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COPPER-MANGANESE ALLOY FOR MARINE ENVIRONMENT

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Studies have been made on the behaviour of copper-manganese alloys, with and without addition of other elements in synthetic sea water, using potentiostatic technique. It is found that 70:30:Cu:Mn alloy has superior corrosion resistance probably because of the homogeneous micro-structure of the alloy. Addition of misch metal further improves corrosion resistance. The corrosion rate values were found to decrease in the following order: 80/20: Cu/Mn, copper, 70/30: Cu/Mn and Cu/Mn misch metal. The anodic Tafel constant (b_a) is found to be 75 ± 5 mV/decade, for copper and its alloys. Addition of manganese to copper shifts the open circuit potential in cathodic direction. It also marginally increases the hardness.

Key words: Copper-manganese alloy, sea water, deoxidation, impedance

INTRODUCTION

Copper alloys find applications in heat exchangers, pumps, valves and also in propellers of sea going vessels. The corrosion resistance of these alloys is attributed to the formation of an oxide film, which shows better protective properties for alloys of copper than for pure copper.

In this paper, the electrochemical behaviour of copper-manganese alloys of varying compositions in synthetic sea water is considered.

EXPERIMENTAL

Materials

Analar grade copper and manganese and misch-metal of known composition (60% Ce; 10% Fe; lanthanides 30%) were used for casting the alloys. The melting was done in pit-type furnace followed by casting in graphite moulds. The copper-manganese alloys with an area of 1 cm^2 were fitted in teflon, and used for electrochemical studies. For oxidation studies, specimens of cylindrical shape with an area of 4.5 cm^2 have been used.

Metallography

Specimens were prepared as per standard metallographic procedure and were etched in 3% $FeCl_3$ (acidified) solution and photomicrographs were taken at a magnification of 250X.

Hardness

Hardness values were obtained using Rockwell machine and reported in BHN-scale.

Oxidation behaviour

Oxidation studies have been conducted, using an oven and a muffle furnace and the rates have been determined from the increase in weight after an oxidation period of 10 hours.

Potentiodynamic studies

Pure copper and copper-manganese alloys were polarized potentiodynamically, using a potentiostat (Princeton Applied Research, U.K.) in combination with universal programmer (P.A.R. Model 175) with X-Y recorder, at a scan-rate of 2mV.s^{-1}

Potential vs time studies

Cu:Mn and Cu-Mn-misch metal alloys were annealed and stress-relieved and the potential values were recorded as a function of time w.r.t. S.C.E., using Philip's microvoltmeter (Model No. 799A).

Impedance measurements

Impedance measurements were carried out at a potential of 250 mV, within the frequency range of 10 KHZ to 60 mHZ using Solartron frequency response analyzer, Model 1180. The amplitude of applied A.C. perturbation was 10 mV

Weight-loss studies

Corrosion rates were determined in synthetic sea water from the difference in weight before and after corrosion for various periods. Concentrations of manganese and copper in solution were analyzed, using Atomic Absorption Spectrometer Model No.380 made in U.S.A.

Heat treatment

The alloys were annealed at 1223K and stress relieved at 673K for 15 hours in an inert-atmosphere.

RESULTS AND DISCUSSION

Table 1 gives the corrosion rates obtained from Tafel extrapolation and by direct corrosion tests.

TABLE-I: Corrosion behaviour of Cu-Mn alloy in synthetic sea water

Materials	i_{corr} ($\mu A.mm^{-2}$)	b_a ($mV.decade^{-1}$)	Wt loss ($mg.cm^{-2}$)	O C P (mV vs SCE)
Copper	14.5	80	—	—240
Cu:Mn/80:20	15.0	50	0.70	—305
Cu:Mn/70:30	9.0	75	0.53	—240
Cu:Mn/76:24 with misch metal	3.5	70	0.46	—340

It is clearly seen that i_{corr} of 70:30/Cu:Mn alloy and Cu:Mn-misch metal are lower than 80/20: Cu/Mn alloy and pure copper in synthetic sea water. Weight loss measurements also support this trend. Anodic Tafel slopes of 70:30/Cu:Mn and the alloy containing misch metal are identical, indicating no change in the mechanism of dissolution.

Table II gives the hardness values for pure copper and Cu-Mn alloys. From hardness values, it appears that addition of

TABLE-II: Comparison of hardness values

Material	Hardness
Cu:Mn/80:20	64
Cu:Mn/70:30	69
Cu:Mn/76:24 (deoxidised with cerium)	116

manganese marginally increases the hardness, while addition of misch metal increases it considerably. The micro-structure of copper-manganese alloys are shown in Figs. 1,2,3. The

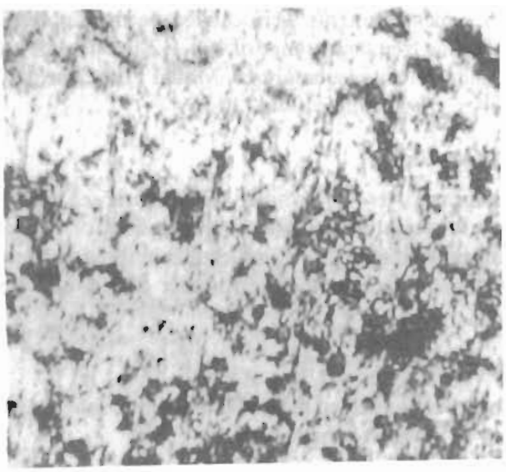

Fig. 1: Microstructure of 80/20 Cu:Mn alloy

70:30/Cu:Mn alloy reveals homogeneous distribution of micro-constituents (Fig. 2) and absence of acicular phases, while alloy with misch metal reveals inclusions at grain boundaries and grains proper (Fig.3). The 80:20 Cu:Mn alloy reveals a nonuniform distribution (Fig.1) of micro-constituents.

Fig.4 shows the potential-time curves for copper-manganese alloys, with and without heat treatment. It is seen that annealing followed by stress-relieving treatment makes the potential values more positive, both for 70:30/Cu:Mn alloy and the Cu-Mn-misch metal. It is seen that annealing without stress-relieving has no beneficial effect, as far as O.C.P. is concerned, in Cu:Mn/70:30 alloy. But in the case of alloy containing misch metal, annealing appears to change the O.C.P. values to a more positive direction.

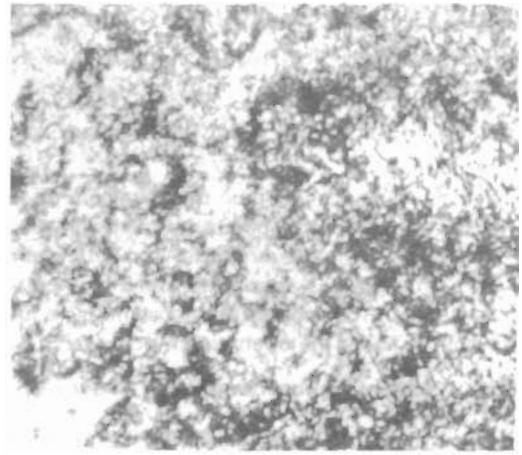

Fig.2: Microstructure of 70/30 Cu:Mn alloy

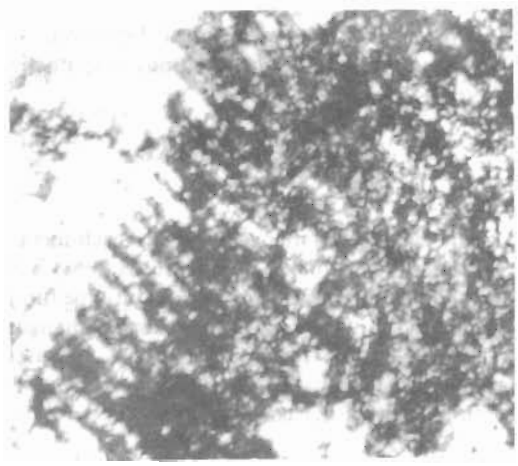

Fig.3: Microstructure of 76/24 Cu:Mn + misch metal

Fig.5 shows the impedance behaviour of copper-manganese alloys in synthetic sea-water. It indicates that R_{ct} (charge transfer resistance) values increase in the following order, Cu:Mn/80:20, Cu:Mn/70:30 and the Cu:Mn/76:24 alloy with misch metal confirming the results obtained by potentiodynamic as well as weight loss experiments.

Table III shows the dissolution of copper and manganese in synthetic sea water, as a function of time. It is clear that increase in

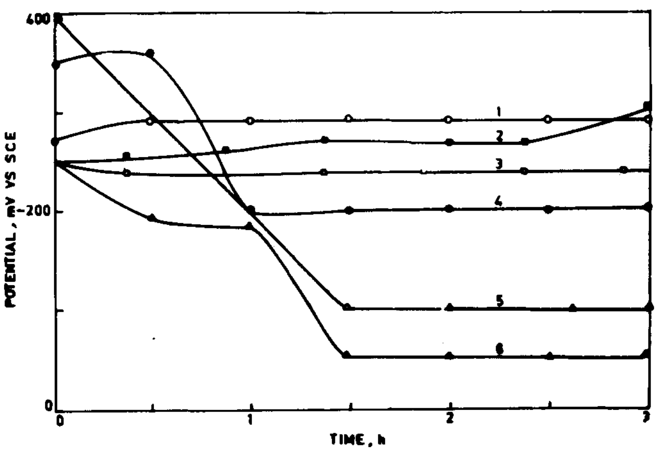

Fig.4: Potential time curves for copper-manganese alloys, with and without heat treatment
1. 76:24/Cu:Mn-misch metal alloy as cast
2. 70/30/Cu:Mn alloy annealed at 1223K
3. 70/30/Cu:Mn alloy as cast
4. 76:24/Cu:Mn alloy annealed at 1223K
5. 76/24/Cu:Mn alloy annealed at 1223K
6. 70/30/Cu:Mn alloy annealed at 1223K and stress relieved at 673K

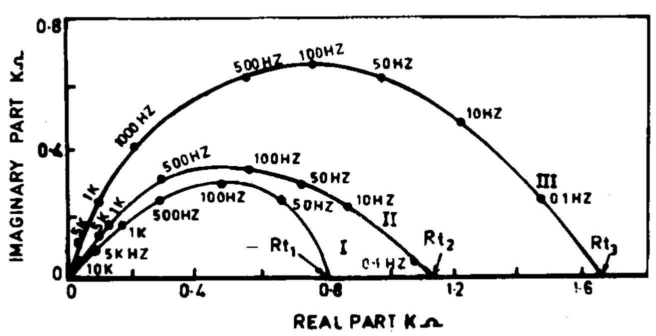

Fig.5: Impedance behaviour of copper-manganese alloy in synthetic sea-water
I-80:20/Cu:Mn alloy
II-70:30/Cu:Mn alloy
III-76:24/Cu:Mn misch metal alloy

the manganese content of the alloy, suppresses the dissolution rate of copper. It is also seen that the dissolution of copper and manganese are almost identical for the 80:20/Cu:Mn alloy, while the tendency for selective dissolution of Mn is more in 70:30 Cu-Mn. The electrochemical behaviour of 80:20 alloy may be explained from the total loss of Cu + Mn ions, which is always more than the corresponding values of Cu + Mn for the 70:30 alloy. The superior behaviour of 70:30/Cu:Mn alloy is attributed to the homogeneous micro-structure of the alloy matrix.

TABLE-III: Dissolution of Cu and Mn-ion in 3% synthetic sea water as a function of time, for copper-manganese alloys

	80:20/Cu:Mn alloy		70:30/Cu:Mn alloy	
Hrs.	Cu μg.100ml-1	Mn μg.100ml-1	Cu μg.100ml-1	Mn μg.100ml-1
2	37	35	5	30
6	80	70	10	50
10	97	95	18	70
16	100	116	25	95
18	105	115	27	90
20	110	105	30	81
24	120	70	30	61

CONCLUSIONS

It is concluded that 70:30/Cu:Mn alloy has superior corrosion resistance properties in synthetic sea water. Addition of manganese to copper improves both the corrosion and oxidation resistance properties. Addition of misch metal to Cu-Mn alloys further improves the corrosion resistance properties.

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