MECHANISM OF INTERGRANULAR CORROSION OF NiCu ALLOYS

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Abstract - The objective of this study is to simulate intergranular corrosion (or intergranular attack, IGA) of Monel 400 (70Ni-30Cu) tubes that occurs occasionally in practice. In general the hypothesized factors of IGA for Monel 400 tubing could be crevices, dissolved oxygen, low pH, reduced sulfur species, and precipitation of impurities at grain boundaries. Electrochemical techniques including cyclic polarization and long-term potentiostatic polarization were used to test two heats of Monel 400 tubing that had behaved differently in practice. To simulate the situation within a crevice or under a deposit, cupric ions were added to the base solution, which was either neutral or acidic in pH. The effect of thiourea as a representative reduced sulfur compound was investigated. The results show that in neutral solution IGA occurs with little sensitivity to metallurgy and does not require thiourea, but in acid solution it only occurs with thiourea addition, and particular grain boundary microstructures are more susceptible.

Key words: intergranular corrosion, Monel 400, thiourea

Introduction

Monel 400 (70Ni-30Cu) recently achieved its centenary as a versatile though moderately expensive alloy [1]. It has found a variety of uses, such as steam generation, heat-exchanger tubing, cladding for splash zones on offshore structures and riser pipes, and service in HF and caustic environments.

The good performance of Monel 400 in most applications can be attributed to its combination of a noble character, due to Cu, and a moderately passivating tendency, due to Ni. Pitting, as usually defined, is hard to sustain, and the difference in standard potentials between Cu and Ni is not large enough to make de-alloying a routine occurrence.

Stress corrosion cracking of Monel 400 is rare, but has occurred in oxygenated hot water, especially at sites of local cold-work [2-4]. It can also be made to crack in slow strain rate tests in various media [5] and is susceptible to cracking in the presence of lead [6]. Like all nickel base materials, Monel is susceptible to reduced sulfur compounds, including on occasion the action of sulfate-reducing bacteria [7-11]. Such behavior is consistent with the usual sensitivity of nickel to adsorbed S^0 [12]; the noble character of copper is also compromised by the presence of reduced sulfur. There are indications that Monel can be damaged by chemical cleaning formulations [13,14], and this can possibly be interpreted using electrochemical kinetic studies [15-17]. Such studies are, however, hard to interpret with regard to the possible role of de-alloying of Ni, which requires a different approach illustrated in the present paper.

One concern with Monel is its variable susceptibility to intergranular corrosion, often called IGA, which may be the underlying mechanism of some reported cases of pitting or underdeposit attack [18-22]. In industrial plant where the redox potential fluctuates, corrosion may propagate by alternate phases of highly localized (intergranular) and more uniform dissolution.

The present work was based on the hypothesis that IGA of Monel could have an underlying de-alloying mechanism. Since copper alloys such as brass are easily de-alloyed in copper salt solutions, such as Cu I in NaCl or ammonia [23-26], and since practical cases of Monel corrosion often involve deposits where Cu ions can accumulate, we have used acidic and neutral $CuSO_4$ solutions and focused on the region very near the Cu equilibrium potential, where Ni can dissolve but not Cu, or at least, Cu cannot dissolve at a microstructurally significant rate. Thiourea was used in some experiments as a source of reduced sulfur.

Experimental Procedures

Materials

Two heats of Monel 400 tubing (66% Cu, 31% Ni, balance mainly Mn and Fe) were acquired. These materials had behaved differently in practice, with one showing more sensitivity to IGA.

Samples for electrochemistry were cut and mounted in heat-resistant resin so as to expose an arc of the tube cross-section, with surface areas from 0.05 to 0.21 cm^2. Larger samples exposing the tube wall could not be used, as the IR drop became unacceptable.

Pure nickel (Goodfellow; <17 ppm total impurities) was acquired in the form of 2 mm rod and similarly mounted to expose a surface area of 0.0314 cm^2. Pure copper (>99.9%) was mounted to expose 0.0256 cm^2. All samples were attached to Cu wires for electrical connection.

Electrochemistry

The three-electrode electrochemical cell was a 500 ml glass vessel with a water jacket for heating and temperature control. A platinum counter electrode and saturated mercury/mercury sulfate electrode (MSE) were used for most experiments. PAR 2263A and Gamry Instruments, Reference 600 software-controlled systems were used to make the electrochemical measurements. In some experiments, a copper rod was used as reference electrode. Argon (Prepurified, 99.998%) was used for deoxygenation.

Initial potentiodynamic studies were done at 80^0C on copper, nickel and the two Monels in 0.125M H_2SO_4 + 0.125M Na_2SO_4 with a room-temperature pH of 1.13 (pH at 80^oC of 1.41). Long-term potentiostatic studies were done at potentials of 0 and 10 mV vs. Cu in a similar solution containing 0.05M $CuSO_4 \cdot 5H_2O$ with or without excess Cu_2O to ensure Cu I saturation, with a room-temperature pH of 1.56. All experiments were done with and without the addition of 30 ppm (0.4 mM) thiourea, or sometimes other concentrations. Neutral-solution experiments used simple mixtures of Na_2SO_4 and $CuSO_4$.

Microscopy and analysis

Monel samples that were exposed in the long-term potentiostatic or ZRA experiments with Cu II in the solution were examined by SEM and EDX, both in surface view and as polished cross-sections.

Results and Discussion

Figure 1 illustrates the potentiodynamic behavior of nickel, copper and the ‘bad’ and ‘good’ Monels (Monel 1 and Monel 2, respectively) in acid sulfate. No passivation is evident in the anodic behavior of the Monels, showing that the presence of enriched Cu hinders passivation by Ni.

The ‘bad’ Monel 1 shows a distinct though slow de-alloying of Ni in the potential range -0.8 to -0.4 V (MSE). Less de-alloying is evident for the ‘good’ Monel 2. It is not possible to tell whether this difference is associated with IGA.

The addition of 30 ppm thiourea eliminates passivity of nickel by creating an aggressive adsorbed sulfur species – probably S^0_{ads} [12] - as shown in Figure 2. There is a large IR drop in this curve; correction reveals that a rapid rise in current density to >150 mA/cm^2 occurs between -600 and -500 mV. Not much change is evident in the behavior of the copper or the two Monels, except that the rate of de-alloying of the ‘good’ Monel 2 increases. Copper shows indications of oxidation to some Cu I species, perhaps Cu_2S, and its dissolution as Cu II is slightly inhibited by the thiourea.

It is not possible to tell from these data whether there is de-alloying occurring near the Cu II dissolution potential, whether this is enhanced by thiourea, or whether any of the corrosion is intergranular.

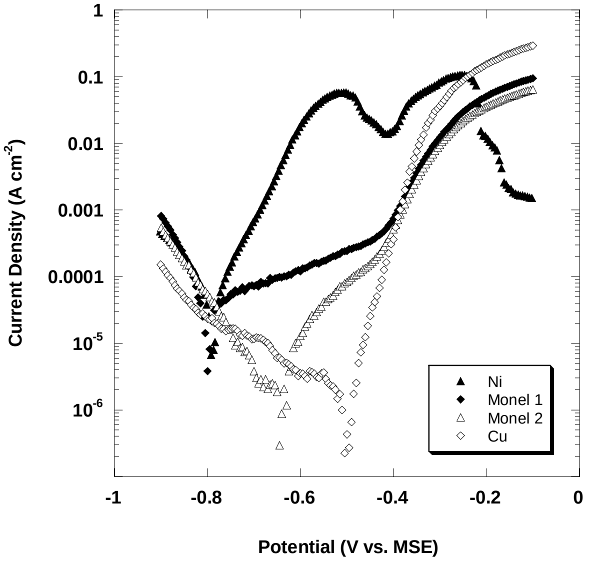

Fig.1. Anodic potentiodynamic polarisation curves for Ni, Cu and two different Monels ('bad': Monel 1; 'good': Monel 2) in 0.125M H_2SO_4 + 0.125M Na_2SO_4 at 80^{o}C. The scan rate was 5 mV/s. No IR correction has been performed.

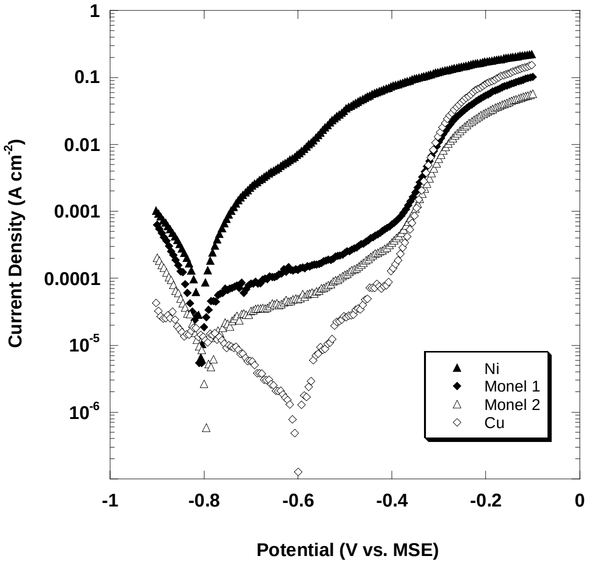

Fig.2. Anodic potentiodynamic polarisation curves for Ni, Cu and two different Monels ('bad': Monel 1; 'good': Monel 2) in 0.125M H_2SO_4 + 0.125M Na_2SO_4 at 80^{o}C, with 30 ppm thiourea added. The scan rate was 5 mV/s. No IR correction has been performed.

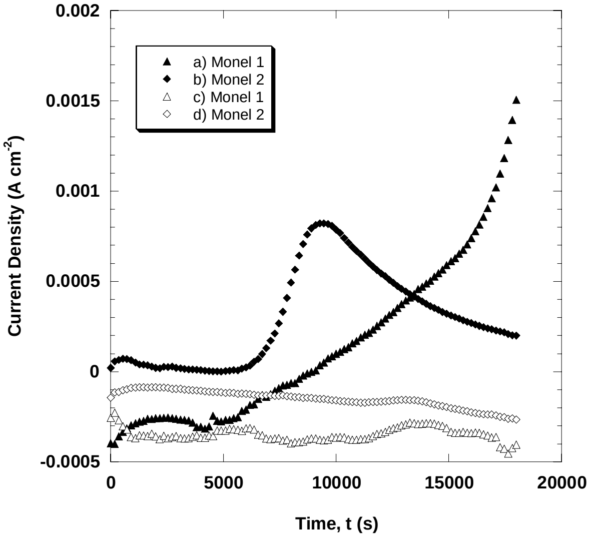

Fig.3. Current-time curves for 5-hour potentiostatic experiments on 'bad' and 'good' Monels in 0.125M H_2SO_4 + 0.125M Na_2SO_4 + 0.05M $CuSO_4$ with (a and b) and without (c and d) addition of 30 ppm thiourea, at 0 mV vs Cu reference electrode, at 80^{o}C.

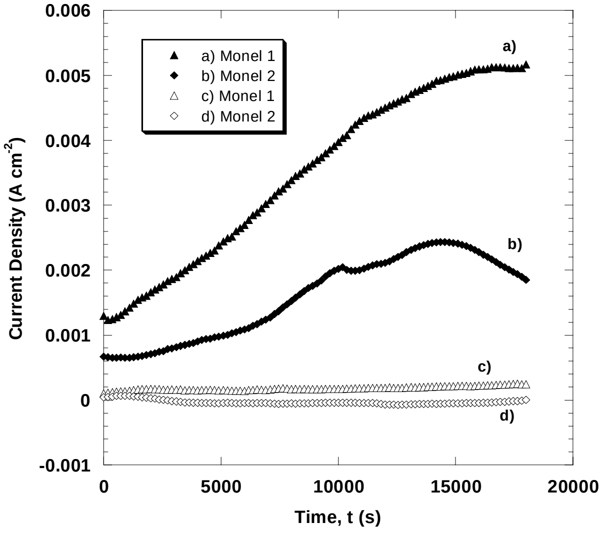

Fig.4. Current-time curves for 5-hour potentiostatic experiments on 'bad' and 'good' Monels in 0.125M H_2SO_4 + 0.125M Na_2SO_4 + 0.05M $CuSO_4$ with (a and b) and without (c and d) addition of 30 ppm thiourea, at +10 mV vs. Cu reference electrode, at 80^{o}C.

Potentiostatic treatment near the Cu equilibrium potential in sulfate solutions with Cu II

These experiments were done with a copper reference electrode and usually lasted 5 hours. For acid solution at 0 mV vs Cu, the currents are low and even cathodic without thiourea, but with thiourea there is a breakaway after about 5000 s followed by a sustained anodic current for both alloys – Figure 3. A clearer distinction between the alloys was obtained by using a potential of 10 mV vs Cu, as shown in Figure 4: now the breakaway is earlier and the difference between the alloys is distinct. The solutions used for Figures 3 and 4 were equilibrated with Cu_2O. Much higher anodic currents were consistently obtained on the 'bad' Monel 1, and the reproducibility of the behavior was excellent.

In neutral solution both alloys showed IGA and it was noticed that the Cu 'equilibrium' potential was more positive than in acid – the Cu is actually corroding slowly to Cu_2O.

There is some way to go before these procedures could be considered as a rapid test for susceptibility to IGA. The behavior is very sensitive to the exact potential applied, and also to stirring. In fact the 'best' discrimination between the heats was obtained in stirred solution without Cu_2O – Figure 5.

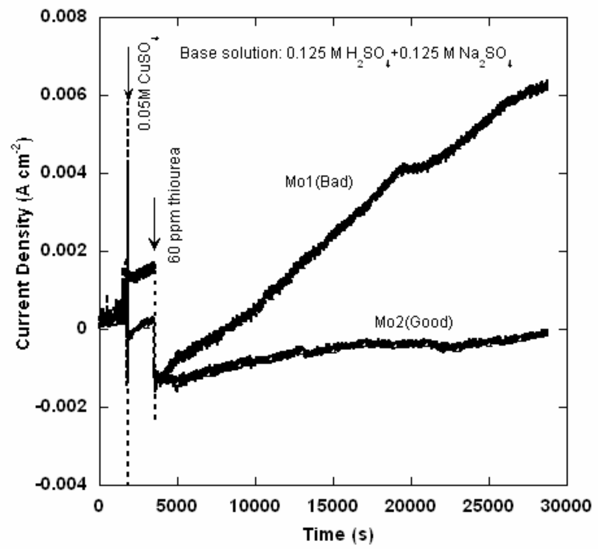

Fig. 5. Similar experiment to Figure 4, but using stirred solution and no Cu_2O addition, and 60 ppm thiourea, showing optimized discrimination between the different heats.

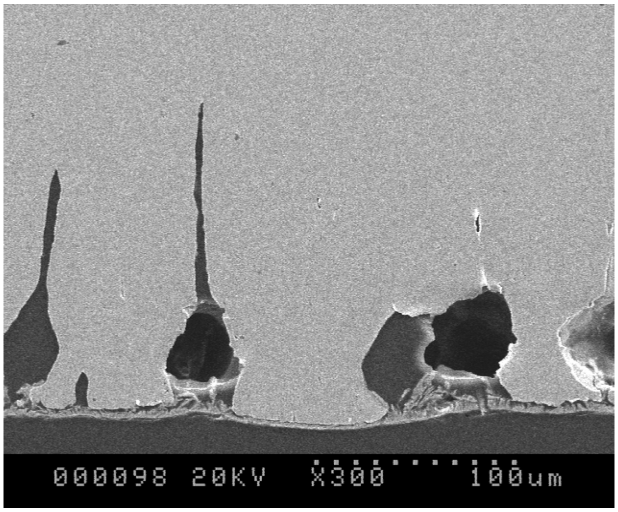

Fig. 6. Cross-sectional microscopy of grain-boundary related slotting corrosion on the 'bad' Monel in the experiment of Figure 5.

Reasons for heat-to-heat differences in susceptibility of Monel to IGA

The alloys used in the present investigation have been studied by SIMS analysis of electropolished surfaces [27]. The presence of nickel boride precipitates on grain boundaries is responsible for the greater susceptibility to IGA of some Monel heats. These precipitates are essentially pure nickel, and dissolve actively, catalyzed by thiourea adsorption. Between the precipitates, Ni is removed by intergranular de-alloying.

Conclusions

1. Susceptible heats of Monel 400 undergo rapid IGA in acidic copper sulfate solution, but only if thiourea is added. In neutral solution IGA is less sensitive to metallurgy and occurs without thiourea.
2. The mechanism of this corrosion involves de-alloying of nickel and is facilitated by active dissolution of nickel boride precipitates.
3. Thiourea promotes this corrosion by depassivating nickel through the formation of S^0_{ads}.

Acknowledgements

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