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EVALUATION OF THE ELECTROCHEMICAL BEHAVIOR OF DUCTILE NICKEL ALUMINIDE AND NICKEL IN A pH 7.9 SOLUTION

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Abstract

The electrochemical behavior of ductile nickel aluminide has been examined in neutral solutions. Features observed in a certain potential range were characterized, and the potentiodynamic sweep parameters affecting them identified. Nickel aluminide behaves essentially as pure nickel, however small differences were observed.

Introduction

Ductile nickel aluminide, Ni_3Al , microalloyed with 200 ppm boron, is a high strength ductile alloy and, therefore, a promising material, for structural applications. Nickel aluminide was developed originally for high temperature applications because of its high yield strength which increases with temperatures up to 1000°C and its good oxidation resistance. Because of many low temperature properties such as excellent ductility (up to 50 %), low density, excellent wear resistance, corrosion resistance and high strength compared to other nickel alloys and stainless steels, nickel aluminide and nickel aluminide alloys are being considered for many low temperature applications such as forging dies, gas & steam turbines, dental drills, pump impellers and aerospace engines. In order to further evaluate this material for new applications, an investigation of the corrosion behavior of a ductile Ni_3Al alloy was undertaken.

To help understand the corrosion behavior of the intermetallic compound, a comparison should be made with the thermodynamic properties of pure nickel and

aluminum. Figure 1 shows the potential-pH diagrams (Pourbaix) of Ni and Al. Figure 2 shows the phase diagram of these two metals.

Earlier work on Ni_3Al had shown that the electrochemical behavior of Ni_3Al is similar to that of Ni (3,4,8). However, in neutral solutions, some differences had been observed in the shape of the potentiodynamic scans. Such differences, which could not be easily reproduced, were related to the following features:

- 1) When scanning cathodic from a positive potential in the passive range (approximately a few hundreds of mV positive with respect to SCE), a cathodic peak appeared at potentials about -900 mV/SCE. This feature will henceforth be called the "cathodic peak".
- 2) On the return scan, from -1 V/SCE (where H_2 evolution is taking place) a cathodic current, whose magnitude is weakly dependent on potential, is observed in the range between -800 and -500 mV/SCE. This feature will henceforth be called the "cathodic current".
- 3) Continuing on the anodic scan, a positive peak appeared, centered around -300 mV/SCE. This feature will henceforth be called the "anodic peak". Fig. 3 shows these features and their names.

As to the cause of these features, it was reasonable to assume that the anodic and cathodic peaks indicate the formation of a surface product and its reduction. To further examine which compounds could be involved, the equilibrium potentials of the reactions of formation of various nickel oxides and hydroxides were calculated from thermodynamic data of pure nickel as well as ordered and disordered Ni_3Al at the pH of interest ($\text{pH} = 7.9$). The results are shown in table 1. The difference in potentials

between Ni and Ni₃Al is ca. 100 mV, the value for pure Ni generally lower than that for Ni₃Al. Figure 4 shows a graph overlaying Ni and Ni₃Al in the potential area from -200 mV to -1000 mV, which covers the potential range of the reactions calculated above. Comparison between the calculated values and the position of the peaks leads one to believe that the only reasonable possibilities are the formation of NiO or Ni(OH)₂. However, a choice between them is probably impossible to make on the basis of their equilibrium potentials.

The cathodic current observed in the range -800/-500 mV was thought to be due to oxygen reduction, since it appeared to be diffusion-limited at a value about -250 $\mu\text{A}/\text{cm}^2$, agreeable with the O₂ concentration in air-saturated solutions and the stirring applied.

It was therefore thought interesting to focus the research on these features, trying to identify the conditions affecting them in order to understand their origin, and at the same time to ascertain if there were differences in behavior between Ni and Ni₃Al. As a consequence, most experiments were restricted to these two materials, except for open circuit potential measurements, which were carried out also on aluminum.

Experimental

The ductile nickel aluminide samples for the experiments were received from the Oak Ridge National Laboratory. The alloy, IC-50, contained 77.0 at. % Ni, 22.2 % at. Al, 0.42 at. % Hf, 0.11 at. % Fe and 0.087 at. % B. The pure nickel and aluminum samples were purchased from Johnson Matthey, the Ni has a purity of 99.998 % and the Al of 99.9995 %. The nickel and nickel aluminide samples were cleaned, placed in a quartz tube which was evacuated, back filled with argon and then sealed before annealing at 1100°C for 1 hr. The aluminum samples were used as received.

Electrodes were made by mounting samples in epoxy resin, cleaned in ethanol and doubly distilled water immediately before use. For all potentiodynamic scans,

surfaces were polished down to 0.02 μm with SiO_2 powder. In the open circuit potential measurements, for the purpose of studying the effect of surface finish, a polish to 14 μm was also employed. The results are summarized in table 2. All experiments were conducted with a buffer ($\text{pH} = 7.9$) made of 50 % saturated sodium borate ($\text{Na}_2\text{B}_4\text{O}_7$) and 50 % saturated boric acid (H_3BO_3), and prepared with doubly distilled water. In most experiments the solution was exposed to laboratory air, but in some cases the solution was deaerated. To do this the cell was purged with nitrogen for approximately 20 minutes before the experiment, at a flow rate of 10 - 20 cm^3/min , in order to eliminate all the oxygen. Also during the experiment the nitrogen was kept running through the electrochemical cell. All voltage measurements were conducted with respect to the saturated calomel reference electrode (SCE).

Electrochemical measurements were conducted with standard laboratory instruments controlled by computers, driven by in-house developed software. Since a fast sweep rate is known to enhance the amplitude of the current transients, the sweep rate was chosen to be 100 mV/s in most experiments.

During the transfer of data to the computer after each potentiodynamic scan, there was a period of approximately 1 minute during which the electrode potential was not controlled. To avoid this, a new program was developed, which saved the data automatically after each scan, while holding the potential constant for about 1 second, and then continuing with the next scan, until the desired number of scans was completed.

The free corrosion potentials of Ni, Al and Ni_3Al were determined by measuring the potential every 5 seconds, while letting the experiment run overnight to be sure that the potential did not change more than 2-3 mV over a long period of time.

To facilitate the visual examination of the electrode surfaces after the experiments, some samples, instead of being encased in epoxy, were mounted in a shrinkable teflon tube, to be able to transfer them in the scanning electron microscope

(SEM) without delay.

Results and Discussion

Open circuit potentials

The results of the free corrosion potential measurements, shown in table 1, indicate that the value for Ni_3Al is not significantly different from that of pure Ni, considering the scatter of the data, confirming previous results (3,4,8). This shows that Ni surface atoms dominate the free corrosion behavior of the alloy. Highly polished surfaces gave more positive corrosion potentials for Ni and Ni_3Al , but not for Al. The scatter of the values is such, however, that it is uncertain whether surface finish has any effect.

Potentiodynamic scans

A typical example of the reproducibility problems in the scans is illustrated in figures 5a and b, for Ni and Ni_3Al respectively. The three features previously described appeared between -1000 mV and -200 mV, as shown in figure 5a, but only on a sample, which was polished immediately before the experiment. These characteristics disappeared when running the experiment again, without moving the sample from the cell or changing the experimental parameters, as shown in figure 5b. In general the features were less evident on Ni_3Al than on pure Ni, suggesting that the surface behavior is changed slightly because of the aluminum in the alloy. An overlaid graph is shown in figure 4 to illustrate this small difference.

The disappearance of the anodic and cathodic peaks was thought to be caused by the formation of a stable passive film at higher potentials, which prevented any further surface reactions. It was, therefore, interesting to see if the formation of this stable layer was related to the value of the positive vertex of the scan, that is, if there was an upper potential limit, below which it was possible to reproduce the peaks in consecutive scans. To evaluate this limit the sample was used in two succeeding experiments with exactly the same parameters. First when the sample was polished

immediately before the experiment and then in a second experiment without removing the sample from the solution, while waiting for approximately 15 minutes at the open circuit potential. With each new sample the upper vertex was 50 mV higher, beginning at approximately +200 mV and continuing until there were no signs of any features the second time the experiment was run.

On Ni the cathodic peak flattened out when the upper vertex was 300 mV and disappeared completely at 400 mV. It was also found that the maximum negative current density at the lower vertex is affected by the value of the upper vertex: if the vertex is greater than 400 mV, the drop in current is approximately 3 mA/cm² from the first scan to the second, whereas, with an upper vertex lower than 400 mV, it did not drop more than 1 mA/cm². When the vertex was 600 mV the cathodic current decreased and at 700 mV it disappeared altogether. At 850 mV none of the peaks reappeared in the second scan.

On Ni₃Al the various features started to flatten out when the upper vertex was 250 mV, and at 300 mV the cathodic current disappeared. The maximum current density became larger in the second scan until the upper vertex reached 400 mV, after which it became smaller. The limit, at which all the features disappeared in the second scan, was found to be 550 mV.

To test for an effect of the lower vertex, the same kind of 2 succeeding scans as above were run, but instead the lower vertex was shortened of 50 mV, beginning at -1000 mV, with each new sample. This did not have any effect on the peaks, which confirmed that the features were eliminated because of a high anodic polarization.

Another point of interest was to evaluate whether the shape of the curves changes with the number of potentiodynamic scans. To do this, the same sample was used in ten succeeding scans from -1000 mV to +200 mV, without changing the solution or the experimental parameters between each scan. In the first set of experiments the old program was used and, therefore, there was a break of ca. 1

minute between each scan. On Ni₃Al the cathodic current became smaller with the number of scans until it disappeared, while the cathodic peak, which had not shown earlier, appeared after four scans and then kept increasing. On Ni the features did not show any changes with time. In the second set of experiments, the new computer program was used, thus eliminating the open circuit wait between scans. Ni₃Al behaved exactly as in the first series of experiments, whereas on Ni the cathodic current got smaller with time and the cathodic peak moved gradually from being at a current density level of -1 mA/cm² to -0.5 mA/cm². It was noticed that the current density at the lower vertex had a tendency to get larger with each scan on Ni, whereas on Ni₃Al it would get larger in the first five or six scans and then get smaller. This happened in both sets of experiments.

Confirmation that the cathodic current observed in the range -800/-500 mV was due to oxygen reduction was obtained by running ten potentiodynamic scans while purging the cell with nitrogen. In these conditions, on both Ni₃Al and Ni, the cathodic current did not occur at all. Also, a steady state was reached faster than in the other experiments. Some of the other features were affected by the deaeration: for instance, on Ni, the cathodic peak did not appear until the third scan, whereas in the aerated solution it appeared immediately.

Figure 6 shows the maximum current density level of the three features and the maximum current density at the lower vertex plotted against the number of scans. Both Ni and Ni₃Al are represented in aerated and deaerated solutions, in order to see if there are any patterns in the variation of the features. This did not seem to be the case. When comparing the graphs for the two different solutions it is obvious that the cathodic current disappears totally in the deaerated solution as the current is positive in all the scans. This furthermore confirms that the cathodic current represents oxygen reduction.

To evaluate whether the anodic and cathodic peaks are related, two succeeding potentiodynamic scans, from -1000 mV to -400 mV, were conducted with

the same sample, under the same conditions, thus stopping the anodic polarization just before the anodic peak. The cathodic peak continued to appear, also the second time the experiment was run. This could be interpreted as the reduction of an oxide film formed in air before the scan, however, more experiments should be performed before drawing the final conclusion.

In order to determine if there are any visual changes on the surface of the samples after running a number of experiments, SEM pictures were taken before and after a series of ten scans. In these experiments the samples were mounted in a shrinkable teflon tube. The pictures did not show any significant changes of the sample surface. Although the different mounting procedure should not have any influence on the results, Ni behaved slightly differently, compared with measurements where the sample was mounted in epoxy resin. The cathodic current disappears after a few scans, whereas it did not disappear when using the other mounting. Also, the cathodic peak does not occur at the beginning, as on epoxy mounted samples, but only after a few scans, at a current density level of -0.5 mA/cm^2 instead of -1 mA/cm^2 .

Conclusions

The open circuit measurements showed, as expected (3,4,8), that Ni_3Al behaves essentially as Ni, when compared to Ni and Al. The fact that the features, first observed in earlier work (3), were reproducible and occurred on both Ni and Ni_3Al further confirmed the electrochemical similarities between Ni and Ni_3Al . When looking at the thermodynamic data in table 1, the anodic and cathodic peaks should appear at ca -600 mV . However, the anodic peak appeared 300 mV higher and the cathodic peak 300 mV lower than -600 mV , which indicates that the reactions of the peaks are irreversible. Since the position of the peaks is essentially the same on Ni and Ni_3Al , it appears as though Al is not involved in the surface reactions on Ni_3Al . It was found that the features disappeared because of a high anodic polarization, maybe forming a very stable passive layer that can not easily be reduced. Also the cathodic current was found to disappear when the O_2 in the cell was eliminated, and it was, therefore,

confirmed that it was due to oxygen reduction. Even though the two materials behave essentially the same way there are small differences in the passivity behavior, for example, the difference in how high an anodic polarization is required before the features disappear. These differences are believed to be due to differences in the passive layer forming on Ni and Ni₃Al. To further investigate these small differences surface chemistry on Ni and Ni₃Al is required.

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References

- 1) R. A. Buchanan and J. G. Kim, " Aqueous Corrosion Characteristics of Nickel Aluminides " University of Tennessee, (1988).
- 2) M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, National Association of Corrosion Engineers, Houston, TX, (1974).
- 3) P. V. Madsen, U. Bertocci, R. E. Ricker and J. L. Fink, " Corrosion Behavior of Ni₃Al Alloy ". National Institute of Standards and Technology (1989).
- 4) R. E. Ricker, U. Bertocci, J. L. Fink and M. R. Stoudt, " Evaluation of the Environmental Induced Fracture Resistance of Ductile Nickel Aluminide ". Environmental Effects in Advanced Materials, edited by R. H. Jones and R. E. Ricker, TMS, Warrendale, PA (1991).
- 5) R. E. Ricker, M. R. Stoudt and J. L. Fink, " Hydrogen Embrittlement of Ductile Nickel Aluminide During Corrosion in Aqueous Solutions ". Hydrogen Effects on Material Behavior, edited by N. R. Moody and A. W. Thompson, TMS, Warrendale, PA, (1990), 499-506.
- 6) Oak Ridge National Laboratory, " Nickel aluminides ".

- 7) U. Bertocci, J. L. Fink, D. E. Hall, P. V. Madsen and R. E. Ricker, " Passivity and Passivity Breakdown in Nickel Aluminide ". Corrosion science, 31, (1990), 471-478.
- 8) R. E. Ricker, D. E. Hall and J. M. Fink, " The Effect of Aqueous Environments on the Fracture Behavior of Ductile Nickel Aluminide ". Scripta Metallurgica et Materialia, 24, (1990), 291-296.
- 9) D. D. Wagman et al., " The NBS Tables of Chemical Thermodynamic Properties " J. of Phy. and Chem. Ref. Data, 11, suppl. 2, (1982).

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