

IMPEDANCE BEHAVIOUR OF SOME COPPER ALLOYS AND MONEL IN SYNTHETIC SEA WATER*M NATESAN, G VENKATACHARI, T M BALASUBRAMANIAN and K BALAKRISHNAN*

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The corrosion behaviour of monel, admiralty brass, aluminium brass, 70Cu-30Ni and 90Cu-10Ni alloys in sea water has been evaluated by impedance method for a frequency range of 1mHz to 10KHz. It has been found that monel exhibits superior corrosion resistance owing to the formation of compact film. In the case of other alloys, the formation of porous corrosion product film protects the metal from dissolution.

Key words: Copper alloys, monel, sea water corrosion, impedance

INTRODUCTION

The most important materials used for heat exchanger service in sea water are monel, cupronickel (70Cu-30Ni, 90Cu-10Ni), aluminium brass and admiralty brass [1]. The corrosion behaviour of these alloys in sea water and in polluted sea water has been determined by coupon method [2,3]. It has been found that the rate of corrosion is of the order monel < aluminium brass < 70Cu-30Ni alloy < 90Cu-10Ni alloy < admiralty metal. The review [4] on the corrosion of metals in marine environment summarises the corrosion behaviour of materials. A survey [5] on the percentage of failure of these materials in heat exchanger service has shown that there is a minimum failure in the case of 70Cu-30Ni alloy and a maximum failure in the case of admiralty brass. Using the polarisation resistance method it has been shown that the correction of Cu-Ni alloys in sea water decreases with time [6-8]. In this paper, the impedance behaviour of the marine alloys is reported

EXPERIMENTAL

The chemical composition of the materials used in the study are given below:

- | | |
|-----------------------|---|
| (i) Monel | - Ni66, Cu32, Fe2 |
| (ii) Admiralty brass | - Cu69-83, Zn29.1, Sn 1.07, Fe 0.005
As 0.031 |
| (iii) Aluminium brass | - Cu77.07, Zn22.76, Sn 0.06, Fe0.047
Al 1.94, As 0.016 |
| (iv) 90Cu-10Ni alloy | - Cu87.25, Ni10.65, Sn0.04, Fe1.37,
Al0.69 |
| (v) 70Cu-30Ni alloy | - Cu65, Zn1.0, Ni33, Pb-0.05, Fe0.7,
Mn 1.0 |

The specimens of 1cm² area with stem were cut from the respective tubes and polished on a cloth wheel. After degreasing with trichloroethylene, the specimens were exposed to synthetic sea water (BS 1391-1952) in a polarisation cell using platinum (3cm × 3cm) and SCE as auxiliary and reference electrodes respectively.

Impedance measurements were carried out using the frequency response analyser (Model 1174, Solartron UK) at the open circuit

potential using the electrochemical interface (Model 1186, Solartron, UK) for the frequency range of 1mHz to 10KHz, under stationary conditions at 30 ± 1°C. The charge transfer resistance (R_t) values were calculated from the difference in impedance values of low and high frequency intercept at real axis and the interfacial capacitance (C_i) values were obtained from the relationship

$$C_i = \frac{1}{2 f_{\max} R_t}$$

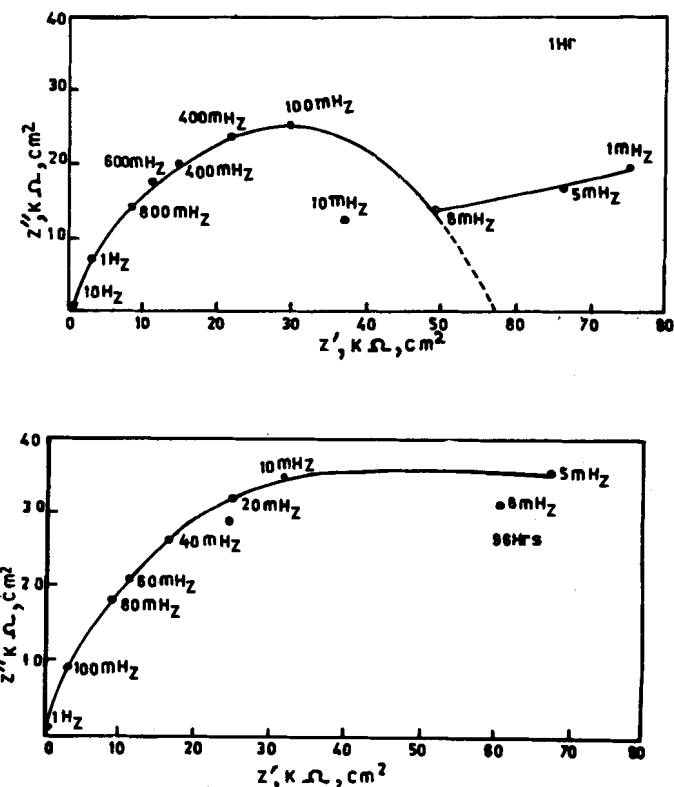


Fig.1: Impedance diagram of monel in synthetic sea water

where f_{max} is the frequency at which the imaginary part is maximum.

RESULTS AND DISCUSSION

Monel

The impedance diagrams of monel in sea water for 1 hr and 96 hrs immersion are given in Fig. 1. Initially due to dissolution reaction, there exists a distorted semicircle at low frequency region. The charge transfer resistance is about $57.5 K \Omega \text{ cm}^2$ and the interfacial capacitance is $28.1 \mu \text{F/cm}^2$. It is found that after 96 hrs immersion, upto 10mHz, the behaviour is a capacitive type due to formation of compact passive layer. The charge transfer resistance is increased to $87.5 K \Omega \text{ cm}^2$ due to reduction in corrosion process. The absence of warburg type behaviour at low frequencies indicates that the corrosion process is anodically controlled. This is indicated in the change in open circuit potential. The potential is shifted from -267 mV to -221 mV in 96 hrs. Moreover, the interfacial capacitance after 96 hrs is $46.1 \mu \text{F/cm}^2$ which also indicates the existence of compact film on the monel.

Admiralty brass

In admiralty brass, the impedance behaviour, as shown in Fig 2, has indicated that the corrosion reaction is cathodically controlled owing to the occurrence of warburg diffusion line at low

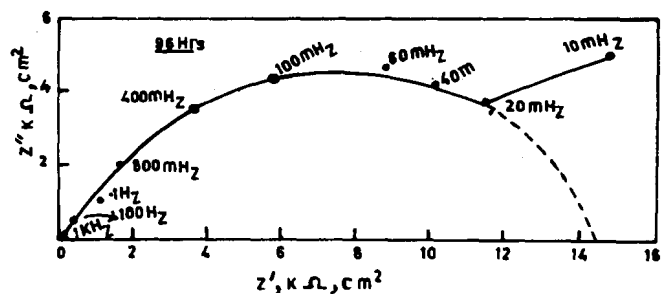
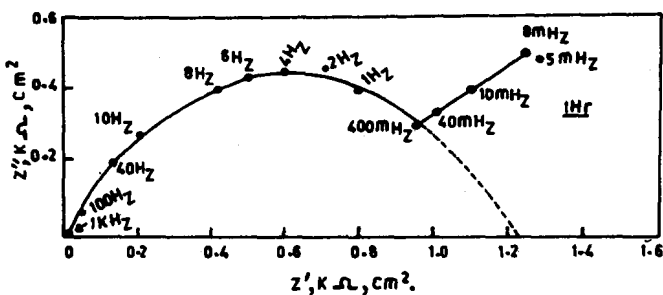


Fig.2: Impedance diagram of admiralty brass in synthetic sea water

frequencies. In this case the open circuit potential is found to shift from -269 mV to -280 mV in 96 hrs. The low frequency distorted semicircle corresponds to the metal dissolution reaction whose charge transfer resistance is $1.2 K \Omega \text{ cm}^2$ for 1 hr and $14 K \Omega \text{ cm}^2$ for 96 hrs. The increased R_t values with time indicate the reduction in corrosion rate owing to the formation of corrosion product film. The C_i values have reduced from $16801 \mu \text{F/cm}^2$ to $1152 \mu \text{F/cm}^2$ within 96 hrs, indicating the formation of porous corrosion product film.

Aluminium brass

The impedance behaviour is shown in Fig.3. Initially, due to

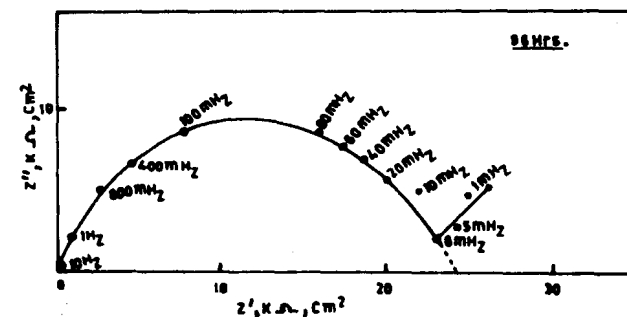
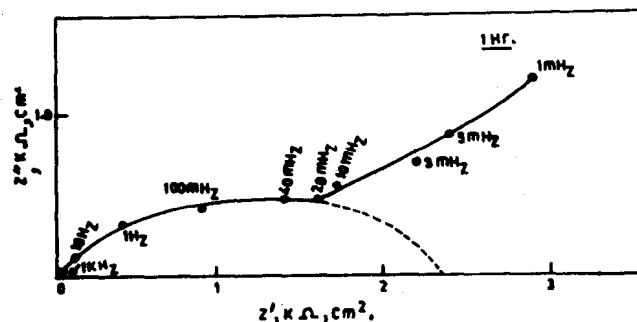


Fig.3: Impedance diagram of aluminium brass in synthetic sea water

O_2 reduction, a well defined warburg diffusion line is observed. After 96 hrs immersion, due to decrease in O_2 reduction reaction, a very little diffusion line is noted. From the extrapolated real axis intercept values, the R_t values for 1 hr and 96 hrs immersion are $2.4 K \Omega \text{ cm}^2$ and $24 K \Omega \text{ cm}^2$. The increased R_t value with time is due to the formation of an adherent corrosion product film which decreases the corrosion rate. The film formed on aluminium brass has been identified as $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_6\text{H}_2\text{O}$ [9]. This film is of porous nature as can be seen from C_i values viz $67204 \mu \text{F/cm}^2$ for 1 hr and $672 \mu \text{F/cm}^2$ for 96 hrs. There is also a shift of open circuit potential in cathodic direction (-280 mV at 1 hr to -298 mV at 96 hrs.).

Cupronickel alloys

The impedance behaviour of 70 Cu-30Ni alloys is shown in Figs.4 and 5 respectively. It can be seen that the behaviour of

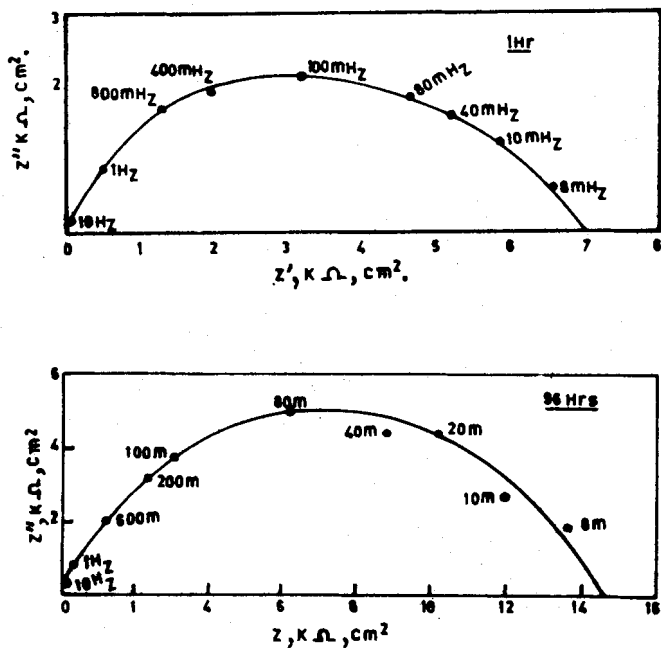


Fig.4: Impedance diagram of 70Cu-30 Ni alloy in synthetic sea water

70Cu-30Ni alloy is different from that of 90Cu-10Ni alloy. The low frequency semicircle is observed in the case of 70Cu-30Ni alloy while a warburg diffusion line is observed in 90Cu-10Ni alloy. The corrosion process in 90Cu-10Ni alloy is cathodically controlled due to appearance of warburg diffusion line. This is also supported from the shift of open circuit potential from -162 mV to -184 mV in 96 hrs. But in the case of 70Cu-30Ni alloy the corrosion reaction is anodically controlled due to the appearance of semicircle in the low frequency region. It is also observed that there is a shift of open circuit potential in anodic direction with time i.e. -309 mV to -236 mV in 96 hrs. The R_i values for 70Cu-30Ni alloy are $7.0K \Omega \text{ cm}^2$ and $14.5K \Omega \text{ cm}^2$ for 1 hr and 96 hrs and C_i value are $2304 \mu\text{F}/\text{cm}^2$ for 1 hr and $139 \mu\text{F}/\text{cm}^2$ for 96 hrs. The decrease in corrosion rate is due to the corrosion product film formation. The film has been reported to consist of inner layer of Cu_2O and an outer porous layer of $\text{Cu}_2(\text{OH})_3 \text{Cl}$ [10]. But in the case of 90Cu-10Ni alloy, the correct R_i values are not possible to get due to diffusion type of behaviour. The approximate R_i values are obtained from the extrapolated semicircles to real axis. The values are $8.5 K \Omega \text{ cm}^2$ and $7.0K \Omega \text{ cm}^2$ for 1 hr and 96 hrs immersion. Among the two alloys the higher R_i value is found in the case of 70Cu-30Ni alloy, indicating its better corrosion resistance.

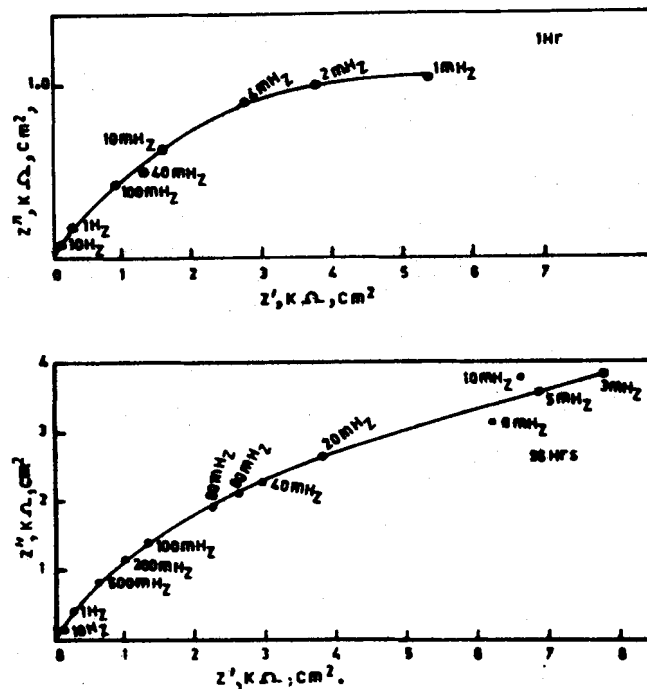


Fig.5: Impedance diagram of 90Cu-10Ni alloy in synthetic sea water

CONCLUSION

The impedance studies have shown that the monel exhibits superior corrosion resistance due to formation of compact film. The other alloys such as admiralty brass, aluminium brass and cupronickel alloys initially corrode and subsequently the formed corrosion product film protects the metals.

REFERENCES

1. H H Uhlig, *Corrosion and Corrosion Control*, John Wiley, New York (1964)
2. T P May, E G Holmberg and J Hinder, *De Ckema Monographian Bank*, (1962) 253
3. T P May and B A Weldeon, *Congress International de la corrosion marine et des Salissures, cames, France*, (1964) p 141
4. F W Fink and W K Boyd, *DMIC report 245*, Bayer and Company Inc, Ohio (1970)
5. H A Todhunter, *Power III*, (1967) 57
6. F P I Jsseling, *Corros Sci*, 14 (1974) 97
7. B S Syrett, *Corros Sci*, 21 (1981) 187
8. D D Macdonald, B S Syrett and S S Wing, *Corrosion*, 34 (1978) 281
9. D C Epler and J E Castle, *Corrosion*, 35 (1979) 451
10. C Kato, J E Castle, B G Ateya H W Pickering, *J Electrochem Soc*, 127 (1980) 1890 and 1987