

Chemical and electrochemical studies on chromate passivation of brass

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BRASS is found to corrode by a process known as dezincification. There are three types of dezincification: (i) Selective corrosion of zinc in brass (ii) redeposition of copper on brass surface and (iii) a combination of processes (i) and (ii). The corrosion is manifested on brass either as 'layer type' when the attack is laterally distributed or as 'plug type' when the attack is concentrated to points resulting in pitting and finally perforation.

Dezincification by deposition theory was supported by electron optics studies.

Restricted supply of oxygen, high temperature and contact with chloride ions increase the incidence of dezincification. Proper alloying, especially with small quantities of tin, aluminium, antimony, arsenic, phosphorus, etc. increases corrosion resistance of brass. Provision of electrical insulation against contact with nobler metals and alloys should be a part of designing complexes with brass. Crennel and Sawyer¹ could cathodically protect naval brass in 3.5% sodium chloride by depressing its potential to -600 mv (w.r.t. Ag/Ag Cl electrode) by impressed current. Sugawara and Elica² found that the electro-chemical nature of brass is essentially similar to that of copper. Muller³ and Akimov and Golubev⁴ reported appreciable protection of zinc and copper against atmospheric corrosion after treatment in dichromate solution. Clarke and Andrew⁵ attempted to passivate brass following the last method. They observed that presence of chloride ions in the passivation solution produced best results. The process has been further studied by Sinha et al.⁶

This paper describes results of the passivation of brass obtained by chemical and electrochemical methods. The effect of time of etching and of the presence of Cl⁻ ion has been studied.

It is thought that a prior etching of brass and specific concentration of Cl⁻/SO₄²⁻ is essential to achieve a good passivation. In chemical passivation this is done by incorporating Cl⁻ ions. In the electrochemical process this is achieved by impressing anodic current on brass.

SYNOPSIS

Laboratory methods for inducing accelerated dezincification of brass have been established. These methods have been used to estimate the corrosion resistance of passivated specimens.

Studies have been made on the effect of varying the period of treatment by pickling and passivation solutions to obtain optimum conditions for chemical passivation of brass. The possibility of electrochemical passivation of brass has been studied. It has been established that anodic etching of brass in lieu of chemical etching by Cl⁻ ions can initiate subsequent passivation.

Experimental

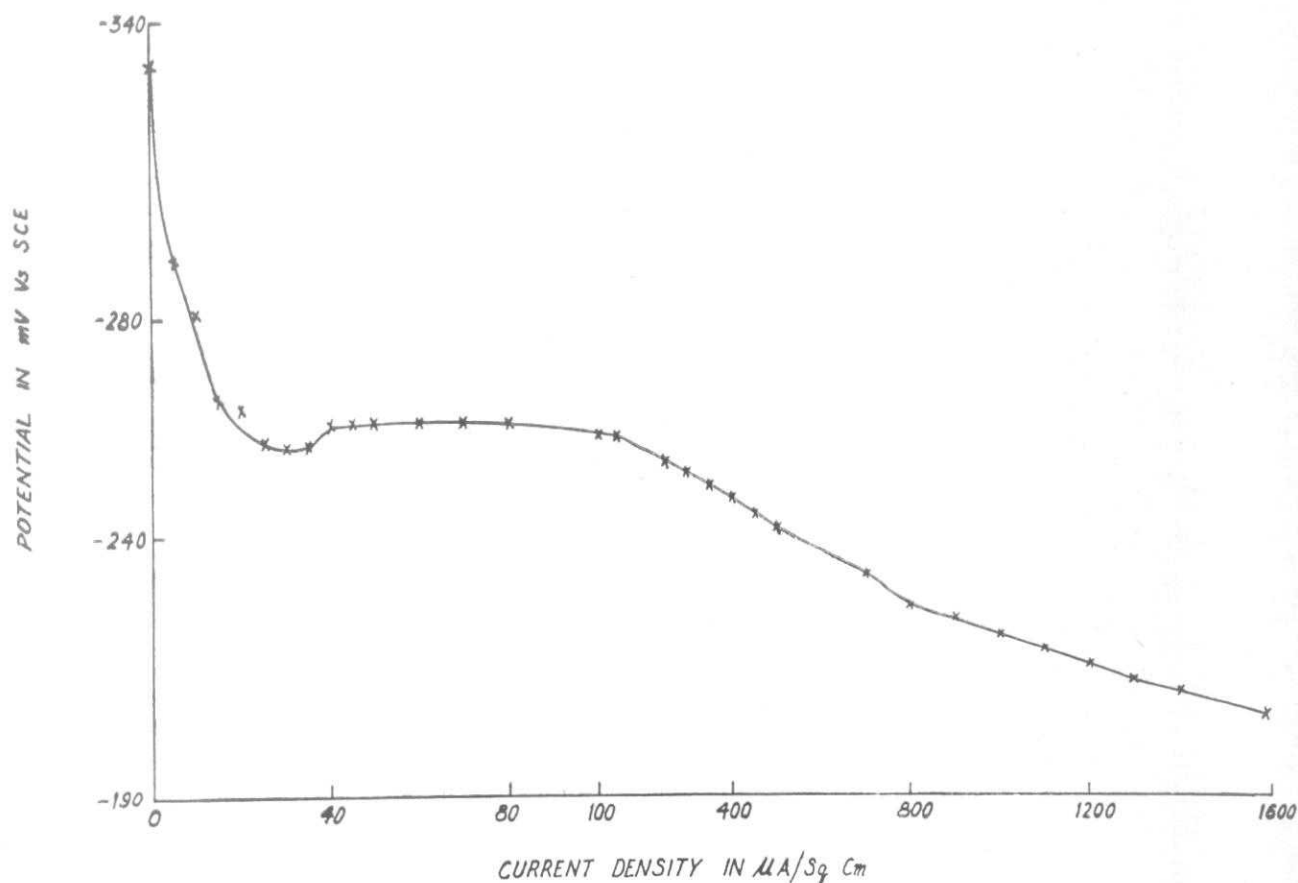
Brass (Cu 60%, Zn 40%) panels 5 cm × 2.5 cm of thickness 18 SWG after abrading by No. O emery were degreased with toluene and methanol.

Bare panels were then exposed for varying periods in a standard humidity cabinet, a C.R.L. beaker, to salt water spray, to aerosol salt fog (5% NaCl) and immersed in salt water. Pronounced dezincification was observed in the aerosol salt fog exposure.

Chemical passivation

Brass panels were dipped in 10% sulphuric acid for 3 minutes, washed, force-dried, weighed and pickled at room temperature in a solution in water of 22.4% dry potassium dichromate and 7.36% of sulphuric acid for (a) 30 seconds and (b) 2 minutes. The pickled panels were washed, force dried and weighed again. The panels were then passivated by immersion in a solution containing 20% potassium dichromate, 1% sodium chloride, 5% sodium sulphate and 1.1% of sulphuric acid for 10, 30, 60 and 180 seconds. The composition and strength of these solutions are same as that used by Clarke.⁵ The panels were then washed, dried and weighed. The adherence of the passivated film was examined by rubbing with a filter paper. One set of panels was treated for 2 mts. by 7.3% (w/v) hydrochloric acid containing 10% stannous chloride to strip the passivated film. The treated panels

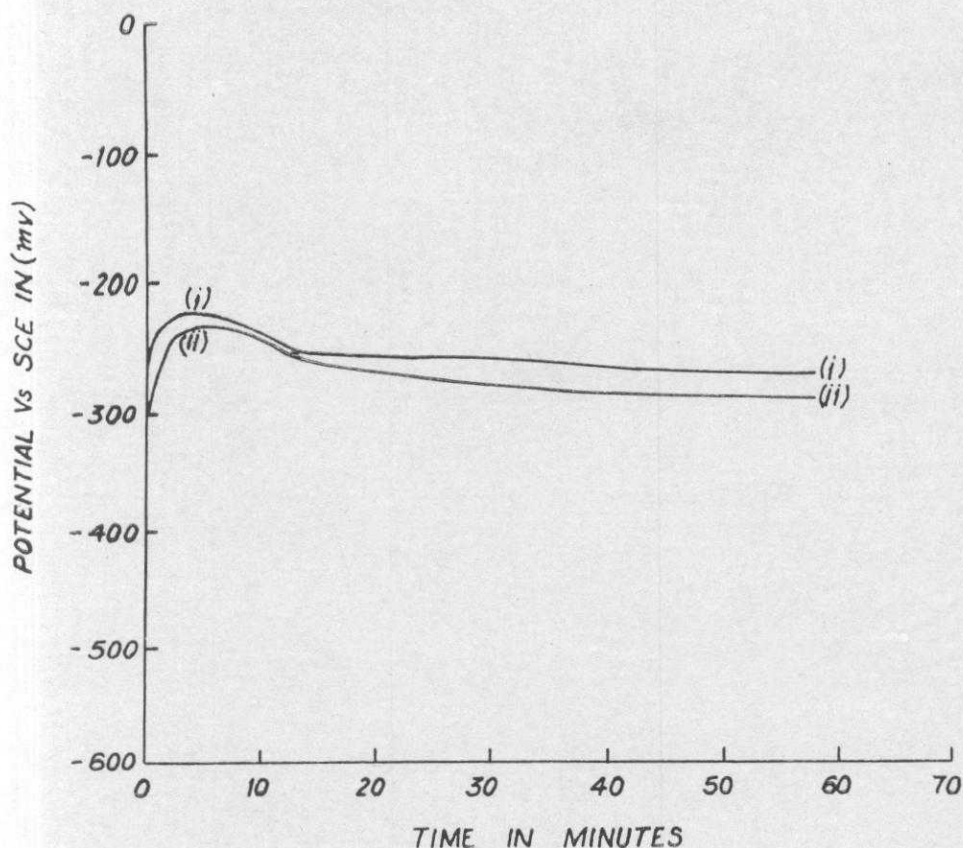
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1 Effect of anodic polarisation of brass in 5.0% NaCl solution

TABLE I Particulars of pickling and passivation treatments and the performance of treated brass specimens in adhesion and aerosol tests

Sl. No.	Pickling time (seconds)	Passivation time (seconds)	Loss in weight after pickling (mg)	Film weight (mg)	Adhesion test	Performance in aerosol test
1.	Control	—	—	—	—	Considerable dezincification after 5 hrs. 45 mts.
2.	30	(i) 10	53.0	2.5	No stain on paper	No dezincification. White corrosion product on edges only after 192 hrs.
		(ii) 30	67.6	6.7	Very slight stain on paper	do
		(iii) 60	63.6	6.7	do	do
		(iv) 180	63.6	8.6	Slight stain on paper	do
3.	120	(i) 10	151.7	3.6	No stain on paper	No dezincification. White corrosion at edges only after 200 hrs.
		(ii) 30	154.0	6.5	Very slight stain on paper	do
		(iii) 60	145.6	6.9	Slight stain on paper	do
		(iv) 180	206.1	9.6	do	do



2 Effect of different C.D. on brass in 5.0% NaCl solution, (i) CD-68 μ a (ii) CD -55 μ a

were washed, dried and reweighed. Another set of panels was exposed to 5% NaCl aerosol spray and the time elapsed from first exposure to appearance of dezincified spots were noted. Results are reported in Table I.

Electrochemical passivation

(a) A high power battery having large resistances in series was used to impress constant current to brass panels immersed in NaCl solution. The change in potential, measured by a potentiometric recorder, was plotted as a function of different current densities impressed (Fig. 1). Such curves were also obtained by using 18% of sodium chromate solutions at pH value adjusted by adding concentrated sulphuric acid at various current densities.

(b) As brass suffered from dezincification at current densities between 40 and 100 μ A, variation of electrode potential of brass with different current densities between 40 and 100 μ A were determined and potential time curve drawn. Typical curves at potentials obtained with 55 μ A and 68 μ A current densities are given in Fig. 2.

(c) Brass panels with passivated films obtained in sodium chromate solution described in para (a) above were tested for the adherence of the passivated film by rubbing with a filter paper and for their corrosion

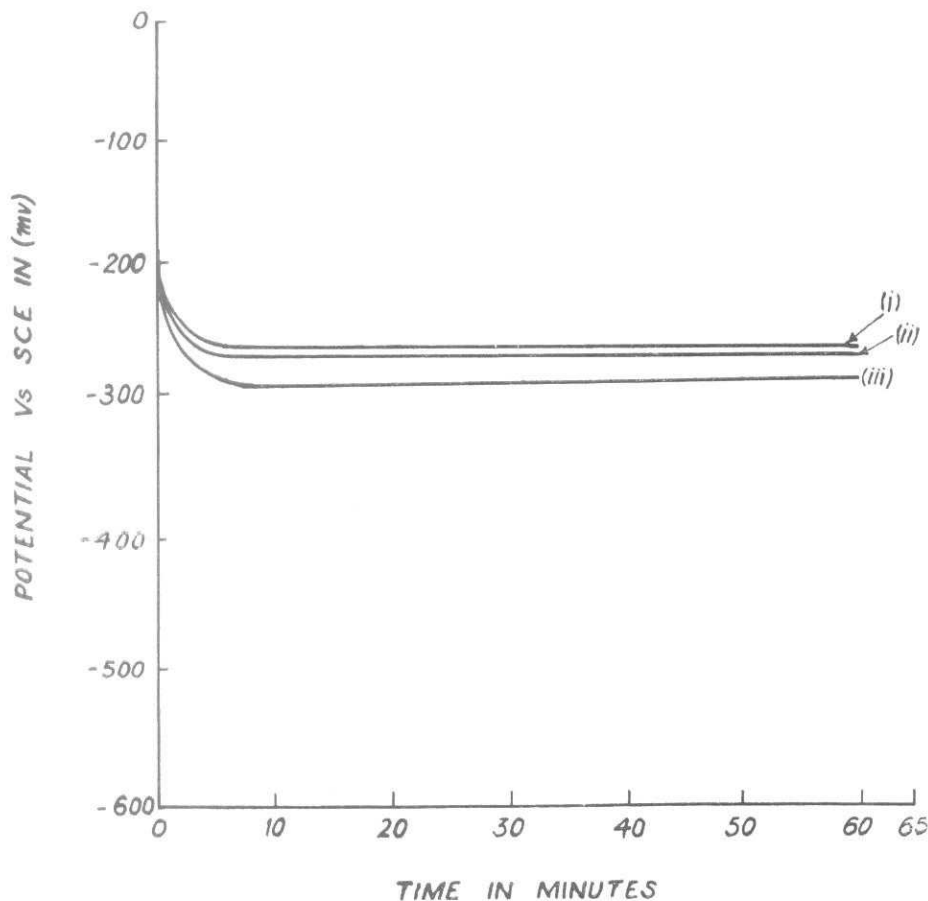
resistance by measuring their electrode potentials when immersed in 5% NaCl solution. The potential time curves at three different current densities are reported in Fig. 3.

Adhesion of the passivated film was judged by rubbing with a filter paper to see if any stain was produced on the paper.

Results and discussions

In the chemical process the increase in the time of pickling results in more metal loss with practically no gain in the character of the passivated film. The passivation film obtained after 30 seconds pickling followed by 10 seconds passivation is equally tenacious and corrosion resistant compared to that obtained by 2 mts. pickling followed by 10 seconds passivation. Similarly, though the film weight of the passivation film increasing time of passivation, no substantial gain is achieved in the character of film. Hence 30 seconds pickling followed by 10 seconds passivation treatment is considered ideal. Moreover, the film obtained under these conditions was found to be adherent.

In the electrochemical process with NaCl alone it was observed (Fig. 1) that the potential remained unchanged while the impressed current was raised from 40 to 100 μ A cm². Brass was found to have suffered from dezincification during this period. To ascertain



3 Examination of the film on brass passivated at different C.D. in 5.0% NaCl solution (i) CD-55 μa (ii) CD-48 μa (iii) CD-31 μa

the exact current density when brass suffers from maximum dezincification, Fig. 2 was obtained by impressing current densities between 40 and 100 $\mu A/cm^2$. All the curves show initial rise in potential which gradually fall to become steady after 15 minutes. However, at current density of 55 $\mu A/cm^2$ the metal loss is highest and maximum dezincification was visible. Hence it is concluded that for dezincification 55 $\mu A/cm^2$ is the limiting current density beyond which the process of dezincification seems to be retarded.

Passivation of brass was carried out in acidified sodium chromate bath at current densities of 31, 48 and 55 $\mu A/cm^2$. The maximum adherence was observed in case of passivation of 55 $\mu A/cm^2$. The passivated films obtained with current densities of 31 and 48 $\mu A/cm^2$ had poor adhesion and at current densities higher than 55 $\mu A/cm^2$ practically no passivated film was visible. The electrode potentials of passivated panels in 5% NaCl solution (Fig. 3) plotted against time, show that the potentials start at -200 mv vs SCE and fall with time. Steady potential is, however, reached by the brass passivated as 55 $\mu A/cm^2$ current density, which also shows the most positive potential.

Brass, like Cu, is only slightly attacked by sodium chloride. Anodic polarisation supplements this attack

and induces active dissolution of the alloy. Near a specific current density (55 $\mu A/cm^2$) there is maximum dissolution of brass redeposition of copper resulting in severe dezincification and when some copper and zinc ions are freely formed on the surface of brass due to the influence of anodic current, these ions react with the chromate and with lapse of time form small crystals on the surface of brass which become perfect on drying and confer passivation.

References

1. Grennel, J. T. and Sawyer, L. J. E. : 1962, Jr. App. Chem. 12 (4), 170.
2. Sugawara Hideo and Elica Hideaki : Corr. Sci., 1967, 6, (8).
3. Muller, E. Z. : Electrochem., 193, 45, 242.
4. Akimov, G. C. and Golubev, A. T. : Zb. Prikl. Khim., 1939, 12, 1920.
5. Clarke, S. G. and Andrew, J. F. : 1962, Proceedings First International Congress on Metallic Corrosion, Butterworths, London, pp. 173-177.
6. Sinha, D. P., Sanyal, S. K. and Sanyal, B. : 1967, Jr. Sci. Tech. 5. (1), 27.

Discussions

Dr S. C. Sircar (Indian Institute of Technology, Kharagpur) : I would like to know whether the experiments were done under constant current or constant potential condition.

How was passivation assessed ?

Mr S. K. Sanyal (Author) : We carried out our experiments under constant current.

Passivation was checked by exposure to corrosive environment e.g. humidity cabinet and also by observing the trend of potential of the passivated panel when immersed in NaCl solution.