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Anodic Polarization Behavior of Fe-Ni Alloys Fabricated by Ion Implantation

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ABSTRACT

Surface alloys have been fabricated by implantation of 25 keV nickel ions into polycrystalline iron to doses ranging from 8.5×10^{15} to 3.4×10^{16} ions/cm². Their aqueous corrosion characteristics have been studied under conditions of anodic polarization at 30°C in a helium-deaerated sodium borate buffered boric acid solution (pH 8.5) containing 2400 ppm chloride ion. The pitting- and general-corrosion characteristics are comparable to nominally equivalent bulk commercial alloys and are superior to those of pure iron. A high strength maraging steel is shown to exhibit an increase in pitting-corrosion resistance due to the implantation of chromium ions.

Ensuring an adequate supply of critical materials such as nickel to meet national economic and strategic needs is a goal of the Bureau of Mines metallurgy research program. Ion implantation offers the potential of extending the usefulness of our supply of critical materials without sacrificing chemical or physical properties.

A group of iron-nickel alloys has been fabricated by the implantation of low energy metallic ions into the surface regions of polycrystalline iron. These alloys have been designated as surface (s) alloys (1) since the alloyed region extends only to a depth of 200Å below the iron surface. A potentiodynamic study of the characteristics of these alloys has been conducted in order to determine their characteristic critical current densities (i_c) and pitting potentials (E_p). These two parameters are an indication of the relative general- and pitting-corrosion resistances, respectively, and can be compared to equivalent parameters determined for commercial bulk alloys of known corrosion resistance. E_p is an operational parameter measured in an identical manner for all of the data reported here and is equivalent to the "critical breakdown potential" reported by other authors (2).

The surface alloys were prepared by implanting 25 keV nickel ions into 99.99% purity polycrystalline iron samples. The details of the technique have been extensively described elsewhere (3), and only a few brief remarks are made here. Prior to implantation, the iron surfaces were prepared using mechanical grinding, electropolishing, and high vacuum treatments that also have been described elsewhere (1, 4). The result of these surface preparations was a residual oxide coverage less than 10Å in thickness and a residual carbon surface impurity coverage of less than 1×10^{16} atoms/cm². The 25 keV nickel ions had a mean penetration depth of 38Å, and the final implant depth distribution was shown experimentally to be essentially Gaussian in character, with approximately 99% of the nickel located within the first 150Å (3). The surface alloy concentration has been defined, therefore, as the average concentration over this 150Å implant region. Implantation of nickel ions was used to fabricate surface alloys of 6 atom percent (a/o) (a dose of 8.50×10^{15} Ni⁺ ions/cm²), designated as Fe-6(s)Ni, and 25 a/o (a dose of 3.40×10^{16} Ni⁺ ions/cm²), designated as Fe-25(s)Ni. Tertiary surface alloys containing 15 a/o Ni (a dose of 2.05×10^{16} Ni⁺ ions/cm²) and 10 a/o Cr (a dose of 2.08×10^{16} Cr⁺ ions/cm²), designated as Fe-10(s)Cr-15(s)Ni, also were

fabricated and studied. A commercial maraging steel, Vascomax 250 (V-250), was implanted with 25 keV chromium ions to a total dose of 2.08×10^{16} Cr⁺ ions/cm². This resulted in an average concentration of 10 a/o chromium over the first 200Å.

The potentiodynamic polarization studies of both the surface and the bulk alloys were conducted in a high purity boric acid solution buffered to pH 8.5 with the addition of sodium tetraborate decahydrate and containing 2400 ppm Cl⁻ (as NaCl). The solutions were deaerated with helium, and the area in front of the electrode was rapidly stirred with the same gas to minimize the effects of diffusion on the polarization results. The polarization tests were conducted in standard 1-liter glass polarization cells that were cleaned with boiling HNO₃. The planar electrodes (test alloys) were mounted in an O-ring sealed Lexan electrode holder. The tests were conducted at 30°C with a polarization scan rate of 10 mV/min. The initial applied potential was -100 mV with respect to E_R , where E_R was the rest potential recorded after the electrode had stabilized following a cathodic reduction process. The electrode potential was maintained using a Wenking 70TSI potentiostat and was scanned with a Wenking VSG72 scan generator.

Results

The surface alloys, bulk alloys, and metals reported here were studied under identical electrochemical con-

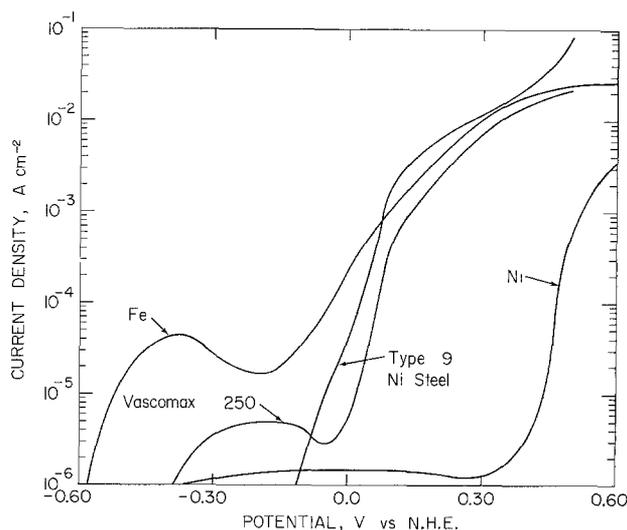


Fig. 1. Anodic polarization behavior (in a borate-buffered solution with 2400 ppm Cl⁻ addition) of polycrystalline iron and nickel and two commercial alloys.

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Key words: ion implantation, surface alloys, anodic polarization, pitting potential, Fe-Ni.

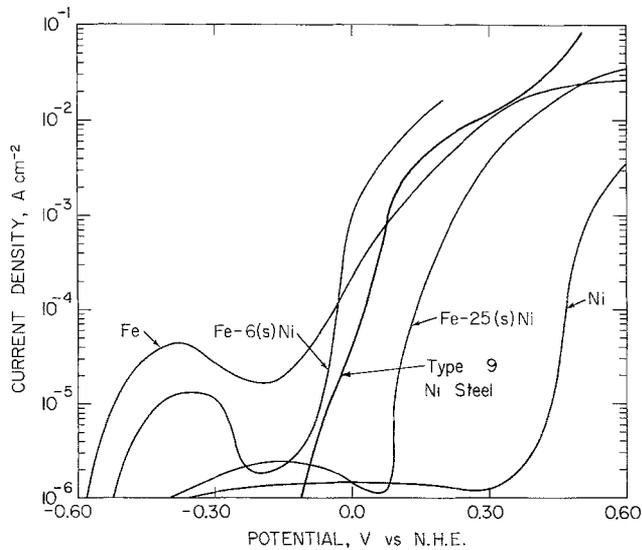


Fig. 2. Anodic polarization behavior (in a borate-buffered solution with 2400 ppm Cl^- addition) of the surface alloys Fe-6(s)Ni and Fe-25(s)Ni compared with that for polycrystalline iron and nickel and one commercial alloy.

ditions. Figure 1 shows the results obtained for polycrystalline iron (99.99%), nickel (99.5%), V-250 (18% Ni), and Type 9 nickel steel (9% Ni) under these specific conditions. Each curve in this figure and in subsequent figures represents the average of a minimum of four tests. Figure 2 shows the results obtained for the Fe-6(s)Ni and Fe-25(s)Ni alloys compared with those obtained for pure iron, nickel, and Type 9 nickel steel. The electrochemical behavior of iron in a borate-buffered solution of pH 8.5 without the presence of Cl^- indicates an i_c of $1-3 \times 10^{-5}$ A/cm² with a definite passivation region extending from -0.20 to $+1.10$ V vs. NHE (5, 6), the normal hydrogen reference electrode. The addition of 2400 ppm Cl^- reduces the length of the passive region, increases i_c to 4.5×10^{-5} A/cm², and shifts E_p to -0.14 V vs. NHE. E_p was determined graphically for each alloy by the intersection of tangents drawn from the passive region and the region of the current density vs. applied potential curve that exhibited the steepest slope. For those polarization curves that did not exhibit active dissolution regions, E_p was determined as the potential at which the current density was equal to 1×10^{-6} A/cm², generally the lowest measurable current density in these experiments. A comparison of the results obtained for iron with the results obtained for the Fe-Ni surface alloys shows three effects due to the surface alloying: (i) a substantial reduction in i_c ; (ii) a shift of the crossover potential, E_o , toward the noble direction; and (iii) a shift of E_p toward the noble direction. The values for these parameters obtained directly from the curves in Fig. 2 are summarized in Table I.

Figure 3 contains the results for the Fe-10(s)Cr-15(s)Ni alloy, 316 L stainless steel (18% Cr, 12% Ni), Inconel 625 (61% Ni, 21.5% Cr), and the iron and nickel data from Fig. 1. The electrochemical parameters of interest are summarized in Table II and again indicate that the resistance to pitting corrosion is enhanced by surface alloying. In Fig. 4 results are shown

Table I. Electrochemical parameters from Fig. 2 where $i_c \equiv$ critical current density, $E_o \equiv$ the crossover potential, and $E_p \equiv$ the pitting potential

Metal	i_c (A/cm ²)	E_o (V vs. NHE)	E_p (V vs. NHE)
Iron	4.5×10^{-5}	-0.58	-0.14
Fe-6(s)Ni	1.3×10^{-5}	-0.52	-0.12
Type 9 Ni steel	$<< 10^{-6}$	-0.12	-0.12
Fe-25(s)Ni	2.5×10^{-6}	-0.40	0.08
Nickel	1.5×10^{-6}	-0.36	0.41

Table II. Electrochemical parameters from Fig. 3

Metal	i_c (A/cm ²)	E_o (V vs. NHE)	E_p (V vs. NHE)
Fe-10(s)Cr-15(s)Ni	$<< 10^{-6}$	-0.09	-0.09
316 L SS	1.5×10^{-5}	-0.30	0.52
Inconel 625	1.1×10^{-5}	-0.20	0.59

Table III. Electrochemical parameters from Fig. 4

Metal	i_c (A/cm ²)	E_o (V vs. NHE)	E_p (V vs. NHE)
Iron	4.5×10^{-5}	-0.58	-0.14
Vascomax 250	5.0×10^{-6}	-0.39	0.01
Vascomax 250 + 10(s)Cr	2.0×10^{-6}	-0.13	0.05

for the electrochemical behavior of V-250 + 10(s)Cr, as compared with V-250 and pure iron. The relevant electrochemical parameters are summarized in Table III.

Discussion

The implantation of nickel ions into polycrystalline iron has been shown (Fig. 2) to produce results similar to those previously reported for Fe-Cr surface alloys (1). These results indicate a general trend, similar to those observed for Fe-Cr and Fe-Ni bulk alloys, for E_p to become more noble with increasing concentration of the alloying element. A similar type of behavior in bulk alloys has been interpreted by many in-

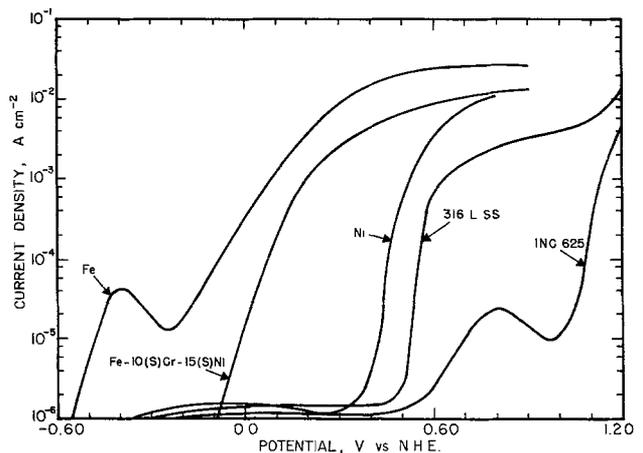


Fig. 3. Anodic polarization behavior (in a borate-buffered solution with 2400 ppm Cl^- addition) of a tertiary surface alloy, Fe-10(s)Cr-15(s)Ni, compared with that for polycrystalline iron and nickel and two commercial alloys.

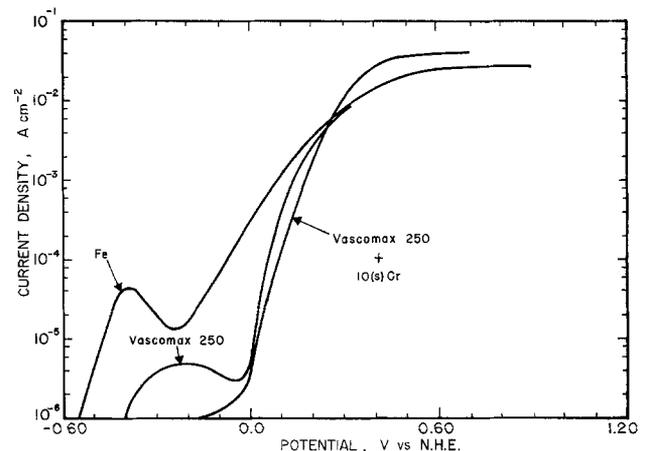


Fig. 4. Anodic polarization behavior (in a borate-buffered solution with 2400 ppm Cl^- addition) of a maraging steel, after implantation of 25 keV Cr^+ ions to an average concentration of 10 a/o.

investigators (2, 7, 8) to indicate an increase in the resistance of the alloy to pitting corrosion. Increasing the resistance to general corrosion by increasing either the nickel and/or the chromium concentration in bulk alloys is a well-known phenomenon. The electrochemical data reported here for the Fe-Ni surface alloys are interpreted as indicating that, since the active, passive, and transpassive regions for the surface alloys are similar to those for the equivalent bulk alloys, the over-all corrosion behavior could be expected to be the same. It has been reported previously (1) that the electrochemical results for an Fe-5% Cr bulk alloy were essentially identical to those for an Fe-6(s)Cr alloy up to a potential of +0.20V vs. NHE. At more anodic potentials, the implanted region was completely dissolved and the subsequent electrochemical behavior of the Fe-6(s)Cr alloy resembled that of pure iron. This was interpreted as indicating that as long as the alloyed surface region remains intact, the over-all corrosion resistance properties are the same. Similar conclusions are reached in this paper for the Fe-Ni surface alloys.

Table I shows that there is a decrease in i_c and an increase in E_p with increasing nickel implant concentration. The i_c approached a limiting value of 1.5×10^{-6} A/cm², the same value measured for pure nickel. The effect of the implanted nickel can be seen also as a shift of E_0 toward the same value as that for pure nickel. The decreasing i_c reflects the decreasing anodic dissolution; the increasingly more noble E_p reflects an increased resistance to pitting corrosion. The Fe-25(s)Ni alloy exhibits a more noble E_p than that measured for an Fe-19(s)Cr alloy (1) and has a pitting-corrosion resistance approximately equal to that of an Fe-12% Cr bulk alloy (1) (assuming that the surface alloyed region remains intact).

Two Fe-Ni commercial alloys, V-250 and Type 9 nickel steel, were tested. In addition to iron and nickel, the V-250 contains significant amounts of Co, Mo, Mn, and Ti. These additional alloying elements are probably detrimental to the over-all corrosion resistance since i_c for the V-250 was higher than that for the Fe-25(s)Ni alloy and the E_p was less noble than that for the surface alloy. The addition of the chromium, via implantation into the V-250, resulted in a decrease in i_c and a more noble value of E_p . The results for the V-250 + 10(s)Cr are interpreted as indicating a region of anodic dissolution, followed by pitting (indicated by the rapid rise in current density). The i_c was deter-

mined as the highest current density measured before the applied potential reached the value of E_p . A comparison of the results for the Fe-6(s)Ni alloy with those for the Type 9 nickel steel shows that the surface alloy exhibited a substantially higher i_c than the Type 9 nickel steel (which in fact exhibited no i_c at all). Also, the Type 9 nickel steel had an E_p slightly greater than that of the Fe-6(s)Ni alloy.

The commercial alloys, Inconel 625 and 316 L stainless steel (with an i_c of approximately 1.0×10^{-6} A/cm²), each exhibited a much more noble E_p than the Fe-10(s)Cr-15(s)Ni alloy. The results for this multiple implant are comparable to those for the Type 9 nickel steel and the Fe-19(s)Cr alloy (1).

The implantation of nickel and chromium ions into iron and steels has been shown to have the potential for fabricating alloys with good general- and pitting-corrosion characteristics. In addition, high strength steels such as V-250 can have their surfaces alloyed to increase resistance to corrosion while at the same time retaining their designed bulk strength characteristics.

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HPLC Analysis of the Stereoisomers Obtained by Electrohydrodimerization of *p*-Hydroxybenzaldehyde

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ABSTRACT

In contrast to previous reports, high pressure liquid chromatographic analysis (HPLC) of the 4,4'-dihydroxyhydrobenzoin formed by the electrohydrodimerization of *p*-hydroxybenzaldehyde showed that the ratio of *dl*- and *meso*-isomers did not vary significantly with various reduction mediums, the cathode material, or the concentration of aldehyde.

The electrochemical reduction of aldehydes and ketones in a divided cell leads to glycol/pinacol dimers

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Key words: electrohydrodimerization, *p*-hydroxybenzaldehyde, high pressure liquid chromatography, *dl*/*meso* ratio, glycol formation.

in good yield under a variety of conditions (1, 2). Aldehydes and nonsymmetrically substituted ketones dimerize to form a mixture of stereoisomers and, by varying the reaction conditions, the ratio of *dl*/*meso*-isomers can be varied (1, 2). Also, the use of an