The Effect of Copper on Crevice Corrosion of Stainless Steels

Roger Francis, FNACE, *RFMaterials, Glossop, Derbyshire, United Kingdom*
Glenn Byrne, *Rolled Alloys, Blackburn, Lancashire, United Kingdom*

Crevice corrosion leaks on superduplex stainless steel sprinkler heads occurred in a firewater sprinkler system operating at 22 °C. Tests showed that copper deposits from corroding copper alloys could act as very efficient cathodes and stimulate dissolution during the regular breakdown and repassivation of the passive film in crevices. Several other service failures have occurred because of a similar mechanism, which had not been previously reported.

Superduplex stainless steels (SS) such as UNS S32760 and UNS S32750 have been widely used in seawater systems because of their excellent resistance to crevice corrosion. Reviews of service experience have shown satisfactory performance with Alloy Z100 (UNS S32760) up to ~40 °C.[1]

In the late 1990s, there were some unusual leaks of S32760 sprinkler heads in the firewater system on an offshore platform. The leaks were in the accommodation module with a typical temperature of 22 °C, and they took the form of crevice corrosion of the threads of the sprinkler heads.

It was found that aluminum bronze heads were used initially because of the long delivery time of the superduplex SS heads. These corroded rapidly, however, from galvanic corrosion with the superduplex SS piping and were replaced with superduplex SS heads.

Examination and Testing

An initial examination of the S32760 sprinkler heads showed severe crevice corrosion of the threads, despite the relatively low temperature in the accommodation module. Just outside the creviced area, coppery-colored deposits were clearly visible. It was thought that these deposits might have originated from the reduction of soluble copper corrosion products formed during the corrosion of the bronze sprinkler heads.

To determine whether this was possible, 50-mm square plates (3-mm thick) were fitted with polyacetal crevice washers, as described in ASTM G78.[2] The washers were loaded with nylon-coated disc springs to produce a load of 27 N/mm^2, which provided a tight crevice similar to that found in a screwed joint. The samples were immersed in synthetic seawater containing 50-mg/L cupric ions at 20 °C and the water was continuously aerated with compressed air. After three weeks, the plates were examined and coppery deposits were seen outside the crevice (Figure 1). These were confirmed as copper by x-ray analysis using scanning electron microscopy.

Discussion

The copper deposits normally would be expected to have a potential of ~ –250-mV vs. a saturated calomel electrode (SCE) and would be anodic to superduplex SS in aerated seawater.[3] The water in a sprinkler system only flows intermittently, however, so the environment in the crevice will gradually acidify and experience an increase in

chloride content. This follows the crevice corrosion model of Oldfield and Sutton.[4] Crevice corrosion will not initiate on superduplex SS until the pH drops to 0.5 in seawater (the depassivation pH) at 20 °C. Hence, the environment in the crevice at 20 °C should have a higher chloride content than seawater and a pH level between 0.5 and 8. The anodic polarization diagram in Figure 2 was generated for S32760 in 4 M sodium chloride (NaCl) solution at pH 1, and it shows an active peak below the threshold current density (CD) of 10 μA/cm², which is needed to initiate crevice corrosion.[4] The active peak potential is ~–250 mV vs. SCE, similar to that of copper in aerated seawater, so there would be no galvanic corrosion of the copper in contact with the superduplex SS crevice.

When a SS has a crevice, the creviced area is the anode and the area surrounding the crevice is the cathode. The passive film on SS is continuously breaking down and reforming in chloride-containing solutions. At 22 °C in seawater, the rate of repassivation is rapid and localized corrosion does not normally occur. If, however, a more efficient cathode is available, that cathode can stimulate increased dissolution when the passive film breaks down.

Figure 3 shows the cathodic polarization curves for a S32760 superduplex SS sample (~600 mm²) in aerated, synthetic seawater at 20 °C, and also when it is coupled to a ~6-mm² copper sample. The significant depolarization of the cathodic reaction of S32760 when coupled to copper shows the much greater efficiency of copper as a cathode. This is what is believed to have stimulated the initiation of crevice corrosion in the sprinkler heads when repassivation would normally occur.

Service Experience

Crevice corrosion of SS caused by the presence of copper under conditions when corrosion is not normally expected to occur is not reported in the literature, but unreported examples have occurred. A UK chemical processing plant suffered serious leaks in austenitic SS pipework due to the presence of copper deposits.[5]

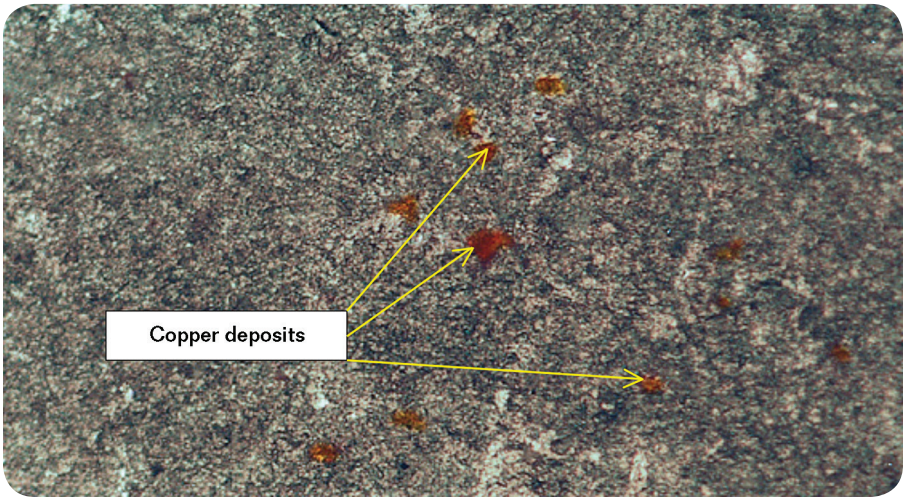

FIGURE 1 Copper deposits on superduplex SS after three weeks in aerated seawater plus 50 mg/L cupric ions.

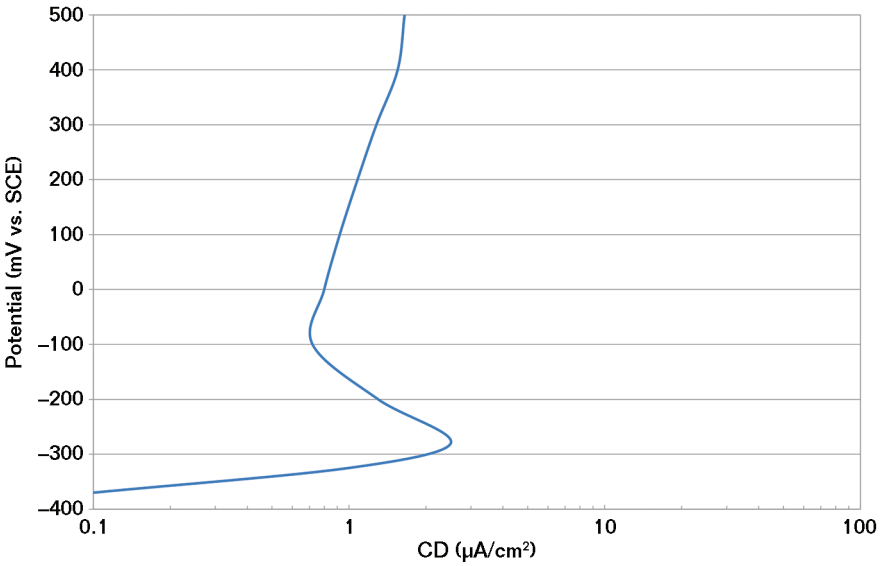

FIGURE 2 Anodic polarization curve for S32760 superduplex SS in 4 M NaCl at pH 1.

Severe crevice corrosion of a 2205 (UNS S32205) duplex SS coupling occurred in a reverse osmosis desalination plant with chlorides ~4,000 mg/L in the process fluid.[6] The coupling threads had been cleaned with a brass brush prior to assembly, and it is believed that corrosion of the brass residue led to the formation of copper deposits that stimulated crevice corrosion in a similar manner to that described in this article.

Conclusions

- Copper deposits may form as part of the cathodic reaction after dissolution of copper alloys coupled to SS.
- If these deposits are adjacent to tight crevices, they can act as cathodes that are more efficient than SS.
- This can result in failure to repassivate the passive film during regular film breakdown cycles, which can

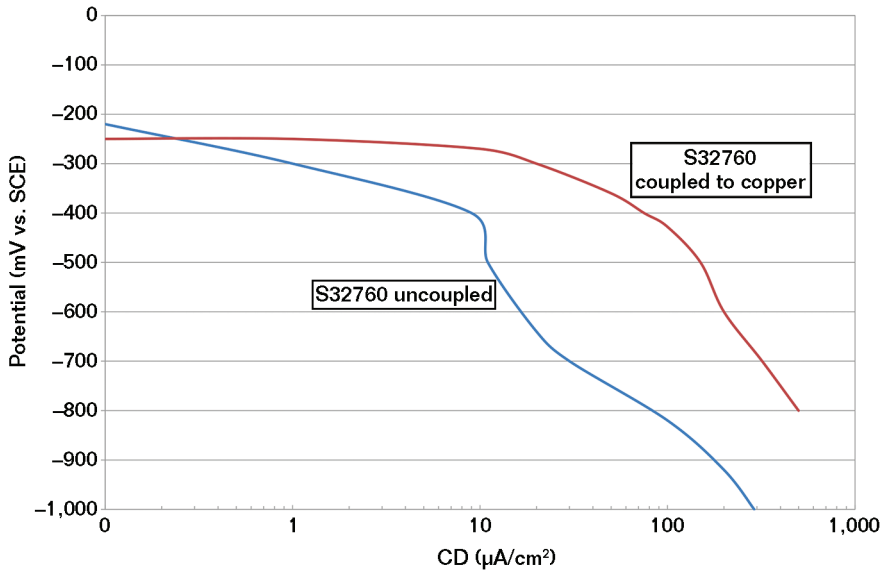

FIGURE 3 Cathodic polarization curves for S32760 superduplex SS in aerated, synthetic seawater: uncoupled (blue curve) and coupled to ~6 mm² of copper (red curve).

then lead to the initiation of crevice corrosion when it would not normally occur.

- This mechanism has caused several unexpected service failures.

Acknowledgments

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ROGER FRANCIS, FNACE is the director of RFMaterials, 1 The Lodge, Hadfield, Glossop, Derbyshire, SK13 1QN, United Kingdom, e-mail: rfrancis@rfmaterials.com. He has been a corrosion engineer for 40 years with extensive experience with SS and copper alloys in many environments, particularly marine. He has B.Sc. and M.Sc. degrees and a Ph.D.; and certifications as C.Eng. and MIMMM. He is a Fellow of NACE International and ICorr and received the NACE T.J. Hull Award in 2014. He has been a member of NACE since 1992.

GLENN BYRNE is the director of Global Projects and Technology at Rolled Alloys, 16 Walker Industrial Park, Blackburn, Lancashire, BB1 2QE, United Kingdom, e-mail: gbyrne@rolledalloys.com. He has 30 years of experience in the application of SS in many industries, and is interested in microstructure and property relationships, welding, corrosion, fracture, and fatigue of alloys. He has a B.Met degree and a Ph.D. and is certified as C.Eng. and MIMMM. MP