

SELECTIVE REMOVAL OF TIN AND PHOSPHORUS IN PHOSPHOR BRONZE*G SUBRAMANIAN, V ANANTH, P S MOHAN and T M BALASUBRAMANIAN*

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[Received: 1987 February; Accepted: 1987 December]

The aim of the present study is to quantify the selective removal of tin and phosphorus in phosphor bronze wire exposed at shore site at Mandapam after mechanical polishing. The samples were withdrawn from exposure monthwise and cumulatively. Corrosion rates were determined after pickling the corrosion product. The stripped corrosion product was analysed for tin using atomic absorption spectrophotometer (AAS) and for phosphorus using photocolormeter. These were plotted along with corrosion rates. The average values of tin and phosphorus in the corrosion product are 4.6% and 12.8% respectively, whereas the parent alloy contained phosphorus: 0.4%, tin: 5% and copper: balance. The severity of the atmosphere for corrosion is discussed on the basis of meteorological data. The chemical analysis is supported by the scanning electron micrograph (SEM).

Key words: Phosphor bronze, atmospheric corrosion

INTRODUCTION

Theoretical considerations [1] on the fundamental studies on corrosion of alloys date back a few decades. The differing rates of reaction between the individual components of the alloy and the environment is a complex one, compared to the reaction in the case of pure metal. Initially, the components of an alloy react with the environment at rates which are not in accord with more fractions and during this time the surface becomes enriched with nobler metal.

Any of the following may happen: (1) The reaction rate may decrease to negligible or low level by virtue of the protective nature of either of the modified surface alloy layer or of a corrosion product layer. (2) The planar surface becomes unstable and local penetration occurs. This situation has great relevance in the industrial sphere since it leads to high rates of selective removal and often a loss of ductility and structural integrity. (3) Selective removal ceases in a short time but gives way to a non-selective reaction of the alloy with the environment without loss of stability of the planar surface and at an appreciable rate which increases with the driving force.

A well known phenomenon belonging to the second category is dezincification of brasses [2]. Similar type of de-alloying is rarely observed in tin bronzes also [3]. The phosphorus which is added as deoxidiser to copper plays a major role in the mechanical property of bronzes. Tin bronzes containing 0.2 to 0.5% of phosphorus are called phosphor bronzes. These are marked with good electrical conductivity. These are used in trolley wires and springs. Usually the corrosion rate of these bronzes in normal atmosphere is very low. But the corrosion rate of phosphor bronze in marine atmosphere is relatively high [4]. The miniaturising of equipments to save space and materials, necessitated a thorough study on this material in tropical marine environment. In the present study, the first phase deals with the analysis of the corrosion product which points out the existence of selective leaching of the components

of the alloy. The result of chemical analysis is supported by the SEM of the sample.

EXPERIMENTAL

The alloy used in the present study was of commercial grade. The nominal composition and the analysis of the alloy are presented in Table I.

TABLE-I: Composition of phosphor bronze

Nominal	Analysis
P: 0.5wt%	P: 0.4%
Sn: 5wt%	Sn: 5.0%
Cu: Balance	Cu: Balance

Phosphor bronze received in the form of 3mm dia drawn wire was cut to size of 150mm long rods, etched in 10% HCl for 3 minutes, polished on a cloth wheel using emery compound to have reproducible mirror polish and degreased in trichloroethylene.

Triplicate samples were removed each time from the exposures, derusted in 10% HCl and the corrosion products were analysed for phosphorus and tin using photocolormeter and AAS respectively. A set of samples were also exposed for metallographic study. Further more, visual observations on the panels were recorded during the exposure period.

The exposure site is located on the shore of Bay of Bengal in the Gulf of Mannar, 30m away from the water line and 3m above the sea level. The longitude and latitude of the site are 79° east and 9.2° north. The location of the yard admits the wind directly from the sea, only during the south-west monsoon periods which prevail from March to September. The north-east monsoon prevails during October to February and the wind from Palk strait has to

cross the land of about 2 km to reach the exposure yard.

The presence of shallow waters along with the submerged rocks in front of the exposure yard favours splashes and carry over of a considerable quantity of seawater droplets by the high velocity wind during south-west monsoon.

Meteorological data for the site were recorded regularly using the equipments supplied by Meteorological Centre, Pune, India.

RESULTS AND DISCUSSION

The monthly salinity and rainfall data are presented in Figs. 1 and 2. Higher salinity values were due to the carry over of sodium chloride from the sea by high velocity wind prevailed during south-west monsoon. Heavy rainfalls were recorded during north-east monsoon. Visual observations on the panels over the exposure period reveals that for the initial period of 3 to 4 months, dark brown corrosion product was observed. After this, tenacious, adherent bluish green product was observed on the rods exposed for one year and above. The exponential decrease of the cumulative corrosion rate indicates the protective nature of the corrosion product.

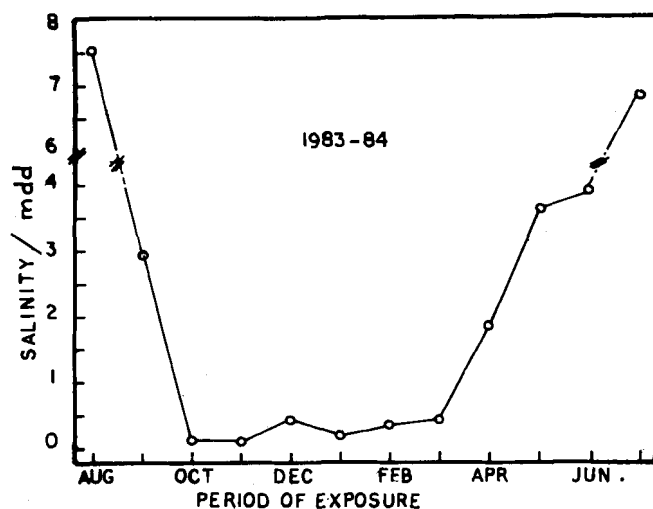


Fig. 1 Monthly atmospheric salinity values at shore site

Fig. 4 presents the percentage of tin and phosphorus in the corrosion product stripped monthwise and the monthly corrosion rate of phosphor bronze. Fig. 3 shows similar analysis of corrosion product stripped cumulatively alongwith cumulative corrosion rate. Phosphorus content in the corrosion product stripped monthwise shows higher percentage during the months December to March. The lowest phosphorus content in the corrosion product is about 4% which is ten times the concentration of phosphorus in the parent alloy. The lower atmospheric pollution (salinity) during December to March coincided with higher leaching of phosphorus and the higher rainfall recorded during the same period accelerated the formation of phosphorus compounds. The corrosion product analysis of tin showed an average value of 4.6%. If equal corrosion of tin and copper would have taken place, they should be in the same pro-

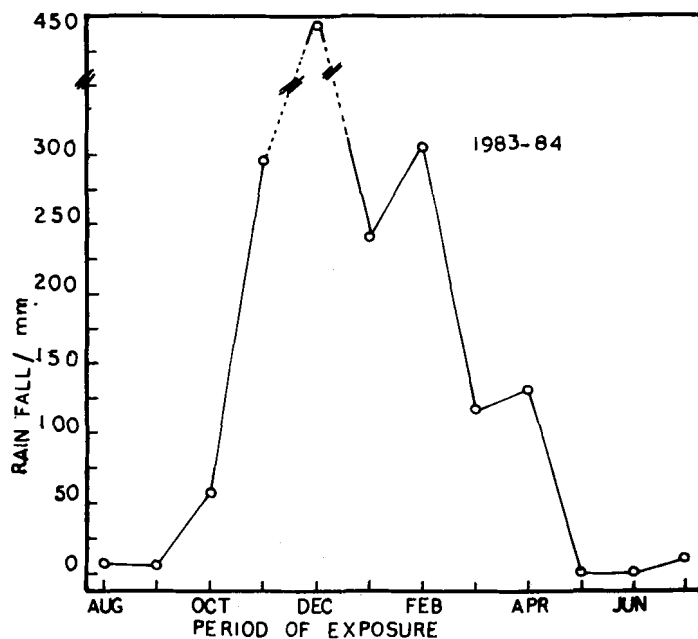


Fig. 2. Monthly total rainfall values at shore site

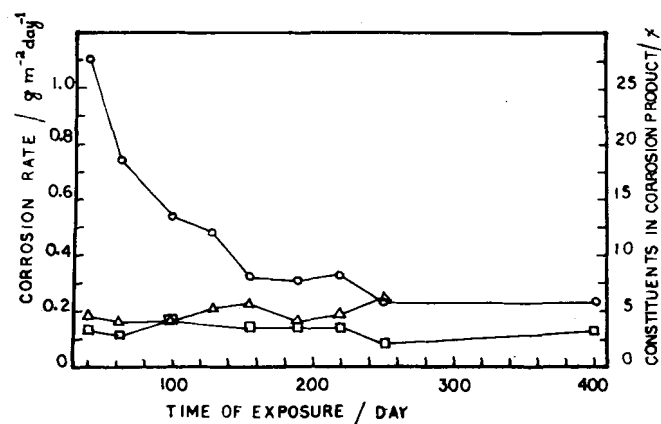


Fig. 3: Cumulative corrosion rate of phosphor bronze and its corrosion product analysis: o-Corrosion rate Δ -phosphorus content \square -Tin content in corrosion product

portion as in the parent alloy, which amounted to 3.75% of tin. This higher value is due to the position of tin in the electrochemical series compared to copper.

It is also found that presence of moisture increases the corrosiveness of halogen gases and their compounds considerably and at elevated temperatures. Halogens react rapidly with copper-tin alloys forming volatile tin halides [5]. Considering the possibility of the above facts and free energy of formation, the following products PCl_3 and $SnCl_4$ are more favoured which ultimately forms

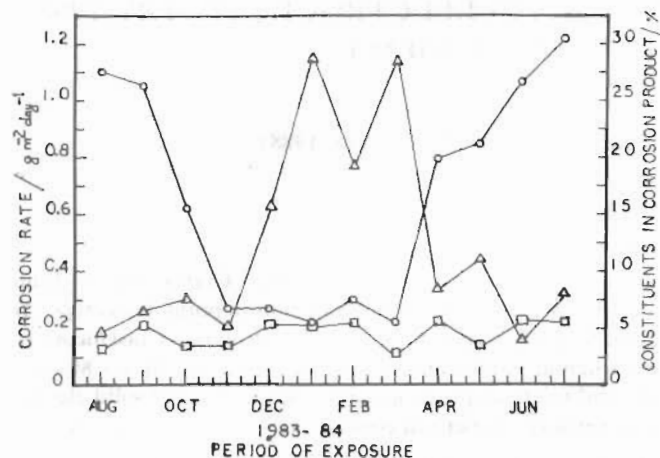


Fig. 4: Monthly corrosion rate of phosphor bronze and its corrosion product analysis: \circ -Corrosion rate Δ -Phosphorus content \square -Tin content in corrosion product

tin tetraphosphide, a white crystalline compound, insoluble in water and soluble in hydrochloric acid. A favourable condition might have existed during the course of exposure that part of SnCl_4 formed on the surface of the rod might have escaped through evaporation. (The vapour pressure of stannic chloride is approximately equal to that of water at 30°C). This could be the reason for the constant amount of tin reported in the corrosion product analysis.

Addition of arsenic, antimony or phosphorus to the copper base alloys is recommended for marine application to curtail the selective leaching of zinc from brass. In the present case, phosphorus itself is leached out and hence the possibility of inhibiting the dealloying by addition of phosphorus becomes impossible in this tropical-marine atmosphere. The selective leaching of phosphorus and tin from the bronze is further envisaged by the presence of copper enriched surface of copper-tin-phosphorus system in the scanning electron micrograph (Fig. 5).

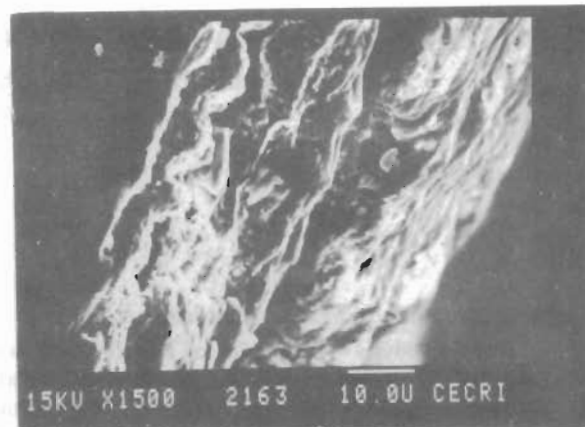


Fig.5: SCM of phosphor bronze after exposure for 2½ years

CONCLUSIONS

Phosphor bronze is having relatively higher corrosion rate, due to the chloride pollution prevailing at this tropical marine atmosphere. Selective leaching of phosphorus in phosphor bronze is more favoured in comparison to the leaching of tin. Leaching of phosphorus from phosphor bronze is higher during the lean period of corrosion rate and favoured by the screening effect of the salinity by the rainfall.

Acknowledgement: The authors wish to thank Dr. K Balakrishnan, Coordinating Head of Corrosion Science and Engineering Section for his interest in this work. Their thanks are due to M/s Augustin Ramakrishnan and Karupiah, Scientists, CECRI, Karaikudi, for their help rendered in carrying out the analysis of corrosion product and scanning electron micrograph.

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