The Role of Inclusions in Crevice Corrosion of High-Alloy Austenitic Stainless Steel Tube Used in Seawater-Cooled Condensers

N. Mukhopadhyay, T.R. Jayaraman, S. Baskaran, and Y. Kalpana

In view of the reported superiority of high chromium-nickel-molybdenum austenitic stainless steel tube over copper alloy tube in seawater-cooled condensers, two such compositions were tested for crevice corrosion performance in seawater using a Campbell test rig. Tube of one particular alloy composition was free of crevice attack in seawater testing, whereas tube of the other alloy composition experienced extensive crevice attack. Anodic cyclic polarization test results carried out in the laboratory were in agreement with the field test results for these alloys. It was thus concluded that inclusion morphology, together with alloy composition, should be considered in the selection of tube materials for condenser applications.

1. Introduction

COPPER alloys that traditionally have been used as condenser tubes in seawater become unfit for use when seawater is polluted with sulfide ions in low concentrations due to accelerated corrosion.[1,2] Stainless steels containing 2 to 4% molybdenum have often been considered for use under such conditions, because molybdenum provides a significant improvement in crevice corrosion resistance of stainless steels. Kesten[3] reported that molybdenum in steels actually deactivates the localized sites involved in sulfide ion attack by forming molybdenum sulfide, which is a highly insoluble substance, thereby providing resistance to localized corrosion. AISI type 316 stainless steel has been used as condenser tubing,[4,5] but its crevice and pitting performance was poor. Subsequently, many of the high-alloy austenitic and ferritic stainless steels, developed both for the purpose of chemical process industries as well as sea and brackish water, have been suggested by the manufacturer for use as condenser tubes.

The major localized corrosion problem in seawater with regard to stainless steel condenser tubes is crevice corrosion occurring at shielded surfaces due to either a loose deposit or to

N. Mukhopadhyay, T.R. Jayaraman, S. Baskaran, and Y. Kalpana, Corporate R & D, Bharat Heavy Electricals Limited, Hyderabad, India.

marine growth. With this in mind, the authors conducted long-term studies in natural seawater using a Campbell apparatus[6] at a coastal power station with tubes of two commercial austenitic stainless steels containing equivalent amounts of chromium and higher amounts of nickel and molybdenum than standard AISI type 304 steel. The performance of these two steels under crevice corrosion conditions in unpolluted seawater is reported below. Field test results were corroborated by an electrochemical test to illuminate the mechanism of corrosion. The results show that, in spite of a high molybdenum content, one of the two alloys suffered from crevice attack caused by structural heterogeneities such as inclusions. This consideration is of practical importance in the specification of stainless steels as condenser tubing materials for use in seawater.

2. Experiment

To study the crevice corrosion susceptibility of stainless steel tubes, the crevice design of the Campbell apparatus (Fig. 1) was used. According to this design, a crevice condition is created at the bottom end of each test tube by inserting a tapered nozzle made of a nonmetallic material. The nozzle has a taper of 2° with respect to the axis of the tube, which creates a crevice site. In this study, natural seawater was made to flow into each test tube through a hole in the nozzle. A 250-mm long array of test tubes was held vertically by two plates at the top and bottom. Seawater in the unchlorinated and filtered condition was pumped into an overhead tank, from which water flowed continuously in the Campbell apparatus throughout the test. The layout of the test facility and the methods of monitor-

Table 1   Chemical analysis of stainless steel condenser tubes

| Tube material(a)	C	Mn	Si	S	P	Cr	Ni	Mo	Cu	Fe
					Composition, wt%					
Type 304 stainless steel ...	0.08	2.00	1.00	0.03	0.045	18.0-20.0	8.0-10.0	...	...	bal
Tube A	0.020 max	1.8	0.5	0.015 max	0.020 max	19.5	25.0	4.5	1.5	bal
Tube B	0.025	1.50	0.50	0.010	0.025	20.25	24.50	6.25	...	bal

(a) Tubes A and B are stainless steels also.
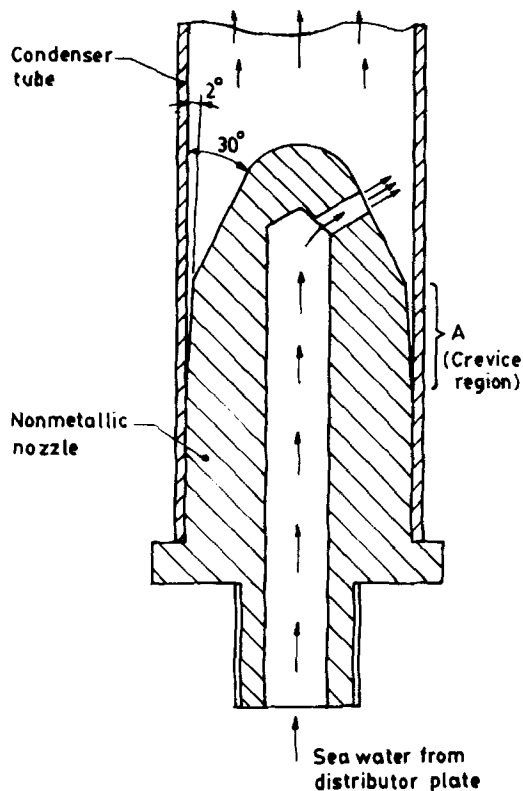
Fig. 1 Campbell corrosion apparatus. Nozzle tapered at location A to create a crevice site between condenser tube and the nozzle in a Campbell corrosion test apparatus.

Table 2 Variation in seawater analysis during exposure of stainless steel tubes

pH	8.5-8.7
Conductivity, mmhos/cm	55.0-75.0
Dissolved oxygen, ppm	5.4-11.0
Ammonia	Nil
Sulfide	Nil

ing seawater chemistry have been described in a previous publication.[7]

Three different types of commercial stainless steel tubes were used: AISI type 304 and two high Cr-Ni-Mo stainless steels. The chemical analyses of the tubes are given in Table 1. Although the AISI type 304 steel is listed by name, the other two stainless steels are only designated tube A and B, respectively. All of the stainless steel tubes were exposed to seawater simultaneously for 30 days, during which time the seawater was analyzed. Seawater analyses are given in Table 2. The amount of silt or suspended matter in the seawater was found to be insignificant enough to cause any corrosion/erosion of tubes during their exposure. The tubes were removed after 30 days and slit open longitudinally to examine the crevice sites. Metallographic investigations were carried out on the nature of inclusions in the two high-alloy stainless steels by using a scanning electron microscope (SEM). Electrochemical corrosion investigation on the pitting susceptibility of the high-alloy
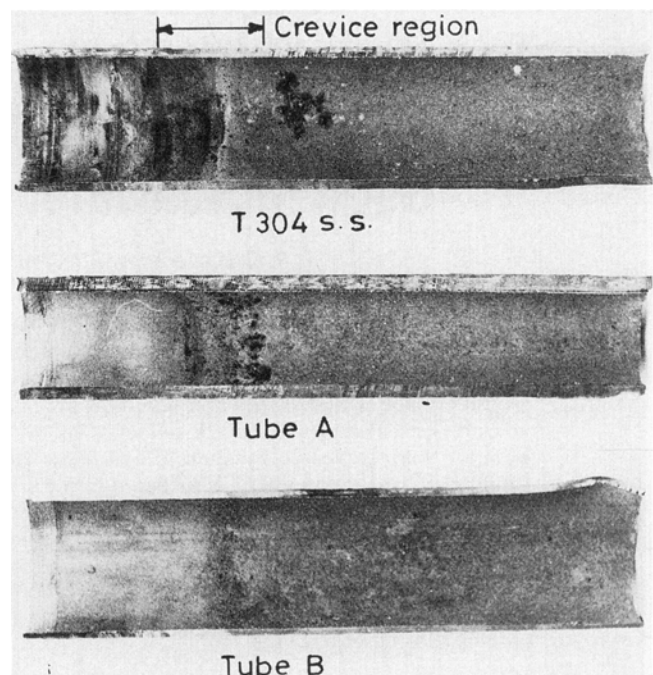

Fig. 2 Relative crevice attack on different stainless steel tubes after exposure in seawater for 30 days.

stainless steels was carried out in synthetic seawater prepared according to ASTM Standard D 1141. Cyclic potentiodynamic anodic polarization curves were recorded for both alloys in a synthetic seawater medium, after stabilization of E_{corr} by starting from E_{corr} and scanning the potential at 1 mV/s up to 1000 mV and then reversing the scan at the same rate back to E_{corr}. All potentials are referred to as saturated calomel electrode (SCE).

3. Results and Discussion

In spite of its established susceptibility to pitting and crevice attack in seawater, type 304 stainless steel was chosen in the current work to be used as a yardstick for comparative evaluation of the performance on the two high-alloy stainless steel tubes, A and B. The seawater analysis carried out during the course of the experiment indicated that the water had sufficient dissolved oxygen to repair any broken film for maintenance of passivity. It is known that crevice corrosion attack usually starts as a differential aeration cell. Slow diffusion of oxygen into the crevice region may not be sufficient to maintain passivity. The surface outside the crevice where sufficient supply of oxygen is available becomes the cathode, whereas the crevice region becomes anodic due to the sluggish supply of oxygen, and thus is unable to maintain passivity.

After exposure in seawater for 30 days, the type 304 stainless steel tube and tube A were severely attacked in the crevice region, and tube B was completely free from such attack. The surface appearance of these tubes is shown in Fig. 2. Although a general rusting was apparent in the crevice region of the type 304 stainless tube, the nature of the crevice attack in tube A was
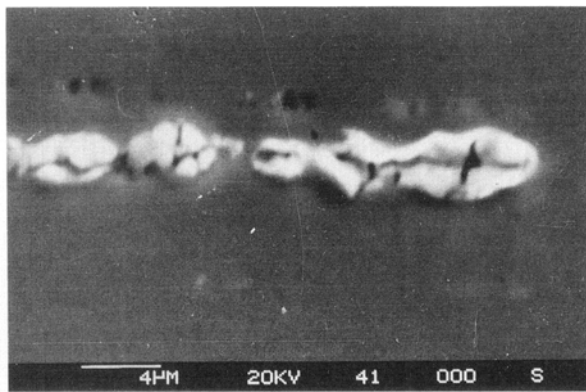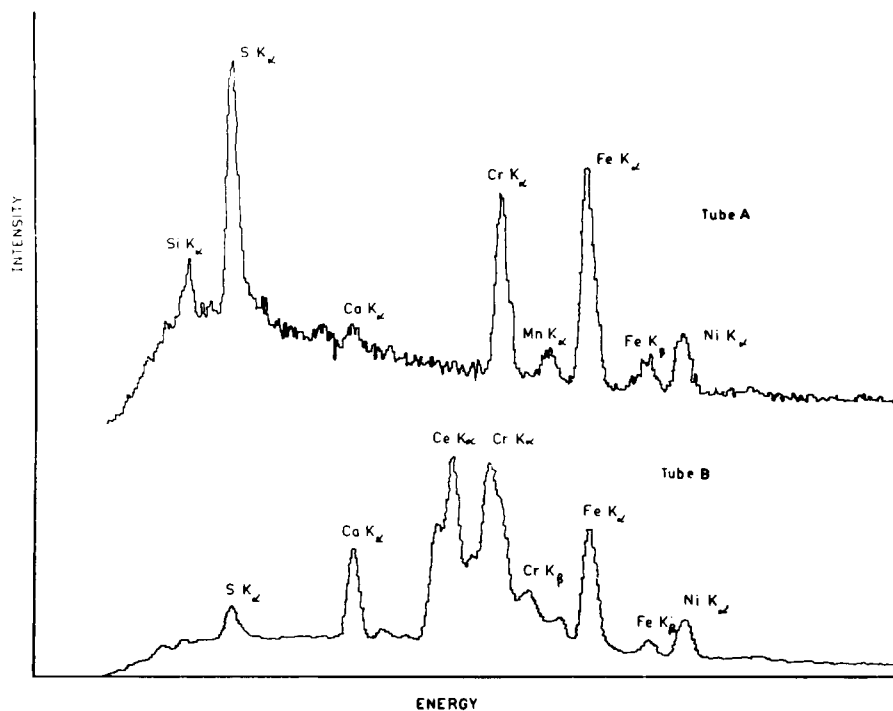
(a)
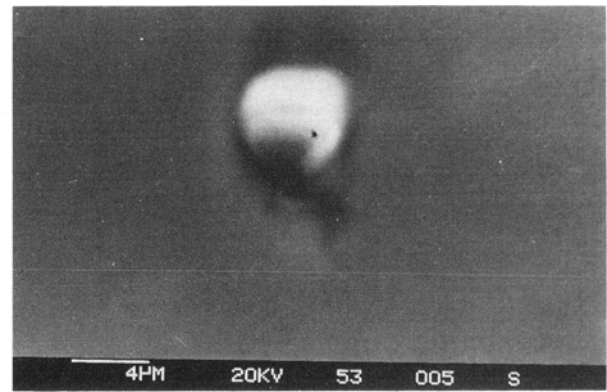
(b)

Fig. 3 Inclusion morphologies of tubes A and B under SEM observation.

Fig. 4 Energy-dispersive X-ray analysis of inclusions shown in Fig. 3.

different. The pits were elongated in nature. It was suspected that an inherent material defect was responsible for elongated pit formation, because 1-month exposure in seawater was not likely to corrode tube A because of its high molybdenum content. Longitudinal sections of tubes A and B were evaluated in the as-polished condition, which revealed evidence of the presence of elongated inclusions in tube A and fine, globular inclusions in tube B. The shapes of these inclusions are shown in Fig. 3. In the SEM micrographs, the elongated inclusions appeared to have formed interconnecting chains that were up to 30 μm long in some places. These inclusions contained cracks. In contrast, the finer inclusions in tube B were globular to elliptical in shape, with an average diameter of less than 5 μm. En-

ergy-dispersive X-ray analysis of the inclusions in tubes A and B was carried out, the results of which are shown in Fig. 4. From the peak positions, it is evident that inclusions in tube A contained predominantly S, Si, Fe, and Cr, in addition to Ca and Mn. The globular inclusions in tube B were characterized by the presence of Ce, Ca, and S, as well as Fe, whereas the Mn peak was barely evident.

Due to the presence of a predominant peak of S in the inclusions in tube A, S content was analyzed in both tubes by means of a LECO carbon-sulfur analyzer, which indicated S contents of 0.004 and 0.007 wt%, respectively, for tubes A and B. Thus, chemical analysis and energy-dispersive X-ray analysis provide an indication of the nature of the inclusions. The inclu-
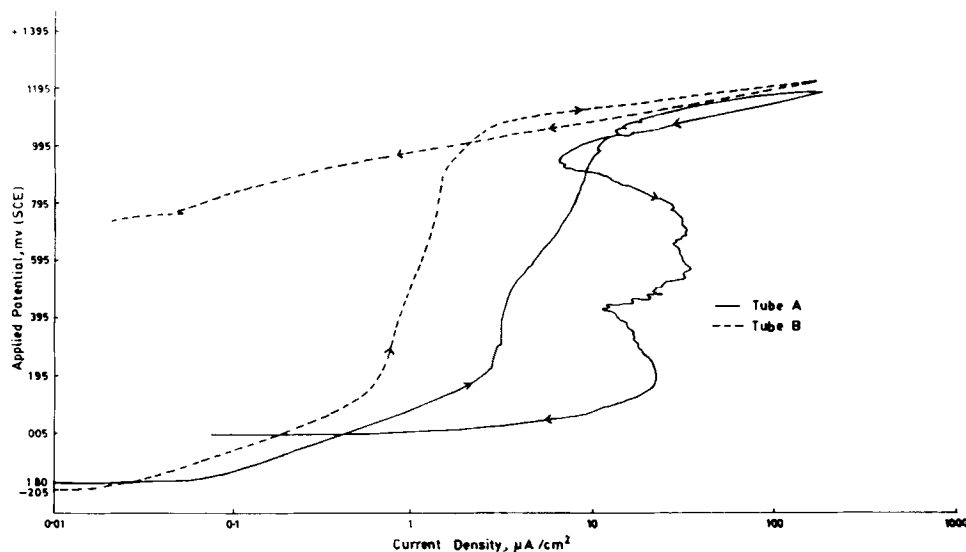
Fig. 5 Cyclic anodic polarization plots of tubes A and B in synthetic seawater.

sions in tube A were characterized by the dominant peaks of S, Ca, and Fe and a weak peak for Mn. Fe and Mn are two well-known common sulfide-forming elements. The presence of calcium as one of the dominant elements in the inclusion is probably due to a ladle addition of calcium to deoxidize the steel, leading to the formation of CaS, because the S in steel has a higher affinity for calcium than for iron and manganese. Hence, Ca can be present in inclusions as small amounts of CaS, along with FeS and MnS. Cracking of inclusions as observed in this work is not uncommon and has been reported by Kozasu and Tanaka[8] as occurring at the onset of plastic instability in steel, thus leading to fragmentation of these inclusions. Regardless of the chemical form of these sulfide inclusions (CaS, FeS, or MnS), they are easily soluble in NaCl solution.[3,9] On dissolution of the sulfide inclusions, a cavity thus forms, exposing the bare metal underneath.[10] Formation of the cavity promotes acidification of the solution within it in an autocatalytic manner and pits propagate. This appears to be the mechanism of localized corrosion observed in seawater with respect to tube A.

Freedom from crevice attack in tube B is notable. The apparent absence of inclusions appears to have been achieved by the ladle addition of the rare earth elements to deoxidize the steel, which otherwise could not be achieved in tube A. Not only do the rare earth elements form several oxides (e.g., La_2O_3, Ce_2O_3), but sulfides (e.g., LaS, CeS) and oxysulfides ($La_2O_2S_2$, $Ce_2O_2S_2$) also are formed.[11] Although the oxides are removed in the slag, the minute globular sulfide and oxysulfide particles are evenly dispersed in the casting instead of accumulating at the interdendritic regions, which occurs in absence of rare earth elements.[12] Hence, hardly any stringers or streaks form during hot working. The rare earth sulfides also do not undergo deformation during hot working.

The cyclic anodic polarization plots obtained for both alloys in synthetic seawater are shown in Fig. 5. The corrosion poten-

Table 3 Results of cyclic anodic polarization tests on specimens of tubes A and B in synthetic seawater (25 °C pH = 8.2)

Parameters	Tube A	Tube B
E_{corr} mV (SCE)	−180	−205
E_{break} mV (SCE)	+1050	+1045
E_{prot} mV (SCE)	...	+975
Limiting current density, μamps/cm^2	28	0.7
Comments	Intense localized attack	Resistance to pit propagation

tial, E_{corr}, of tube B was slightly more active by about 20 mV compared to tube A. Even though the E_{corr} was more active for tube B, the cyclic polarization scan clearly shows that this alloy resists localized corrosion by exhibiting the reverse scan below the forward scan. On the other hand, tube A in spite of exhibiting a slightly more noble corrosion potential (E_{corr} for tube B is −205 mV, and E_{corr} for tube A is −180 mV) exhibits a reverse scan above the forward scan, thereby indicating its poor repassivation kinetics. However, both alloys exhibit high breakaway potential, E_{break} (in this case the transpassive breakdown potential). It is important to note that in spite of the high transpassive breakdown potential and high molybdenum content, tube A exhibited poor repassivation behavior and exhibited polarization characteristics typical of localized corrosion susceptibility. The data obtained from Fig. 5 are summarized in Table 3. Thus, the electrochemical data are in conformity with the relative merits of these alloys under field trial conditions.

Notice that S content in tube B was higher (0.007 wt%) than that in tube A (0.004 wt%). In spite of the higher S content, tube B did not experience any crevice attack. This improved resistance to localized attack appears to have been possible due to a ladle addition of rare earth elements to deoxidize the steel. Therefore, the enhanced S content is not as critical as the shape

and composition of the sulfide inclusions in promoting localized corrosion.

4. Conclusion

Both field trial and electrochemical studies have shown that sulfide stringers can promote localized corrosion in stainless steel. Globularization of sulfides by rare earth element addition can minimize localized corrosion of stainless steel in seawater. High-alloy stainless steel condenser tubes should be free from sulfide stringers for seawater service.

Acknowledgments

References

1. J.C. Gudas and H.P. Hack, *Corrosion*, Vol 35, 1979, p 68

2. B.C. Syrett, D.D. Macdonald, and S.S. Wing, *Corrosion*, Vol 35 (No. 9), 1979

3. M. Kesten, *Corrosion*, Vol 32 (No. 3), 1976

4. W.B. Lawrence et al., "Steam Plant Surface Condenser Study," EPRI Report, EPRI NP/48, 1977

5. T. Otsu and M. Okawa, *Sumitomo Light Metal Tech. Rep.*, Vol 3 (No. 3), 1962, p 205-224

6. H.S. Campbell, "The Campbell Condenser Tube Test Apparatus," Report No. MP 577 and Drg. No. M.U.C.S./002, British Nonferrous Metals Technology Centre, 1973

7. N. Mukhopadhyay and S. Baskaran, *Corrosion*, Vol 42 (No. 2), 1986, p 113

8. I. Kozasu and J. Tanaka, in *Sulphide Inclusions in Steels*, J.J. deBarbadillo and E. Snape, Ed., American Society for Metals, 1975, p 288-292

9. G. Wranglan, *Localized Corrosion*, R.W. Staehle et al., Ed., National Association of Corrosion Engineers, 1974, p 466

10. Z. Szklarska-Smialowska, in *Sulphide Inclusions in Steels*, J.J. deBarbadillo and E. Snape, Ed., American Society for Metals, 1975, p 380-402

11. S.K. Saxena, in "International Symposium on Modern Developments in Steel Making," Jamshedpur, India, 1981

12. E.T. Turkdogan, in *Sulphide Inclusions in Steels*, J.J. deBarbadillo and E. Snape, Ed., American Society for Metals, 1975, p 17