Effect of Copper on Active Dissolution and Pitting Corrosion of 25% Cr Duplex Stainless Steels

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ABSTRACT

Electrochemical studies were made of the influence of Cu on pitting behavior and active dissolution of 25% Cr duplex stainless steels (DSS) in chloride-containing neutral and acid solutions. Alloys with increased Cu content showed higher pitting potentials (E_p) in 1 M hydrochloric acid (HCl) and 3.5% sodium chloride (NaCl) solutions. In HCl, the current density in the active state also was lower for the Cu-containing alloys. However, the critical pitting temperature (CPT) in ferric chloride ($FeCl_3$) was not improved significantly by addition of Cu. Pitting in all environments took place preferentially in the ferrite phase.

KEYWORDS: acid solutions, active corrosion, alloying, chloride, copper, corrosion resistance, critical pitting temperature, duplex stainless steel, hydrochloric acid, pitting, sodium chloride

INTRODUCTION

The effect of different alloying elements on the susceptibility of steels to pitting has been studied widely.[1-18] It is accepted commonly that those elements that shift the pitting potential (E_p) to more positive values (e.g., Cr, Mo, Ni, and N) are beneficial, while those such as S and P, which shift E_p values in the negative direction, are detrimental. For duplex stainless steels (DSS), excellent corrosion resistance arises mainly from the presence of three key alloying elements: Cr, Mo, and N.

The effect of Mo on localized corrosion has been studied extensively.[1-4] Sugimoto and Sawada showed that addition of Mo to SS decreases the current density in the active region in acidic solutions by 2 or 3 orders of magnitude, facilitating passivation.[1] The benefits from Mo were explained by Clayton and Lu, who found that Mo additions provide resistance against localized corrosion (chloride attack) by formation of a stable, amorphous passive film.[2] Newman proposed that Mo enriches at kink or step sites during dissolution of Fe-Cr-Mo alloys in the active state. The pitting process in those alloys was inhibited because Mo reduces anodic kinetics in the pit environment by 5 to 10 times.[4]

N has been used extensively in austenitic and DSS to stabilize the austenite phase and to impart higher corrosion resistance. However, it has been proven that N can form deleterious precipitates in th ferrite phase of DSS and, therefore, can reduce corrc sion resistance of the alloy.[5]

There are different theories as to why N improve localized corrosion resistance. Osozawa and Okato found ammonium in the pitting solution and proposed that N buffers the local pH in the pit through the formation of ammonium ions.[6] Newman propose that, as a result of the slow reaction of N with protons during anodic dissolution, elemental nitrogen enriches the surface, which inhibits the anodic diss

Submitted for publication December 1996; in revised form, April 1997. Presented as paper no. 417 at CORROSION/96, Denver, CO.

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0010-9312/98/000009/$5.00+$0.50/0

lution by covering the kinks and steps in the surface.[7] Ives, et al., suggested N may form ammonium that could combine with active oxidants to form less active compounds, inhibiting pit growth.[8] Other studies based on surface analysis have suggested that N enhances surface segregation, which then enriches the surface with beneficial elements.[9]

Lu, et al., suggested that a synergism between Mo and N improves the resistance to localized corrosion of austenitic SS.[10] That explanation is based on the segregation of N to the surface of the steel, which in a neutral solution may form iron nitride and inhibit the dissolution of iron, assisting repassivation of the pit and stopping the autocatalytic pitting process. However, in acidic solutions, nitrided pure iron actually dissolves faster than pure iron. In alloys with Cr and Mo, whose nitrides are more stable, a more resistant surface layer can develop at the pit site. Synergism between Mo and N also has been suggested by Bond and Dundas[11] and more recently by Olefjord and Wegrelius.[12]

The influence of other alloying elements has been studied in austenitic SS.[6,13] Osozawa and Okato reported the marked effect of N, Cu, W, and Mo on E_p and "critical" current density for a 17% Cr-16% Ni SS.[6] Brigham and Tozer developed some empirical relationships to describe the critical pitting temperature (CPT) when tested in 10% ferric chloride ($FeCl_3$) as a function of the alloying elements Mo, Cu, Ni, Mn, and N.[13] They found that Mo had a beneficial effect in pitting initiation resistance of the alloys, in contrast with Cu and Ni, which apparently showed no effect. N and Si showed some beneficial effect in the presence of Mo.

The beneficial effect of Cu in the corrosion resistance of austenitic and DSS in sulfuric acid (H_2SO_4) environments has been recognized. There also have been some indications that Cu could increase the pitting resistance of DSS in chloride-containing solutions.[14] The mechanism by which Cu may influence the corrosion resistance of SS has been reviewed.[15-19] Some published researches[16-19] have found that Cu additions[17] (from 0.2% to 9%) in SS can decrease the corrosion rate[18] and active dissolution[19] of the steel in acid solutions containing chloride ions. Most of these investigations agree that the beneficial effect of Cu in acid results from the accumulation of metallic Cu on the surface, which reacts with chloride ions to form a protective insoluble salt film[16-17] or by depolarizing the cathodic reactions.[18-19] However, other investigations found no effect of Cu for SS tested in highly-oxidizing chloride-containing solutions (such as 10% $FeCl_3$).[15] Furthermore, other studies on the influence of Cu in austenitic and ferritic SS in H_2SO_4, sodium chloride (NaCl) and mixtures of them have suggested that, despite reducing the active dissolution peak current, Cu was detrimental to passive film stability.[20-23] In NaCl[20] and H_2SO_4, they found that Cu accelerated the dissolution of austenitic steels in the passive region,[21] moving E_p in the cathodic direction and the passivation potential in the anodic direction. In H_2SO_4, a second anodic peak was found at ~ 320 mV_{SHE}, corresponding to anodic dissolution of anodic copper enriched in the surface.[22] Lizlovs labelled Cu as detrimental but depending upon the Mo content in the alloy, suggesting a synergism between these two elements.[23] Ogura, et al., found that Cu improved the resistance against stress corrosion cracking (SCC) and intergranular corrosion,[24] and Streicher found increasing crevice corrosion resistance on adding Cu to a number of different SS.[25] Bernhardsson suggested that Cu additions of ~ 1.8% to UNS S32550[1] extended the applicability range to intermediate concentrations of H_2SO_4 up to 45°C and more.[26] However, he reported the effect of Cu as "disputed" (marginally positive or negative) depending upon the concentration in the alloy. Combrade and Audouard suggested Cu is beneficial because of the synergism between Cu and Mo in the ferrite and Cu and N in the austenite.[27] Guha and Clark found that 1.5% Cu in 25% Cr DSS and 1% Cu in 28% Cr DSS was sufficient to achieve optimum corrosion resistance.[28] The role of Cu has been labeled as controversial particularly because Cu-rich precipitates in the ferrite could be initiation sites for pitting,[29] but there are some indications that Cu can increase the pitting resistance of DSS in chloride-containing solutions.[14]

A previous study on the effect of microstructure on pitting of DSS showed that pits always occurred in the ferrite phase, even where the austenite composition indicated a smaller pitting resistance number (PREN) than that of the ferrite.[30,2] The partitioning of copper to austenite, known to occur and seen in the present results, could be a contributory factor in avoiding pitting in the austenite if copper were beneficial in increasing pitting resistance.

The purpose of the present work was to determine whether the influence of Cu on the pitting corrosion resistance of 25% Cr DSS is large enough to account for this. The effect of Cu on the CPT in $FeCl_3$, as well as its effect on E_p in neutral and acidic NaCl solutions, has been studied.

EXPERIMENTAL

Materials

Samples from two melts of the same 25% Cr DSS, Ferralium SD40† (UNS S32550) with different copper contents (in the form of 20-mm [0.787-in.] wrought bars) were annealed at 1,020°C for 2 h and

[1] UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE) and cosponsored by ASTM.
[2] PREN = % Cr + 3.3% Mo + 16% N.
† Trade name.

TABLE 1
Melt Composition (wt%) of Super DSS Used

Sample	Cr	Mo	N	Cu	Ni	Mn	Si	C	S	P
High-Cu	25.92	3.19	0.20	1.62	5.90	0.96	0.47	0.030	0.007	0.024
Low-Cu	25.8	3.33	0.215	0.56	6.34	0.87	0.49	0.025	0.005	0.016
Nil-Cu	24.84	3.84	0.27	0.075	6.93	0.46	0.35	0.012	0.001	0.015
22% Cr	21.5	3.00	0.165	NA[A]	5.7	NA	NA	0.019	NA	NA

[A] NA = Not analyzed

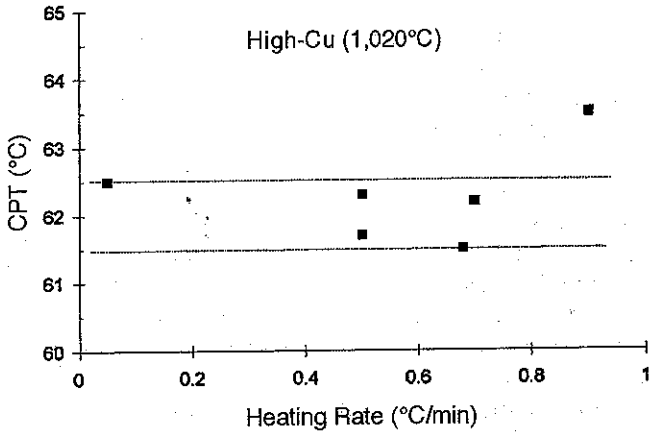

FIGURE 1. *Influence of rate of temperature change on CPT results for high-Cu DSS by ZRA test in $FeCl_3$.*

then water quenched. This temperature has been found to yield the best corrosion resistance for these Cu-containing materials.[30] These are designated as high-Cu (1.62% Cu) and low-Cu (0.56% Cu). A 25% Cr DSS without Cu (0.075% Cu), UNS S32750 (designated nil Cu) also was tested, after annealing at 1,060°C for 2 h and water quenching. Finally, a 22% Cr DSS, designated 22% Cr, was tested as-received. Table 1 shows the melt composition of the alloys. Generic identification is given as UNS S32550 for the high-Cu alloy, UNS S32750 for the nil-Cu alloy and UNS S32205 for the 22% Cr alloy (The low-Cu alloy was prepared specifically for the purposes of this research and does not have a UNS denomination).

After annealing, the outer part of the bar was removed by machining followed by wet grinding with 600-grit paper to produce samples in the form of rods 8.5 mm (0.335 in.) in diameter. The 22% Cr DSS were supplied as a thick plate which was machined to produce a cylindrical sample of 8.5-mm diameter. The end face of the samples (the surface to be tested) was machined carefully to give a smooth finish, then further wet ground to 4,000-mesh finish and degreased immediately before use. A few samples were polished to a 1-μm finish for metallographic observation and microanalysis. The chemical composition of the different phases was determined on an electron probe using a current of 10 μA at 20 KeV. Analysis was made at intervals of 2 μm. With this information, an average composition for each phase (ferrite and austenite) was calculated.

Both the high-Cu and nil-Cu (1,060°C) samples were examined as thin foils by transmission electron microscopy (TEM) to ensure no unwanted phases were present.

CPT Determination

CPT were determined using a method[30] similar to the zero-resistance amperometry (ZRA) test of Salinas-Bravo and Newman.[31] In the test, the current between two DSS samples connected through a sensitive micro-ammeter was measured, and their potential was recorded against a saturated calomel electrode (SCE) via a high-impedance buffer amplifier. The test solution was 250 mL of 10% $FeCl_3$, prepared according to the ASTM G 48 method,[32] in a glass cell immersed in a thermostatic water bath. The solution was unstirred during the test. To avoid crevice corrosion, the cell was arranged so that both specimens could be lowered just to touch the liquid surface with only the end face wetted. This defined the area under test (no attack was ever seen on the sides of the bar) without the need for coatings or gaskets.

An output from the ammeter, the temperature of the test solution (as measured with a temperature sensor accurate to ± 0.25°C, and the potential were all logged simultaneously every 3 s on a personal computer using a 16-bit analog digital converter. Usually the CPT was determined by coupling a high-Cu sample with the test sample. For the nil-Cu, the two samples were identical. The criterion used to determine CPT of the samples was the temperature at which the current measured increased to a value of 5 μA. In this work, a heating rate of 0.5°C/min was used normally. Checks carried out at higher rates (0.7°C/min and 0.9°C/min) showed no significant change at the lower rate and ~ 1° at the higher (Figure 1). Reducing the rate of temperature increase to 0.05°C/min actually caused a slight upward shift in CPT (within the limits of error). Typically variation between duplicates was < 1°. Heating rate was controlled by regulating the heater power, and the rate of rise was essentially constant for this well-insulated bath. Some heat may have been lost by conduction

along the sample, slightly lowering the temperature of the specimen face, but conditions were the same for all samples.

Anodic Polarization Experiments

Potentiodynamic sweeps in hot 3.5% NaCl solution (0.6 M) and 1 M HCl at a rate of 1 mV/s were used to characterize active and pitting behavior, but a higher rate of 4 mV/s was used for the cyclic voltammograms. The tests were carried out in a glass three-electrode cell held in a water bath at the test temperature (above CPT of the samples). In all experiments, the rod under test was supported in a holder on the lid of the cell as described above, such that the end face just touched the surface of the test solution. The counter electrode was a platinum wire, and the reference electrode was a SCE at the same temperature. All potentials are given against the SCE. After grinding the sample, it was immersed in the solution, and its free corrosion potential was measured. During the potentiodynamic sweeps in NaCl, the current density of the sample was logged every 3 s until the current density exceeded 100 $\mu A/cm^2$. At that moment, the potentiostat was switched off, and the experiment finished. The potential at which the current density reached 50 $\mu A/cm^2$ was considered as E_p. Normally E_p was far below the transpassive region (at ~ 1,000 mV). After testing, some samples were etched electrolytically for 3 s in 40% potassium hydroxide (KOH) at an applied voltage of 2.5 V to allow ferrite and austenite to be distinguished in the optical microscope. The samples then were examined for pits.

Anodic potentiodynamic sweeps (1 mV/s) were carried out in 1 M HCl at two temperatures. The current density was logged every 3 s until pitting started.

In some cases, samples were exposed for 200 s at –327 mV, rinsed in distilled water, dried, and observed by optical microscopy to identify the dissolved phase and site of pitting.

RESULTS AND DISCUSSION

Copper Effect on the CPT

The effect of Cu on CPT of the DSS is shown in Figure 2. The plots show the potential of the coupled electrodes against the SCE and the galvanic current between the two samples as a function of the temperature. When the high-Cu samples first were coupled at 25°C, the galvanic current observed was very low (< 1 μA) and essentially constant. Similarly, the potential of the galvanic couple was constant at ~ 480 mV_{SCE}. As the temperature was raised, small current transients (suggested to be metastable events[31]), started to appear well below the CPT. Stable pitting events were indicated when the current steadily increased, crossing the threshold of 5 μA. As

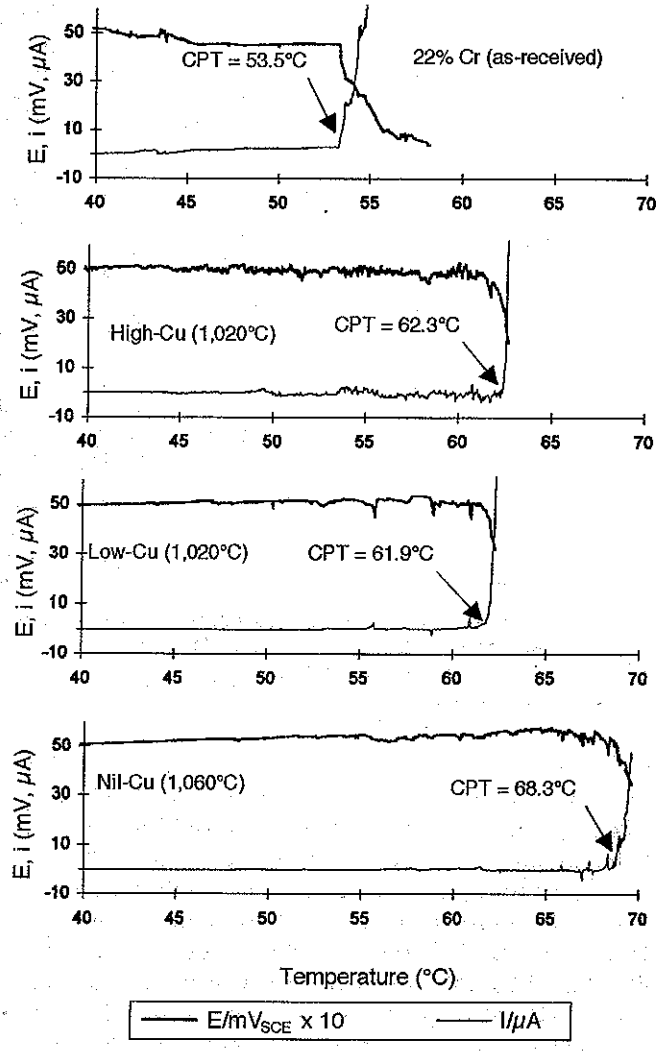

FIGURE 2. *CPT for DSS with different Cu content as determined by the ZRA test.*

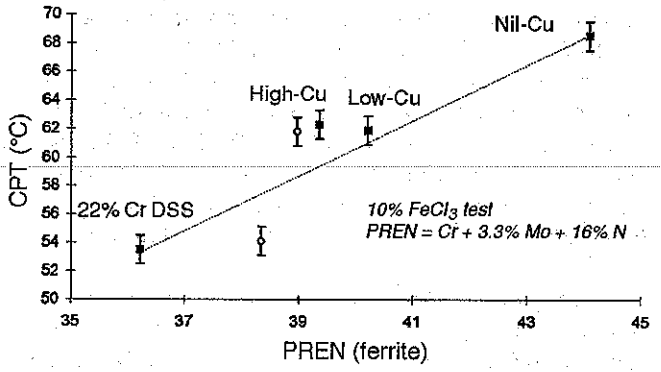

FIGURE 3. *Comparison between CPT of DSS as determined by ZRA test and PREN for ferrite phase of alloys tested.*

current transients began, the potential started to fluctuate downward, until a final permanent decrease occurred simultaneous with the increase in couple current, indicating the onset of pitting. CPT obtained

TABLE 2
Average Compostion (wt%) of the Phases for Each Alloy

Sample	Phase	%	Cr	Mo	N[A]	Cu	Ni	P	PREN[B]
High-Cu	Ferrite	47 ± 1	26.4 ± 0.3	3.7 ± 0.2	0.05	1.3 ± 0.1	4.6 ± 0.1	0.04 ± 0.01	39.3 ± 1.0
	Austenite	53 ± 1	23.1 ± 0.2	2.4 ± 0.1	0.33	1.95 ± 0.1	7.36 ± 0.1	0.02 ± 0.01	36.2 ± 0.6
Low-Cu	Ferrite	56 ± 1	26.8 ± 0.4	3.8 ± 0.2	0.05	0.50 ± 0.05	5.4 ± 0.2	0.03 ± 0.1	40.2 ± 1.1
	Austenite	44 ± 1	23.9 ± 0.3	2.6 ± 0.2	0.43	0.64 ± 0.06	8.1 ± 0.2	0.02 ± 0.01	39.2 ± 1.1
Nil-Cu[C]	Ferrite	59 ± 1	27.9 ± 0.8	4.7 ± 0.6	0.05	0.05 ± 0.03	5.1 ± 0.6	0.03 ± 0.02	44.1 ± 2.7
	Austenite	41 ± 1	24.4 ± 1.6	3.0 ± 0.6	0.60	0.07 ± 0.04	8.0 ± 1.5	0.02 ± 0.02	43.8 ± 3.6
22% Cr	Ferrite	47 ± 1	23.1 ± 0.5	3.7 ± 0.3	0.05	NA[D]	4.3 ± 0.4	NA	36.2 ± 1.3
	Austenite	53 ± 1	20.1 ± 0.6	2.4 ± 0.5	0.26	NA	6.9 ± 0.6	NA	32.1 ± 1.6

[A] Nitrogen in ferrite is taken as a saturation value ≈ 0.05%, the rest partitions to the austenite.
[B] According to PREN = % Cr + 3.3% Mo + 16% N.
[C] Sample annealed at 1,060°C.
[D] NA = Not analyzed.

for the high-Cu sample was 62.3°C.[30] For the low-Cu and nil-Cu alloys, the potential of the coupled electrodes and the galvanic current followed the same behavior as described for the high-Cu sample. The low-Cu sample gave a CPT of 61.9°C, a difference within the limits of error. The 22% Cr DSS gave a CPT of only 53.5°C, but the nil-Cu steel gave a CPT of 68.5°C, which probably could be attributed to higher levels of Cr, Mo, and N. Figure 3 plots the CPT values for these four alloys as a function of the PREN of the ferrite phase (where pitting is seen), calculated from microanalysis of the steels (Table 2). Additional results are included for the high-Cu alloy annealed at temperatures of 1,060°C and 1,100°C, taken from previous work[30] (without results for annealing at 1,120°C, that give excessively low CPT).

It was evident that, except for the two well matched steels (high-Cu and low-Cu), the higher Cu content gave marginally higher CPT. This difference was within the limits of error, and overall, the high-Cu results were close to the general trend. No beneficial effect of Cu could be substantiated from this test.

Enrichment of Cu in austenite certainly could not explain why pitting took place in ferrite, rather than austenite, despite a much higher PREN, in the acidic $FeCl_3$.

Effect of Copper on Anodic Polarization in 1 M HCl

Anodic polarization curves for samples of low-Cu and high-Cu duplex in 1 M HCl solution at 65°C are shown in Figure 4. This temperature was just above the CPT for these samples. The active peak was found in the range between –330 mV and –250 mV, depending upon the alloy. The peak current density for low-Cu was ~ 3,300 μA/cm². That for the high-Cu sample was < 2,500 μA/cm². E_p was substantially higher for the high-Cu sample. A small peak was evident just below the main active peak, at ~ –325 mV, in both the high-Cu and low-Cu alloys. A similar peak has been described by Newman[33] as responsible for the anomalous cathodic behavior of pits on type 304L steel (UNS S30400), arising from dissolution of the Cu from the steel.[34] In tests at 70°C (Figure 5), the active peak heights decreased with increases in Cu content, with no subsidiary peak visible for nil-Cu. E_p increased with increased Cu content. Higher E_p values were observed in the Cu-containing alloys despite their lower PREN values (i.e., levels of Cr and Mo were highest in the nil-Cu steel).

Effect of Copper on Anodic Polarization in 3.5% NaCl

Potentiodynamic curves for low-Cu and high-Cu in 3.5% NaCl solution at 65°C are shown in Figure 6. There was no active peak, and the passive current was < 3 μA/cm². The highest value of E_p was obtained for the high-Cu ($E_p \approx 220$ mV), while the low-Cu gave a lower value ($E_p \approx 150$ mV). Duplicate tests had essentially the same outcome. These E_p values were similar to those observed in 1 M HCl described above. When all three 25% Cr DSS were tested at 70°C (Figure 7), the nil-Cu showed the lowest E_p at ~ 20 mV_{SCE}, with both high- and low-Cu giving E_p values of close to 180 mV_{SCE}.

There was a clear correlation between Cu content and increased E_p values. When three samples

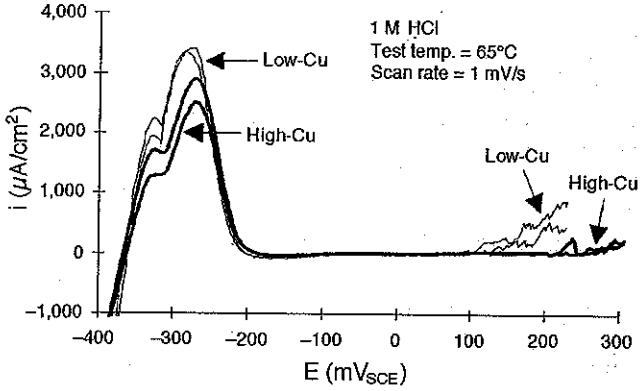

FIGURE 4. *Comparison of polarization curves for high-Cu and low-Cu DSS in 1 M HCl at 65°C.*

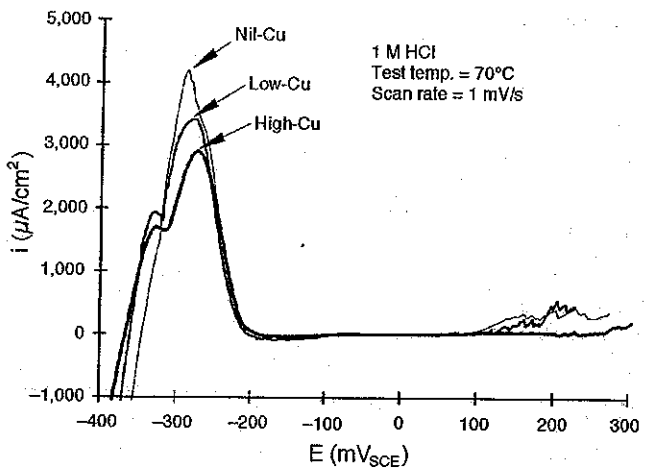

FIGURE 5. *Comparison of polarization curves for high-Cu, low-Cu, and nil-Cu DSS in 1 M HCl at 70°C.*

with different Cu contents were polished to 1 μm and anodically polarized (at a rate of 1 mV/s) until an arbitrary current density of ≈ 60 μA/cm² was obtained, subsequent examination showed that many pits were clearly within the ferrite with occasional pits adjacent to ferrite-austenite boundaries. None appeared to have initiated entirely within austenite, whatever the steel.

In NaCl and HCl, E_p was influenced very little as temperature was raised from 65°C to 70°C. In all these tests. E_p was substantially below the rest potential seen in the ASTM G 48 test solution (Figure 2). It was not surprising that the upward shift in E_p caused by Cu addition did not influence the outcome of a CPT test in the highly oxidizing $FeCl_3$ environment.

Cyclic Voltammetry in 1 M HCl

Cyclic voltammograms for nil-Cu steel in 1 M HCl at 70°C showed a large active peak (9 mA/cm²) on the forward and a smaller anodic peak at ~ –330 mV on the back scan (Figure 8). When a small amount of copper chloride ($CuCl_2$) was added to the solution and the experiment repeated, a substantially smaller active current was seen, with two distinct peaks and no peak on the back scan. The same behavior was seen on subsequent cycles. This mirrored the behavior seen with Cu-containing alloys (Figures 4 and 5). Interrupting the reverse scan at less negative potentials than –450 mV gave only one active peak. It was assumed that cathodic polarization could bring about deposition of metallic Cu and that reoxidation occurred on the anodic sweep. Newman and Isaacs saw similar peaks on a platinum microelectrode within a model pit and suggested that Cu in the pit solution was deposited and reoxidized during the sweep.[33] Their calculations gave a reversible potential for Cu in equilibrium with the complex $CuCl_2^-$ of –308 mV_{SCE} (with 0.018 M dissolved $CuCl_2^-$ and 8 M Cl^-), somewhat less negative than the potential apparently required for Cu deposition here. Neverthe-

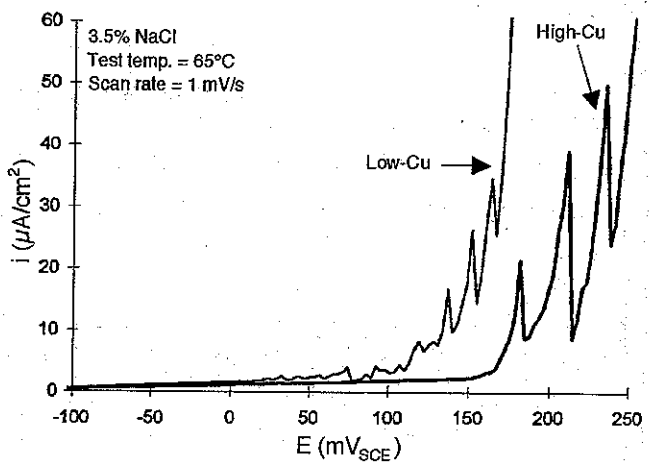

FIGURE 6. *Comparison of polarization curves for high-Cu and low-Cu DSS in 3.5% NaCl at 65°C.*

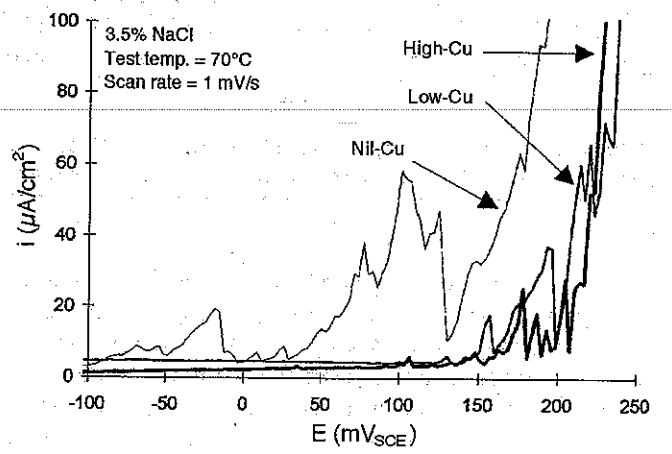

FIGURE 7. *Comparison of polarization curves for high-Cu, low-Cu, and nil-Cu DSS in 3.5% NaCl at 70°C.*

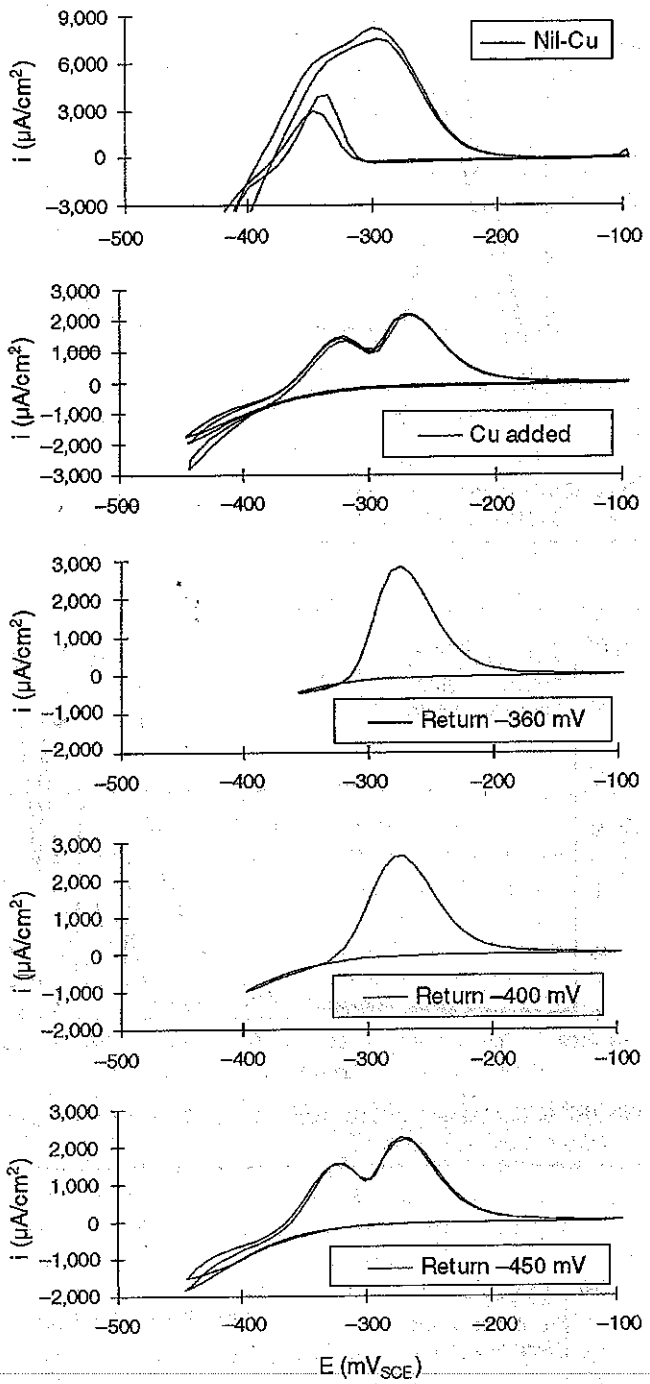

FIGURE 8. *Cyclic voltammograms for nil-Cu DSS in 1 M HCl at 70°C with and without 0.018 M dissolved Cu showing effect of scan limits.*

less, these results suggested that Cu in the alloy may act by first dissolving, then redepositing within a pit and hindering anodic dissolution. It is questionable whether the first active peak seen only in Cu-containing alloys was entirely the result of Cu oxidation.

Distribution of the Alloying Elements

Electron-probe microanalysis (EPMA) of the steels showed Cr and Mo to be enriched in the ferrite phase. Table 2 shows the composition of both phases for each alloy. The level of N present in the ferrite was assumed to be 0.05%, which is a typical saturation concentration. The level in the austenite was calculated from the balance, as suggested by Charles.[35] The high-Cu alloy contained a higher proportion of austenite than the low-Cu or nil-Cu steel.

Calculated PREN values for the ferrite from this table were used to compare the different steels in Figure 3. A reasonable correlation was apparent. It was difficult to distinguish any clear influence of Cu. The PREN values for both phases were quite similar in low-Cu and nil-Cu, but the high-Cu steel showed a significantly lower PREN for austenite yet pits in the ferrite, as reported previously.[30]

The high pitting resistance of austenite seen in the high-Cu alloy did not seem to arise from addition of Cu, but may involve synergism between Mo and N (N levels were substantially higher than in ferrite) or lower levels of residual elements such as P (Table 2).

CONCLUSIONS

- Addition of Cu to 25% Cr DSS resulted in an increase in E_p in potentiodynamic tests above the CPT in 1 M HCl and in 3.5% NaCl.
- Measurements of CPT in acidic $FeCl_3$ did not indicate any beneficial influence of Cu. The strongly oxidizing test solution may have rendered Cu ineffective in inhibiting pitting.
- Cu additions to DSS decreased the size of the active peak for polarization curves in 1 M HCl. A similar reduction was seen if Cu^{2+} ions were added to the solution.

ACKNOWLEDGMENTS

The authors acknowledge financial assistance of Langley Alloys, Ltd.; the provision of laboratory facilities by D.G. Pettifor; helpful discussions by R.C. Newman and O. Khaselev; and sample analyses by C. Salter of Cameca. One author (Garfias-Mesias) acknowledges financial support of Consejo Nacional de Ciencia y Tecnologia (CONACyT).

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