

Localized Corrosion Studies on Materials Proposed for A Safety-Grade Sodium-to-Air Decay-Heat Removal System for Fast Breeder Reactors

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The present investigation was carried out to assess the localized corrosion resistance of materials proposed for the construction of the safety-grade sodium-to-air decay-heat removal system for fast breeder reactors. The materials, such as Alloy 800, 9Cr-1Mo steel, and type 316LN stainless steel, in different microstructural conditions were assessed for pitting and stress-corrosion cracking resistances in a chloride medium. The results indicated that 9Cr-1Mo steel in the normalized and tempered condition can be considered for the above application from the standpoint of corrosion resistance.

Key Words

Alloy 800, breeder reactor materials, corrosion testing,Cr-Mo steel, nuclear power, stress corrosion studies, type 316LN stainless steel

1. Introduction

The 500-MWe prototype fast breeder reactor (PFBR) to be set up in India is a pool type of reactor in which liquid sodium is used as a coolant. Sodium from the primary circuit transfers the heat to the secondary system from where the heat is again transferred to the steam generator to produce steam for running the turbine. During periods of emergency and unplanned shutdowns, the heat from the core of the reactor has to be extracted through a safety-grade decay-heat removal (SGDHR) system comprised of numerous sodium-to-air heat exchanger units.[1] The basic design requirements for the construction of safety-grade decay-heat removal systems are that (1) no pumps, blowers, or valves except dampers should be used, (2) the ultimate heat sink should be air, (3) the system should remove heat directly from the pool of sodium, and (4) the loops should be independent and located in different buildings.[2] The maximum temperature of sodium in the pool is around 815 K, and hence, each loop should be designed for 8 MWt for a hot pool sodium temperature of 815 K.

The coastal atmosphere of the proposed construction site of the prototype fast breeder reactor in Kalpakkam has significant seasonal fluctuations in the salt content of the atmosphere.[3] Because the components would be exposed to the marine atmosphere during fabrication, storage, and between intermittent operation of the decay-heat removal system, deposition of salt over the surface of the component could lead to severe damage due to corrosion.[4] Hence, the materials of construction for the sodium-to-air heat exchangers have to be chosen with utmost care, because their failure could lead to the leakage of sodium into the atmosphere. In the present work, a comparative evaluation of the corrosion behavior of the candidate materials—namely Alloy 800, type 316LN stainless steel, and 9Cr-1Mo steel in different heat treatment conditions—has been attempted to assess their corrosion resistance in a simulated marine atmosphere.

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2. Experimental

2.1 *Materials and Heat Treatment*

The chemical compositions of the materials used in the present work are given in Table 1. The 9Cr-1Mo specimens measuring 120 × 10 × 1.2 mm and 10 × 10 × 1 mm were machined from a thick forged material for stress-corrosion cracking and pitting corrosion studies, respectively. The following heat treatments were given to obtain different microstructural conditions: (1) 1223 K, 15 min, and air cooled, or normalized (This heat treatment was assumed to represent the microstructure in welded condition except for the grain growth region.); (2) 1223 K, 15 min, and water quenched, or hardened, and (3) normalized, heat treated at 1023 K, 1 h, and air cooled, or normalized and tempered.

Alloy 800 specimens 120 × 10 × 2 mm were prepared for stress-corrosion cracking studies from the as-received mill annealed material, and the following heat treatments were given to obtain solution annealed and sensitized conditions: (1) 1323

Table 1 Chemical composition of materials

Element	9Cr-1Mo steel	Alloy 800	Type 316LN stainless steel
Chromium	9.27	19.2	17.9
Nickel	...	30.4	12.12
Carbon	0.09	0.07	0.025
Molybdenum	1.05	...	2.45
Silicon	0.75	0.42	0.975
Manganese	0.67	0.74	1.76
Sulfur	0.003	0.001	0.002
Phosphorus	0.02	...	0.026
Copper	...	0.05	...
Cobalt	...	0.13	...
Vanadium	...	0.05	...
Titanium	...	0.52	...
Aluminum	...	0.49	...
Nitrogen	...	...	0.068

K, 30 min, and 1253 K, 1 h, and water quenched, or solution annealed; and (2) solution annealed and heat treated at 823 K, 100 h, or sensitized. Type 316LN stainless steel alloy specimens 120 × 10 × 2 mm and 10 × 10 × 2 mm were prepared in the solution annealed (1323 K, 1 h) as well as in the solution annealed and sensitized (923 K, 200 h) conditions.

2.2 *Pitting Corrosion Studies*

Pitting corrosion studies were carried out only on type 316LN stainless steel and 9Cr-1Mo steel in different microstructural conditions. Type 316LN stainless steel specimens were tested in the solution annealed as well as in the sensitized conditions in an acidic chloride medium containing 0.5 *M* NaCl and 0.5 *M* H_2SO_4. 9Cr-1Mo specimens in the normalized and tempered conditions were evaluated for their corrosion resistance in 0.5, 0.1, and 0.05 *M* NaCl media.

Potentiodynamic anodic polarization studies on specimens of the above materials were carried out in the respective test solutions at room temperature using a Wenking Potentioscan Model POS 73. The critical pitting potential, E_{pp}, above which stable pits were nucleated at an anodic current density of 25 μA/cm^2, was determined for specimens exhibiting active-passive transition.[5,6] The electrode potentials were measured with respect to a saturated calomel electrode (SCE). After the tests, the specimens were observed using an optical microscope and a scanning electron microscope (SEM) to examine the morphology of corrosion attack.

2.3 *Stress-Corrosion Cracking Studies*

Stress-corrosion cracking experiments were carried out in 5 *M* NaCl and 0.05 *M* NaCl solutions using constant strain (U-bend) specimens of all the materials prepared as per ASTM G-30 standard procedure.[7] The specimens were exposed to alternate wet-and-dry conditions, namely immersing them in the test solution for 7 days and then exposing them to normal atmosphere for the next 7 days alternatively in a cyclic manner. This was to simulate the fluctuating marine atmosphere encountered during service. The specimens were periodically inspected for the presence of pits, cracks, etc. The tests were continued until the specimens cracked, or for sufficiently long durations until significant changes in the surface morphology of the bent region were observed. Specimens that failed, as well as those that underwent long cycles of exposure without failure in stress-corrosion cracking tests, were examined in the SEM and optical microscope.

3. Results and Discussion

3.1 *Pitting Corrosion*

The results of the polarization experiments for type 316LN stainless steel are shown in Fig. 1. Specimens in the solution annealed condition showed excellent resistance to pitting corrosion in the acidic chloride medium. The E_{pp} value (+940 mV) exhibited by the specimen indicated its good pitting corrosion resistance in chloride medium. However, the E_{pp} value of the sensitized specimens decreased to +610 mV, indicating deterioration in pitting corrosion resistance upon sensitization. The SEM observations of specimens showed pitting attack around the inclusions present in the solution annealed specimens and along grain boundaries and triple points in the sensitized specimens (Fig. 2).

In the case of the 9Cr-1Mo steel specimens, uniform corrosion attack with a dark colored thick film on the surface was noticed in 0.5 and 0.1 *M* NaCl solutions. However, in 0.05 *M* NaCl solution, the specimens initially exhibited passivity and then pitting attack was observed at −145 mV (Fig. 3a to c). It is possible that 9Cr-1Mo steel may exhibit a temporary passivity in aqueous solutions containing low levels of chloride ions and thus undergo pitting corrosion. Pitting type of attack in 9Cr-1Mo steels in acidic sulfate or chloride solutions has been reported in the literature.[8] It is well known that pits can act as a precursor to the initiation of stress corrosion and corrosion fatigue cracks.[9,10] Hence, there is a possibility that the presence of pits may increase the stress-corrosion cracking susceptibility of high-strength normalized 9Cr-1Mo steel during service. Optical microscopic observations of the specimens showed severe corrosion attack on their surfaces.

3.2 *Stress-Corrosion Cracking*

The results of the stress-corrosion cracking experiments are given in Table 2. The hardened 9Cr-1Mo steel cracked after 720 h. The surface of the specimen appeared bright, indicating that there was little general corrosion. The time between the crack initiation and failure of the specimen was only 8 h (maximum), indicating a crack growth rate on the order of 3.3×10^{-4} ms^{-1}.

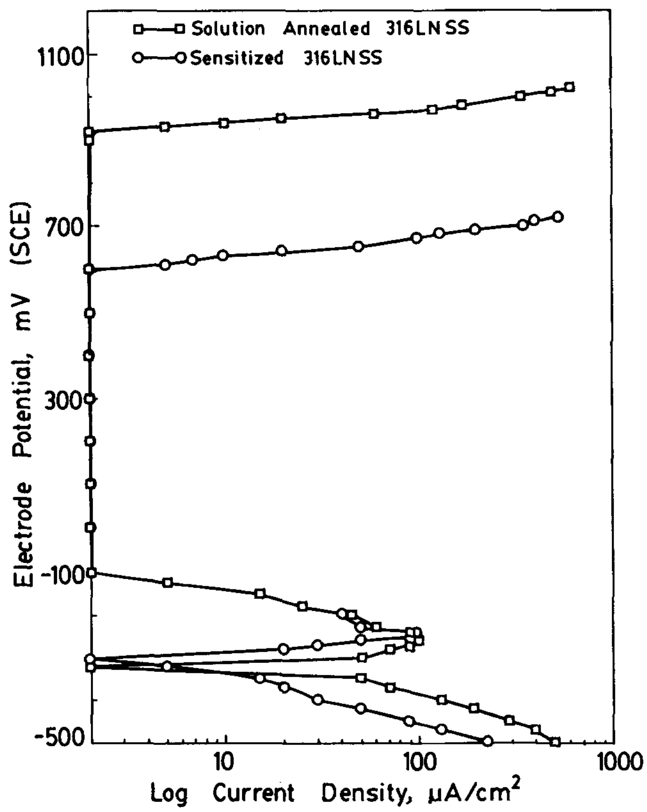


Fig. 1 Potentiodynamic anodic polarization curves obtained for type 316LN stainless steel in acidic chloride medium.

The SEM observation of the fractured surface showed that the crack had initiated in an intergranular mode and propagated in a mixed (intergranular and transgranular) mode (Fig. 4a and b). Propagation of the crack was found to be along the prior austenite grain boundaries.

The normalized specimens were exposed in both 5 and 0.05 *M* NaCl solution to determine whether the difference in the chloride ion concentration had any influence on stress-corrosion cracking resistance. It was found that the normalized specimens tested in 5 *M* NaCl solution failed after 4125, 1875, and 2400 h in three different tests, whereas those tested in 0.05 *M* NaCl solution failed after 1900 and 1475 h. From the above results, it is clear that the chloride ion concentrations in this range does not lead to any significant difference in stress-corrosion cracking susceptibility. However, in the presence of a low level of chloride ions, there is a tendency toward a decrease in the time-to-failure. This can be explained on the basis of the tendency of 9Cr-1Mo steel to pitting attack in low concentrations of chloride ions. During the stress-corrosion cracking tests in 0.05 *M* NaCl solution, many pits were observed on the surface, and no general corrosion was observed. However, in the case of the normalized specimen tested in 5 *M* NaCl solution, severe general corrosion with thick rust layers was observed. Examination of the fractured surfaces in an SEM revealed severe localized attack at many locations near the edge, thus indicating that the pits acted as the crack initiation points in both cases. It was found that the crack initiated in an intergranular mode, propagated in a mixed mode, and failed in a transgranular mode as in the case of hardened steel (Fig. 5a and b). Secondary cracking was also noticed in specimens tested in 5 *M* NaCl solution (Fig. 6a and b). In the case of normalized and tempered specimens, failure was observed after 7000 h. The surface was severely corroded with the presence of layers of loose rust. A notable decrease in the thickness of the specimen was also observed after removing the layers of rust. When a cross section of a failed specimen was observed in an optical microscope, the specimen was found to have failed due to general corrosion (Fig. 7).

The specimens of Alloy 800 in the mill annealed condition did not fail in the stress-corrosion cracking test up to 14,000 h. Specimens in both the solution annealed and sensitized conditions also did not fail up to 10,000 h, and no pits or crevices

Table 2 Stress-corrosion cracking

Material	Heat treatment	Environment	Results
9Cr-1Mo steel	1223 K, 15 min, WQ (hardened)	5 *M* NaCl	Cracked after 720 h
	1223 K, 15 min, AC (normalized)	5 *M* NaCl	Cracked after 4125
	1223 K, 15 min, AC (normalized and tempered)	0.055 *M* NaCl	Cracked after 1900 and 1475 h
	1223 K, 15 min, AC + 1023 K, 1 h, AC	5 *M* NaCl	Failed by general corrosion after 7000 h
Alloy 800	As-received (mill-annealed)	5 *M* NaCl	No cracking up to 14 000 h
	1323 K, 30 min, WQ + (solution annealed)	5 *M* NaCl	No cracking up to 10 000 h
	1253 K, 1 h,WQ		
Solution annealed + (sensitized)	823 K, 100 h	5 *M* NaCl	No cracking up to 10 000 h
Type 316LN stainless steel	1323 K, 1 h, WQ (solution annealed)	5 *M* NaCl	No cracking up to 10 000 h
	1323 K, 1 h, WQ (sensitized)	5 *M* NaCl	No cracking up to 4000 h
	923 K, 200 h		Pits on the surface after 2000 h

Note: WQ, water quenched; AC, air cooled

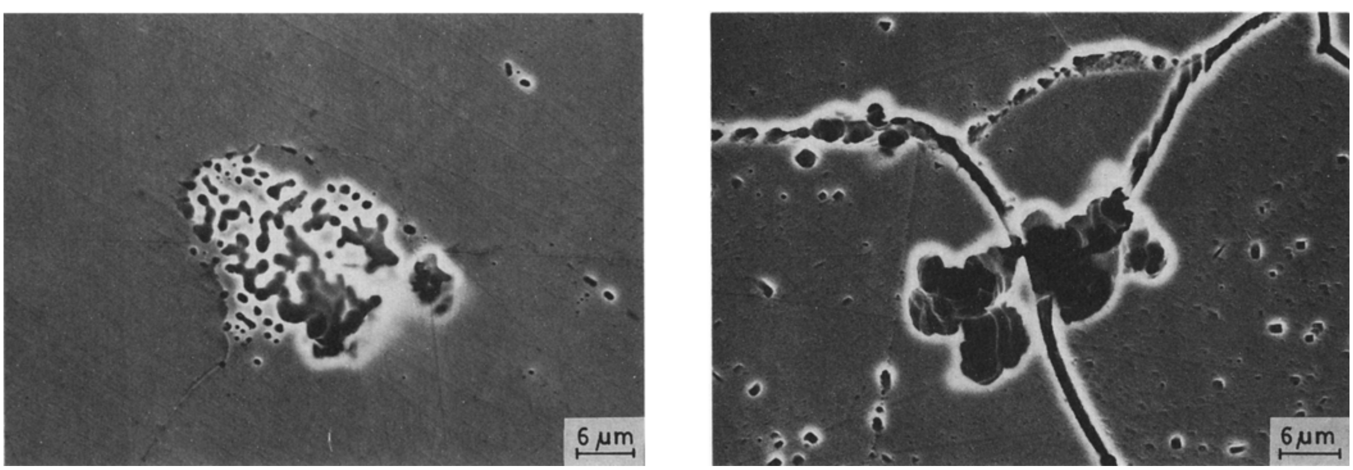
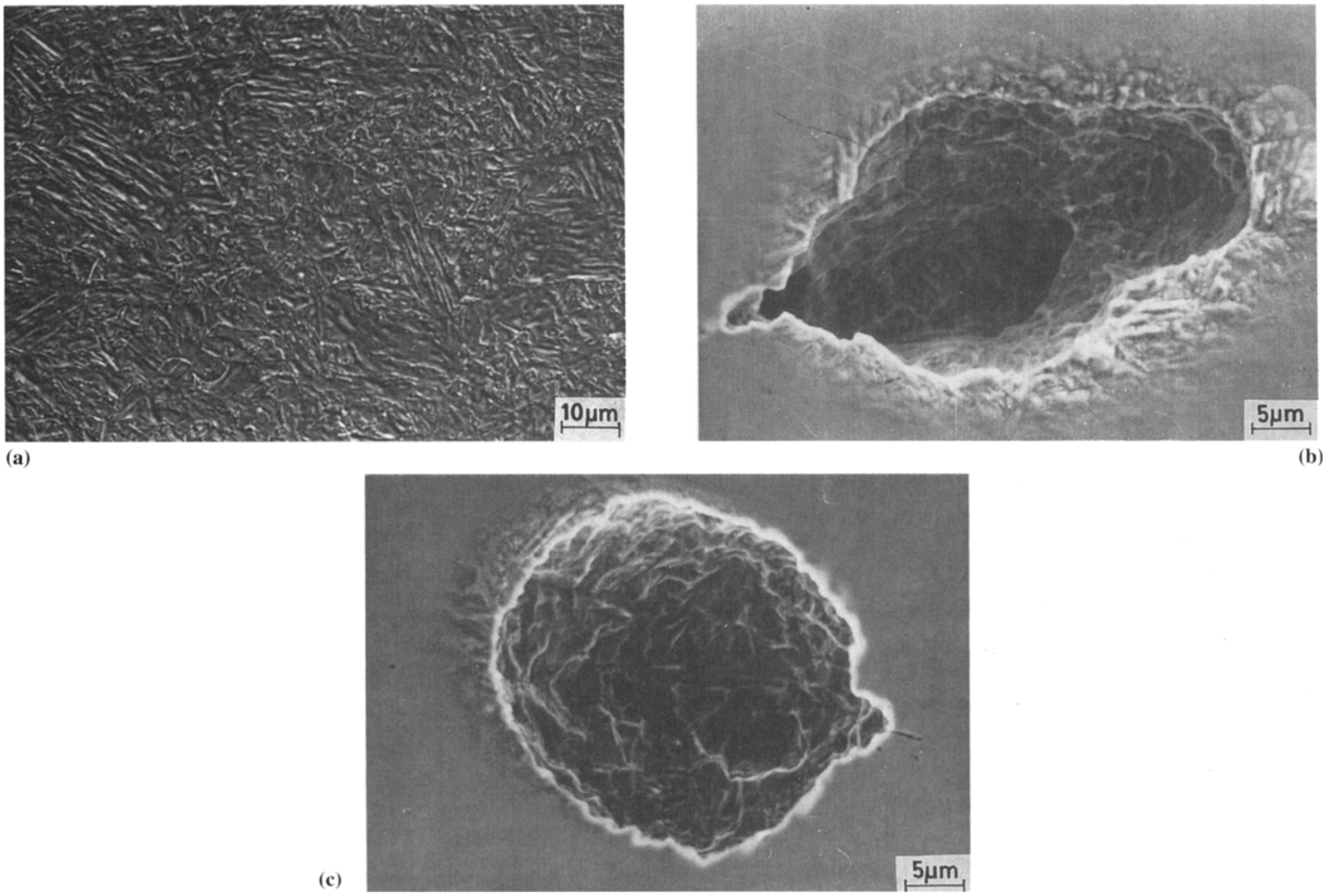
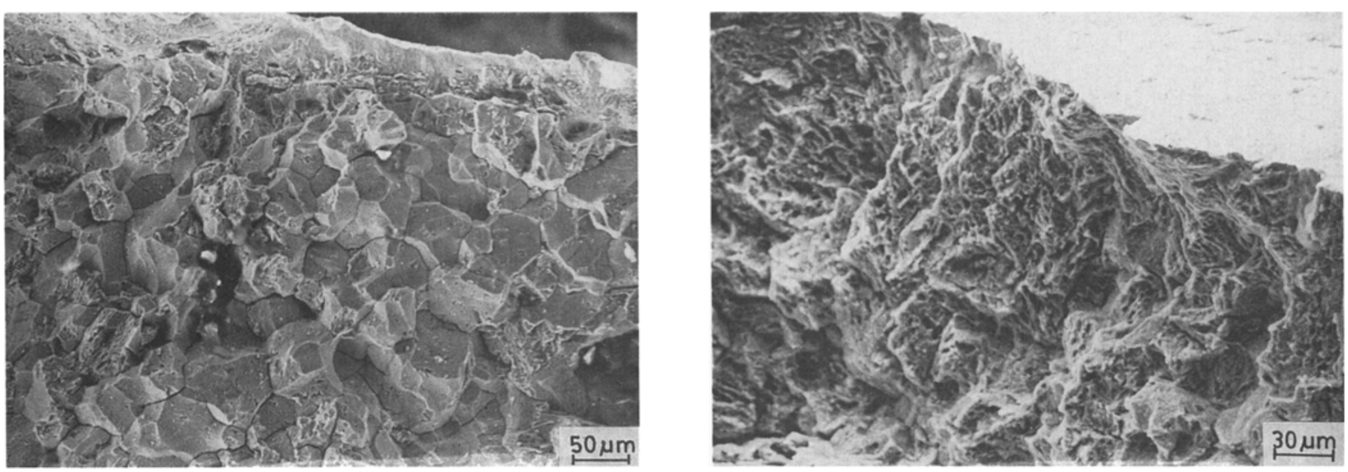


Fig. 2 SEM micrographs of type 316LN stainless steel. **(a)** In the solution annealed condition showing pitting attack at inclusions. **(b)** In the sensitized condition showing pitting attack at the grain boundary.



(a) (b) (c)

Fig. 3 SEM micrographs of 9Cr-1Mo steel. **(a)** General corrosion in 0.5 *M* NaCl medium. **(b)** and **(c)** Pitting attack in 0.05 *M* NaCl medium.



(a) (b)

were observed on the surface. The specimens of type 316LN stainless steel also did not fail after up to 10,000 h of exposure to 5 *M* NaCl solution. However, sensitized specimens exhibited pits at the bend region of U-bend specimens after 2000 h of exposure.

3.3 *Localized Corrosion Resistance*

A number of failures due to pitting and stress-corrosion cracking of austenitic stainless steels in marine atmosphere both in the sensitized and unsensitized conditions have been reported.[4,11-13] Type 316LN stainless steel, due to its nitrogen content, has been reported to generally possess excellent resistance to sensitization.[14,15] However, during long exposures of more than 30 years in designed service-life applications, these steels also will become sensitized and would develop similar susceptibility to intergranular corrosion and intergranular stress-corrosion cracking similar to that of conventional austenitic stainless steels. The minimum operating temperature of the safety-grade decay-heat removal is expected to be maintained around 473 K during shutdown. Even at this temperature, stainless steels can undergo chloride stress-corrosion cracking. It has been reported that, only above about 533 K, chloride salts lose their water of hydration. Consequently, stainless steels are immune from chloride stress-corrosion cracking.[16] In the present investigation, however, only pitting of the sensitized type 316LN stainless steel was noticed after 2000 h of exposure to 5 *M* NaCl solution at ambient temperature.

It is well known that high-strength steels are prone to stress-corrosion cracking and hydrogen embrittlement at ambient temperatures.[17-21] They can fail even in pure water at room temperature.[21] Failure of all of the specimens in the hardened as well as normalized condition shows that 9Cr-1Mo steel behaves similarly to other high-strength steels. In the tempered condition, only general corrosion (failure due to thinning) was apparent. Such general corrosion leading to thinning of the material during manufacturing, commissioning, and service is not likely. In the present work also, no failure of Alloy 800 specimens was observed, even after 14,000 h of exposure at room temperature. Therefore, it can be concluded that the overall ranking of materials in decreasing order of corrosion resistance is Alloy 800, 9Cr-1Mo steel (normalized and tempered), type 316LN stainless steel, and 9Cr-1Mo steel (normalized). Because 9Cr-1Mo steel in the hardened condition exhibited a tendency to crack, it need not be considered for the present application.

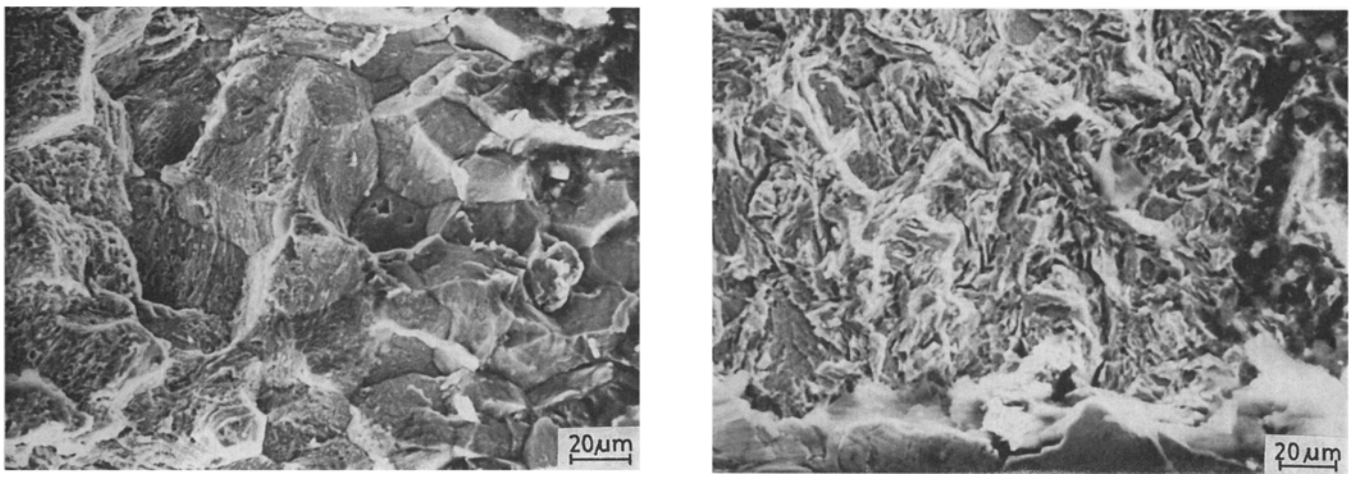


Fig. 5 SEM micrographs of stress-corrosion cracking tested 9Cr-1Mo steel in the normalized condition. **(a)** Crack initiation by intergranular mode. **(b)** Final failure by transgranular mode in 0.05 *M* NaCl medium.

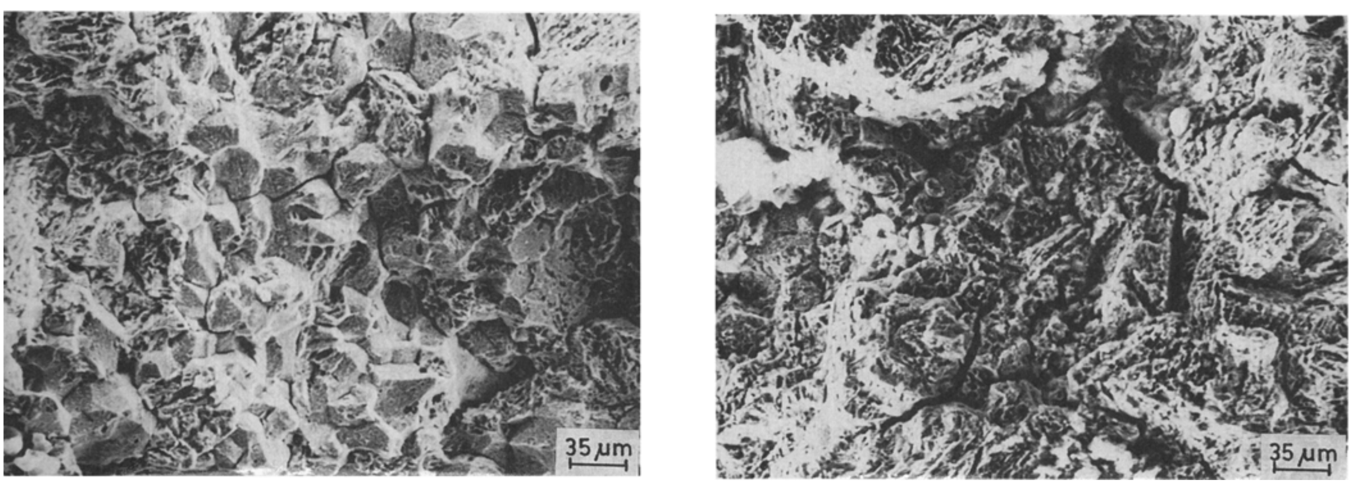


Fig. 6 SEM micrographs of stress-corrosion cracking tested 9Cr-1Mo steel in the normalized condition. **(a)** Mixed (intergranular + transgranular) mode. **(b)** Transgranular mode with secondary cracking in 5 *M* NaCl medium.

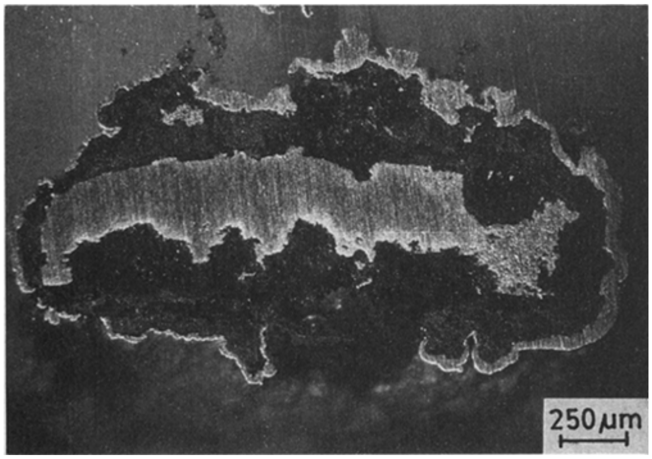


Fig. 7 Optical micrograph showing corrosion products formed on the normalized 9Cr-1Mo steel, which failed by thinning due to general corrosion in 5 *M* NaCl medium.

4. Summary

9Cr-1Mo steel, Alloy 800, and type 316LN stainless steel specimens were evaluated for their corrosion resistance to select the materials of construction for safety-grade sodium-to-air heat exchangers. Corrosion tests were conducted in acidic chloride and neutral concentrated chloride media at room temperature. The following results were obtained.

9Cr-1Mo steel in the as-received condition (normalized and tempered) exhibited temporary passivity and pitting in 0.05 *M* NaCl solution and underwent general corrosion in 0.5 and 0.1 *M* NaCl solutions. Type 316LN stainless steel specimens exhibited excellent pitting corrosion resistance; however, upon sensitizing at 923 K for 200 h, pitting corrosion resistance deteriorated.

9Cr-1Mo steel in both the hardened and normalized conditions failed by stress-corrosion cracking in 5 and 0.05 *M* NaCl solutions, whereas in the normalized and tempered condition the specimens failed by general corrosion in 5 *M* NaCl medium. The stress-corrosion cracks initiated in the intergranular mode and exhibited transition to a mixed mode of failure in both the hardened and normalized conditions. Pits were found to act as crack initiation points for stress-corrosion cracking. In the normalized and tempered condition, general corrosion lead to thinning of the specimens. Alloy 800 did not fail after exposure of up to 14,000 h in the as-received condition and after up to 10,000 h in the solution annealed as well as sensitized conditions in 5 *M* NaCl solution. Type 316LN stainless steel in the solution annealed condition did not fail after up to 10,000 h of exposure to 5 *M* NaCl solution, whereas the sensitized specimens developed pits after 2000 h of exposure. Compared to type 316LN stainless steel, Alloy 800 exhibited better corrosion resistance.

From the present investigation, use of 9Cr-1Mo steel in the normalized and tempered condition is recommended as the material of construction for safety-grade sodium-to-air heat exchangers from the standpoint of corrosion resistance.

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