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Corrosion Failures in Marine Environment

R. KRISHNAN
Naval Chemical & Metallurgical Laboratory, Bombay-400 023

Abstract. This paper gives a brief description of typical marine environments and the most common form of corrosion of materials used in this environment. Some typical case histories of failures pertaining to pitting, bimetallic corrosion, dealloying, cavitation and stress corrosion cracking are illustrated as typical examples of corrosion failures.

1. Introduction

Seawater covers more than 70 per cent of the earth's surface and many common metals and alloys are attacked by seawater or mist-laden sea air. A classification of typical marine environments is given[1] in Table 1. Seawater is a complex, delicately balanced solution of many salts containing living matter, suspended silt, dissolved gases etc. and as such the individual effect of each of these factors affecting the corrosion behaviour is not readily separable.

The most common forms of corrosion are galvanic corrosion, pitting and crevice attack. Because seawater is an excellent electrolyte, severe corrosion often occurs when two different metals are coupled together and exposed to a marine environment. The degree of attack depends on the relative position of the two metals in the galvanic series for seawater. Crevice attack is usually most serious under immersed conditions or in the splash zone. Metals that require plenty of oxygen to continuously repair the breaks in oxide film and thus maintain passivity tend to be susceptible to crevice attack in seawater. Crevices are developed because of design features such as gaskets, washers, rivets etc. It may also be formed by marine fouling organisms settling on the surface. Pitting on metals exposed to the atmosphere may be initiated by discrete salt particles or atmospheric contaminants. Surface features such as inclussions, breaks in the protective film, segregation etc., may also be involved in the initiation of pitting.

Some typical case histories of failures which the Naval Chemical & Metallurgical Laboratory (NCML), Bombay, has studied are discussed below.

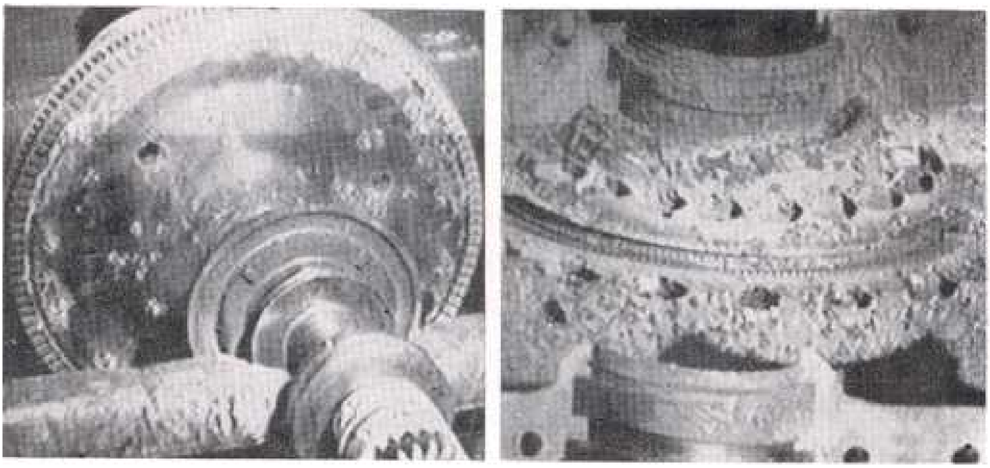
Table 1 Classification of marine environment

S. No.	Marine zone	Description of environment	characteristic corrosion behaviour of steel
	Atmosphere (above splash)	Particles of salt are carried by wind, hence corrosivity varies with height above water, wind velocity, direction etc. Solar radiation may stimulate photo sensitive corrosion reactions. Amount of rainfall and distribution during a time period affects corrosion rate. Tropical marine environments are more corrosive than arctic.	Sheltered surfaces may deteriorate more rapidly than those boldly exposed. Coal dust combined with salt seems to be more corrosive to steel.
2.	Splash Zone	Wet, well aerated surface, no fouling.	Most agressive zone for steels. Difficult to maintain protective coatings.
	Tide zone	Marine fouling is apt to be present. Ample oxygen is available.	Steel in this zone may act cathodically.
	Shallow water	Seawater is usually saturated with oxygen. Pollution, fouling etc. may play an active role.	Corrosion may be more rapid than in marine atmosphere.
5.	Deep Ocean	Oxygen varies, tending to be much lower than at surface. pH is also lower than at surface.	Steel corrosion is often less. Consumption of sacrificial anode is greater deep down.
6.	Mud	Bacteria are often present.	Mud is usually corrosive. Partly embedded panels tend to be rapidly attacked.

2. Pitting

As the name itself implies, pitting is due to localised corrosion as opposed to general corrosion where the metal dissolves uniformly all over the surface. This type of corrosion proceeds with the formation of holes or pits which puncture the passive layer on the metal without much appreciable widening of the attacked area. It is well established now that the occurrence of pitting requires the presence of aggresive anions like chloride, bromide, iodide or oxyhalide in the environment[2]. It is also known that a stagnant medium causes more severe pitting than the flowing one and increased velocities of fluid flow often decreases pitting attack. Pitting generally requires an extend initiation period ranging from several months to even years.

Pitting corrosion observed on the impeller and housing of a two-stage steam turbine after a very short service is shown in Fig. 1. The impeller was made of martensitic grade stainless steel, while the casing was made of plain carbon steel. The turbine was run by super saturated steam. Special quality boiler feed water was converted to steam and fed to the impeller of the steam turbine. Then, the heat of the low pressure



(a) (b)

Figure 1 (a & b). Typical chloride pitting of impeller and housing.

steam was abstracted from it by cooling in seawater in the condenser and water was recirculated. It was observed that the chloride content of the fresh water was more than the specified limits, suggesting that the chloride induced pitting was due to an ingress of seawater through the condenser leakage.

3 Bimetallic Corrosion

When dissimilar metals are in electrical contact in an electrolyte, the less noble metal (anode) is attacked to a greater degree than if it were exposed alone. Similar is the case with the more noble metal (cathode). This behaviour, known as galvanic corrosion, can often be recognised by the fact that corrosion is severe near the junction of the two metals than elsewhere on the metal surfaces. The greater the difference in potential between the two metals, the more rapid will be the galvanic attack.

The aluminium impeller of a pump of a closed loop fresh water recirculating system which has suffered corrosion damage is shown in Fig. 2. The impellers were of a main engine driven pump used to circulate fresh water with 1-2 per cent potassium dichromate to the main engine cylinder liners for cooling. The heat of the warm water was extracted by passing it through the copper coils immersed in seawater. A rubber gasket was provided at each joint between the copper and aluminium tubes.

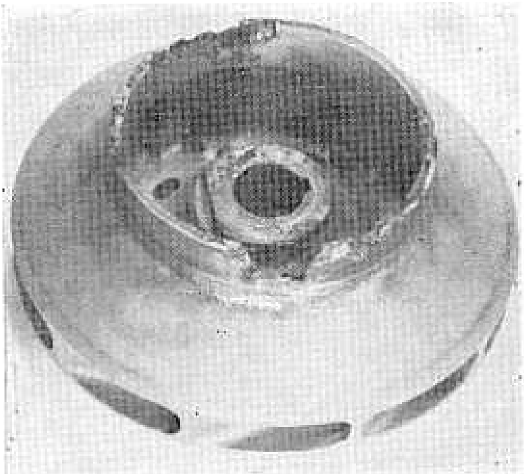


Figure 2. Aluminium impeller failed in service due to galvanic attack.

Chemical analysis of the material of construction of the impeller and the housing revealed that they were of Al-Si alloy as per design specifications. The chemical analysis of the water indicated the presence of copper in the ppm range. The *pH* of the solution was found to be 4.7. Dissolution of copper takes place in the acidified medium. In the stagnant condition, the dissolved copper had formed a galvanic coupling with the aluminium alloy in the electrolyte, thereby leading to the corrosion of less noble aluminium.

4. Dealloying

Dezincification of copper-zinc alloys is the most commonly experienced form of dealloying. Dealuminification of aluminium bronze and denickelification of copper-nickel alloys also comes under this category[3]. Dezincification normally occurs in brasses which contain more than 15 per cent zinc. This is found not only in seawater but also in brackish and fresh water[4].

The crack in the outlet tube end of a forced draught blower of a lubricating oil cooling system made from Muntz metal (60 : 40 brass) is shown in Fig 3. The lubricating oil at a temperature of 60°C is being cooled by seawater passing outside the tube at a pressure of 15 psi. On visual examination, radial cracks with raddish corrosion deposits were observed on the surface. Metallographic examination revealed clear evidence of dezincification. The salinity of seawater coupled with the high temperature was responsible for this failure.

5. Cavitation

As mentioned earlier, cavitation occurs when the material has to stand the impact arising out of collapse of vapour/air bubbles in the fluid. Generally this type of damage is encountered by propellers, cylinder liners, impellers etc.

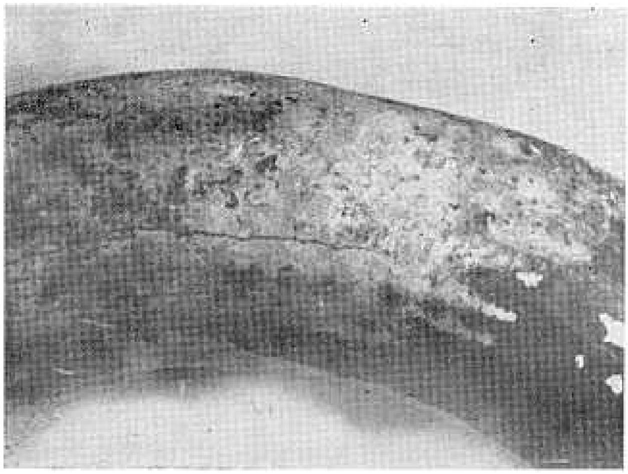


Figure 3. Crack and deposits in a Muntz metal tube.

The cavitation damage suffered by a four pitched propellor blade made of aluminium bronze conforming to BS 1400 AB2 is shown in Fig. 4. The propeller was working at an average speed of 600 rpm. It has been reported that with increase in speed of the propeller gross cavitation can be expected to occur at shorter time periods.

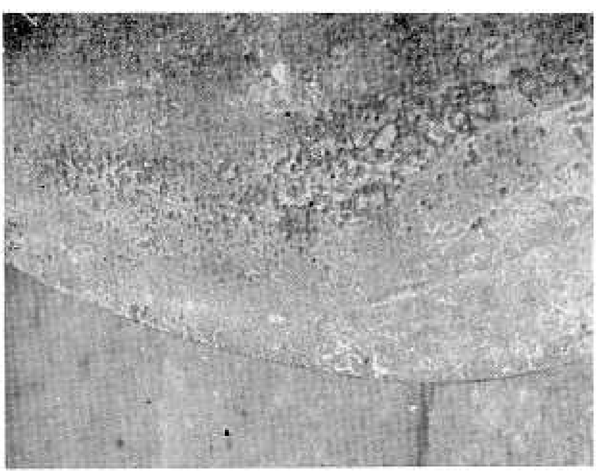


Figure 4. Aluminium bronze propeller blade showing typical cavitation.

6. Stress Corrosion Cracking

Metallic materials when subjected to the conjoint action of a corrosive environment and mechanical stress can, under certain conditions, cause catastrophic failure much below the yield stress of the material. Stress corrosion cracking is a spontaneous damage resulting from a complex interplay of corrosive environment, tensile stresses, and crack sensitive path through an alloy. It is also influenced by temperature. Cracking is generally transverse to the direction of the applied stress and may be transgranular or intergranular in nature.

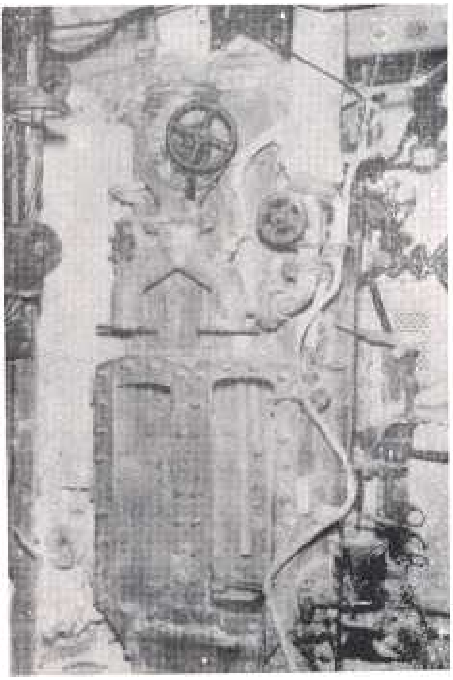


Figure 5. General view of the seawater evaporator.

The general view of the seawater evaporator shell is shown in Fig. 5. It is primarily a heat transfer system, where heat is supplied to the coil by steam and is transmitted to seawater giving fresh water vapour and leaving behind salt and other solid deposits. The evaporator shell was made of 15 inch diameter annealed temper naval brass plate of 3 mm thickness. The shell was fabricated by welding and no postweld stress relieving was reported to have been carried out. Two cracks in the shell body slightly away from the welded zone are shown in Fig. 6. Chemical analysis showed that the tin content of the shell plate was less than the specified minimum of 1.2 per cent. Microstructural examination revealed grain boundary precipitation which was identified to be Cu_3Sn. Abnormal segregation of tin near the crack tip as well as at the grain boundaries was also noticed. Although tin is intentionally added to brass for reducing dezincification, abnormal segregation of tin at the grain boundary has contributed to the failure of the brass in stress corrosion cracking (SCC).

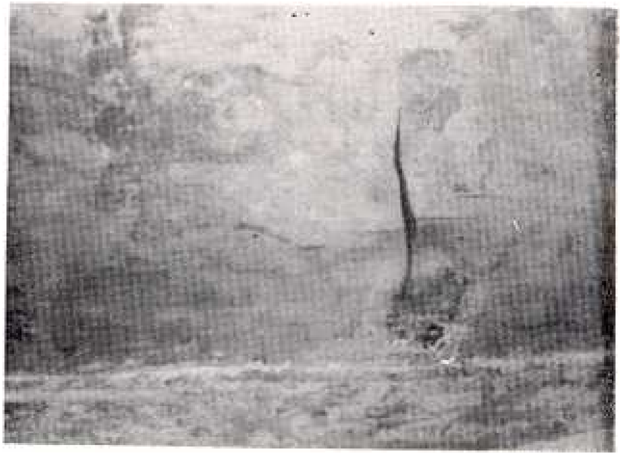


Figure 6. Macrograph showing two cracks on the shell body.

7. Conclusion

The general approach for preventive measures in marine corrosion is either to use inherently corrosion resistant materials or less nobler materials with protective coatings or cladding with superior materials and also by the use of sacrificial anodes or impressed current cathodic protection (ICCP). The NCML at Bombay, while carrying out several failure analysis investigations, has suggested suitable measures to tackle these problems. Development of the aluminium based sacrificial anodes and the lead based ICCP system for the Indian Navy deserves special mention.

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