and these nickel atoms must be removed by either dissolution, surface diffusion, or bulk diffusion before the underlying aluminum atoms can be exposed to the solution and oxidized. Since bulk diffusion, and to a lesser extent surface diffusion, are relatively slow compared to the rate of dissolution during these transients, the rate of aluminum oxidation is limited by the rate of nickel dissolution.

It should be pointed out that these observations may be limited to the alloy and the environments studied. For example, the alloy studied contained only 22 at. % aluminum. This aluminum content may prevent aluminum segregation to the grain boundaries. Also, alloying elements could promote aluminum segregation to the grain boundaries or the nucleation of aluminum rich phases. Any of these could result in a rate of aluminum oxidation that produces negative charge faster than the reduction reactions can remove it at potentials above the hydrogen evolution potential. Also, changes in the environment may have similar results. For example, these experiments were performed in solutions which were open to the air, and dissolved oxygen in these solutions will participate in the reductions reactions. If this oxygen is removed, the extent to which the minimum potential would be reduced is unclear. However, if the rate of aluminum oxidation is limited by nickel removal, as these results indicate, then the minimum potential should be limited to the nickel equilibrium potential which, for neutral solutions as shown in Table II, is above the hydrogen evolution potential. As with any material, testing of the specific alloy and heat treatment in the environment of the planned application should precede the placement of these alloys in service.

CONCLUSIONS

Experiments were designed to evaluate the possibility that nickel aluminide would experience environmentally induced fracture by hydrogen embrittlement in neutral solutions due to local acidification in an occluded region or as a result of hydrogen absorption during the potential transient that follows film rupture. slow-strain-rate experiments were conducted in aluminum chloride solutions of pH 1.4 and 2.7, and the ductility was reduced and intergranular fracture was observed in the lower pH solution only. Since based on hydrolytic equilibria this pH corresponds to relatively large concentrations of the metal ions, it is concluded that environmentally induced fracture by this mechanism is not to be expected in neutral solutions under conditions of restricted transport. As discussed above, this conclusion is restricted to conditions of exposure to bulk solutions and not alternate immersion. During the scratch repassivation experiments, it was found that the potential transient that follows film rupture is not significantly different from that observed on pure nickel and the minimum potentials did not correspond to significant hydrogen fugacities. As a result, it is concluded that hydrogen absorption will not occur in neutral solutions as a result of rupture of the passive film, and applications where cyclic loading and repeated rupture of surface films is to be expected should not result in embrittlement.

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Table I

Selected Hydrolysis Reactions and the Equilibrium pH
for Nickel and Aluminum Ions at 25°C.

Equilibrium pH: $pH_{eq} = pH^0 - A \cdot \log[M^{+n}] + B \cdot \log[M_xO_y(OH)_z \cdot wH_2O^{+nx-(2y+z)}]$

Reactant : Product	w	x	y	z	pH ⁰ ‡	A	B	REF
Ni ⁺² : Ni(OH) ⁺¹	0	1	0	1	6.22	0.50	1.00	(19)
Ni ⁺² : Ni(OH) ₂	0	1	0	2	6.36	0.50	0.50*	(19)
Ni ⁺² : NiO	0	1	1	0	9.66	0.50	0.50*	(19)
Al ⁺³ : AlO ₂ ⁻¹	0	1	2	0	5.62	0.25	0.25	(19)
Al ⁺³ : Al(OH) ⁺²	0	1	0	1	4.91	1.00	1.00	(19)
Al ⁺³ : Al(OH) ₄ ⁻¹	0	1	0	4	5.62	0.25	0.25	(19)
Al ⁺³ : Al ₂ O ₃ (corundum)	0	2	3	0	2.89	0.33	0.17*	(19)
Al ⁺³ : Al ₂ O ₃ ·H ₂ O (boehmite)	1	2	3	0	2.53	0.33	0.17*	(19)
Al ⁺³ : Al ₂ O ₃ ·H ₂ O (diaspore)	1	2	3	0	2.24	0.33	0.17*	(19)
Al ⁺³ : Al ₂ O ₃ ·3H ₂ O (gibbsite)	3	2	3	0	2.41	0.33	0.17*	(20)
Al ⁺³ : Al(OH) ₃ (amorphous)	0	1	0	3	3.22	0.33	0.33*	(20)

‡ pH⁰ is the equilibrium pH for reactants and products at unit activity.

* Note that the activity of a pure solid phase is unity and this term will drop out of the equation.

Table II

Equilibrium Potentials for Selected Dissolution and Repassivation
Reactions for Nickel and Aluminum at 25°C.

General Reaction: $xM + (w + y + z)H_2O \rightarrow M_xO_y(OH)_z \cdot wH_2O^{+nx-(2y+z)} + (2y + z)H^+ + (nx)e^-$

Equilibrium Potential: $E_{eq} = E^0 + C \cdot \log[M_xO_y(OH)_z \cdot wH_2O^{+nx-(2y+z)}] - D \cdot pH$

Reactant : Product	w	x	y	z	n	E^0	C	D	$E_{eq}(pH=7)$	REF
Ni : Ni ⁺²	0	1	0	0	2	-0.236	0.030	0.000	-0.236‡	(19)
Ni : Ni(OH) ₂	0	1	0	2	2	0.140	0.030*	0.059	-0.274	(19)
Ni : NiO	0	1	1	0	2	0.132	0.030*	0.059	-0.282	(19)
Al : Al ⁺³	0	1	2	0	3	-1.676	0.020	0.000	-1.676‡	(19)
Al : Al ₂ O ₃ (corundum)	0	2	3	0	3	-1.504	0.010*	0.059	-1.919	(19)
Al : Al ₂ O ₃ ·H ₂ O (boehmite)	1	2	3	0	3	-1.526	0.010*	0.059	-1.940	(19)
Al : Al ₂ O ₃ ·H ₂ O (diaspore)	1	2	3	0	3	-1.543	0.010*	0.059	-1.957	(19)
Al : Al ₂ O ₃ ·3H ₂ O (gibbsite)	3	2	3	0	3	-1.533	0.010*	0.059	-1.947	(19)
Al : Al(OH) ₃ (amorphous)	0	1	0	3	3	-1.473	0.020*	0.059	-1.887	(20)

* Note that the activity of a pure solid phase is unity and this term will drop out of the equation.

‡ This assumes a concentration of 1 M for the ionic species.

Table III

Average Minimum Potentials Measured During Scratch Repassivation Transients
Against a Saturated Calomel Electrode for Pure Nickel, Pure Aluminum and Nickel
Aluminide (IC-50) in Sodium Sulfate, Sodium Chloride and Nickel Chloride.

SOLUTION	Pure Ni	Pure Al	Ni ₃ Al	E(H ⁺ /H ₂ =1 atm) [‡]
0.5 M Na ₂ SO ₄	-0.450	-1.518	-0.391	-0.626
0.5 M NaCl	-0.561	-1.568	-0.493	-0.614
0.5 M NiCl ₂	-0.588*	-1.296*	-0.430*	-0.537

* Average of two measurements. All others are the average of three measurements.

‡ The potential for an equilibrium hydrogen fugacity of 1 atmosphere as calculated for the measured pH of the solution.

Figure 1 - Results of slow-strain-rate tensile tests in solutions of varying pH on two different Ni_3Al alloys: (a) strain-to-failure or ultimate tensile strength as a percentage of the value observed in air, (b) measured free-corrosion potentials in the same solutions with the equilibrium potentials for a hydrogen fugacity of 10^3 , 10^5 and 10^7 shown, (c) fractograph of a sample tested in 0.5 M Na_2SO_4 , and (d) a fractograph of a sample tested in 0.5 M H_2SO_4 .

Figure 2 - Potentiodynamic polarization curve for a nickel aluminide alloy (IC-50) in 0.5 M H_2SO_4 showing the four potentials at which slow-strain-rate tensile tests were conducted (a) and the ultimate tensile strength ratio observed for the tests at the different potentials (b).

Figure 3 - Diagram of the stress-strain curves obtained for slow-strain-rate testing of a cold-worked nickel aluminide alloy (IC-50): (a) tested in air, (b) tested in 0.5 M H_2SO_4 , (c) tested in air after precharging at the open-circuit, free-corrosion potential in 0.5 M H_2SO_4 for 10 hours, and (d) tested in air after precharging at the open circuit free-corrosion potential in 0.5 M H_2SO_4 for 10 hours followed by outgassing in a vacuum at ambient temperature for over 100 hours.

Figure 4 - Diagram of the phases exposed to each other immediately following film rupture at a crack tip.

Figure 5 - Diagram of the apparatus used to generate bare surface for the measurement of the potential transient that accompanies repassivation.

Figure 6 - Results of the slow-strain-rate tensile tests in the AlCl_3 solutions plotted against pH with the results of the earlier experiments on the same material.

Figure 7 - Scanning electron fractographs of the fracture surfaces observed in the two different AlCl_3 solutions: 0.17 M AlCl_3 (a) and 1.7 M AlCl_3 (b).

Figure 8 - Scratch repassivation transients observed for nickel, aluminum, and nickel aluminide (IC-50) in 0.5 M Na₂SO₄.

Figure 9 - Scratch repassivation transients observed for nickel, aluminum, and nickel aluminide (IC-50) in 0.5 M NaCl.

Figure 10 - Scratch repassivation transients observed for nickel, aluminum, and nickel aluminide (IC-50) in 0.5 M NiCl_2 .

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