# CORROSION BEHAVIOUR OF Cu-Ni SOLID SOLUTION

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(Received 8th Aug. 1977 ; accepted Feb. 1978)

Cu-Ni alloys form an isomorphous series of solid solution which find many applications in engineering industries specially under corrosive environments. Although, in many respects these alloys show close simliarity to the pure metals, their mechanical behaviour and corrosion properties differ considerably In the present paper the corrosion behaviour of Cu Ni alloys has been critically reviewed, and the effect of structural heterogeneities, like lattice contraction, vacancies, coring and twinning on the corrosion behaviour has been emphasised.

Engineering properties of metals and alloys are very closely related to their structure and the relative proportioning of the atoms of the alloying constituents. Corrosion is one of the important properties which is sometimes solely responsible for the failure of a component, and it is so closely related to the alloy composition that many a times even traces of some elements become undesirable. Generally the alloy designers develop an alloy for a certain specific mechanical property and do not pay adequate emphasis on the corrosion behaviour of the alloy. In the present paper an attempt has been made to correlate the metallurgical aspects of Cu–Ni alloys with their corrosion behaviour.

**Metallurgy of Copper–Nickel Alloys**

Copper and Nickel have face–centred–cubic structure, and form a complete range of solid solution. Their atomic radio and lattice parameter being almost identical, their atoms replace each other's position randomly in the lattice structure forming isomorphous substitutional type solid solution. No ordering has been reported in this series of alloys. Hence, there is always a chance of forming localised concentration zones of similar atoms resulting from the random substitution of atoms.

When a copper–nickel alloy is cooled from molten state, the composition of solidifying phase changes along the solidus line shown in fig. 1. The resulting solid phase is developed by the formation of concentric rings and dendrites of varying composition of the alloy. Fig. 2 shows a microstructure of the copper-nickel (59% Cu) in as–cast condition, showing cast dentritic structure. This type of variation in alloy composition from the centre to the grain boundry is

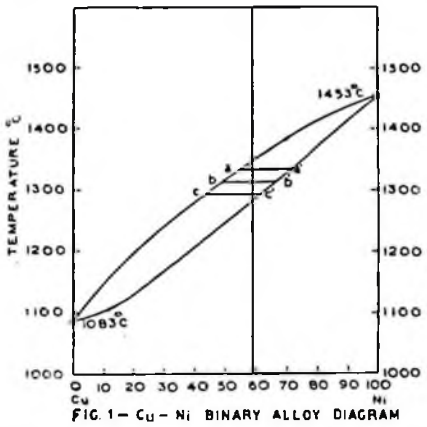


FIG. 1 – Cu – Ni BINARY ALLOY DIAGRAM

known as coring effect and it introduces heterogeneity in the alloy which otherwise has normally a single

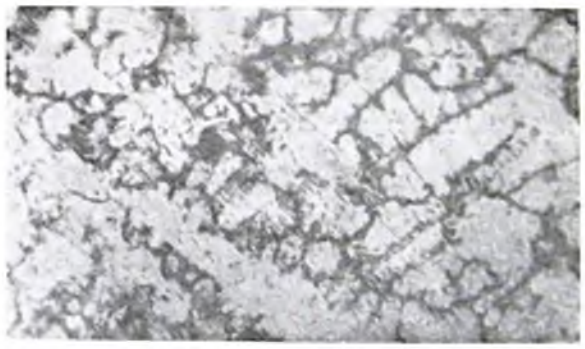


Fig. 2 : Microstructure of Cu–Ni alloy (Cu 59.0%) in as cast condition (Etched–Ferric chloride, Mag—X200).

phase. On cold working and annealing this heterogeneous structure tends to disappear and the cored grains are replaced by new single phase polyhedral grains. But the energy and time required for such treatment is so large that many a times it is impossible to carry out the full treatment in the industry. Fig. 3 shows the micro-structure of the (59%Cu) alloy after annealing for 8 hours at 900°C ; the cast structure has not disappeared even after annealing for such a long time at such a high temperature. When completely homogenised the microstructure will show single phase

polyhedral grains similar to pure metal. Cu–Ni alloys also develop annealing twins, a type of heterogeneity



Fig. 3 : Microstructure of Cu–Ni alloy (Cu 59%) annealed at 900°C for 8 hrs. (Etched-Ferric chloride, Mag—X200).

introduced due to the change in the orientation of the atomic structure.

Besides these types of heterogeneity in the alloy i.e. concentration zones and coring, there are many other types of heterogeneities and defects causing stresses in the metals which are responsible for increasing the corrosion rate of the metal. These disorders and heterogeneities are : (a) Atomic packing on different plains ; (b) changes in grain orientation ; (c) Distortion in lattice structure ; (d) Nature of ordering ; (e) Formation of new phases, their nature and distribution ; (f) Size and distribution of inclusions.

The production method and other engineering operations also introduce defects like dislocations, vacancies, slips, deformation twins etc. which very much affect the corrosion rates.

**Corrosion behaviour of Cu-Ni Alloys**

Pourbaix diagrams for the metal–$H_2O$ system have proved a valuable aid to understand the corrosion behaviour of metals in aqueous solutions. When such diagrams for two or more metals are superimposed over each other the regions of immunity as well as corrosion of the alloy can in many cases be predicted with fairly good accuracy. Fig. 4 shows such a diagram for Cu–Ni–$H_2O$ system. From this diagram, the following observations can be made :

(1) Copper is electropositive to nickel and its

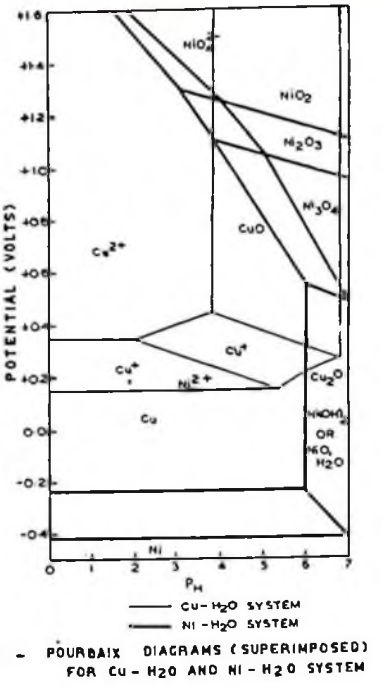



FIG. 4 – POURBAIX DIAGRAMS (SUPERIMPOSED) FOR Cu-$H_2O$ AND Ni-$H_2O$ SYSTEM

immunity region extends up to about 1.6 volts whereas the immunity region for nickel is below –0.4 volts. In both cases the immunity region is maintained up to 6 pH beyond which both the metals form a stable oxide.

(2) At higher positive potential copper passivates in acidic solution having more than 4 pH, and this will provide passivation to Cu–Ni alloys, whereas nickel passivates only in acids having more than 6 pH and potentials more than –0.4 volts. At higher acid concentration and potential, nickel forms a series of oxides $NiO_4^{2-}$, $NiO_2$, $Ni_2O_3$, $Ni_3O_4$, and thus passivates the alloy surface.

From this diagram it is evident that in strong acids either pure copper, Cu–rich alloy or nickel or Ni–rich alloy should be used. In all these cases, nickel is preferentially dissolved, probably due to the formation of a Cu–Ni galvanic cell. But at the same time the formation of an oxide coating due to the shift in the pH in the vicinity of the alloy surface develops adequate corrosion protection. However, under strong acidic media, only Ni and Ni–rich alloys must be used. In alkaline solutions both Ni and Cu will form their stable oxides and retard corrosion rate. Due to the cheapness, Cu–Ni alloys, having up to 30% Ni, are extensively used for marine application.

**Experimental Evidences**

The above-mentioned observations can be confirmed from the results obtained by Goel[1] and others. Goel has prepared ten alloys having compositions given in Table 1. and carried out a systematic study on the anodic polarization behaviour of these alloys.

TABLE 1 Composition of Copper–Nickel Alloys.

| Metal/Alloy Designation | Composition weight % Ni | Cu | Remarks |
|---|---|---|---|
| A | 0.0 | 99.9 | |
| B | 20.4 | 79.5 | The remaining 0.1 to 0.2% |
| C | 27.9 | 72.0 | is impurities such as |
| D | 40.8 | 59.0 | $O_2$, C, Fe, $SiO_2$ etc. |
| E | 49.8 | 50.1 | |
| F | 59.1 | 40.8 | |
| G | 71.7 | 28.2 | |
| H | 79.6 | 20.2 | |
| I | 85.8 | 14.0 | |
| J | 99.9 | 0.0 | |

He has prepared the anodic polarization behaviour diagram (A.P.B.) for these alloys in $H_2SO_4$ solution using a modified Muller's circuit. The details

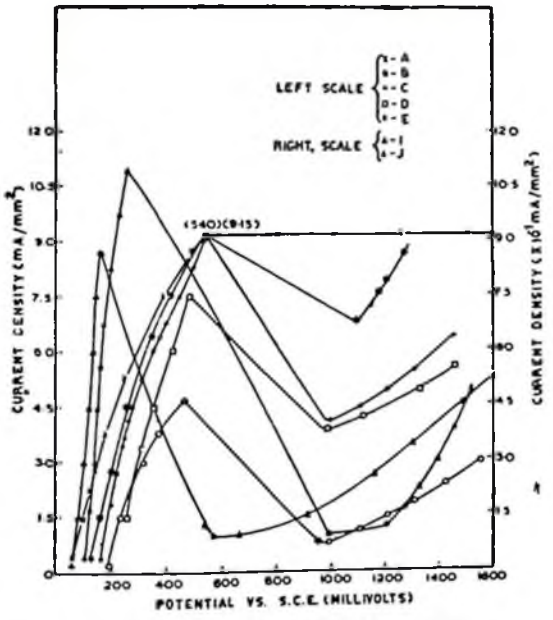



FIG. 5a – ANODIC POLARIZATION BEHAVIOUR OF Cu-Ni ALLOYS (NO – A, D, C, D, E, I & J) IN 0·5M $H_2SO_4$ AT 35°C.

of this circuit and the procedure for the preparation of A.P.B. diagram has been described by Prakash[2].

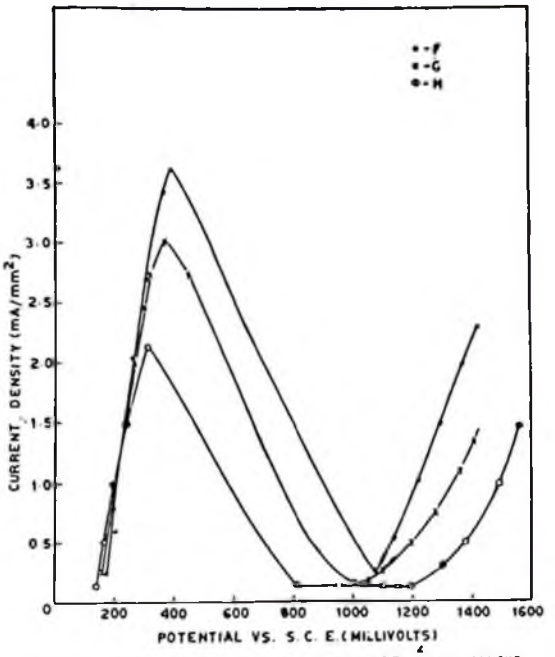



FIG. 5b – ANODIC POLARIZATION BEHAVIOUR OF Cu-Ni ALLOYS (NO. – F, G, H,) IN 0·5M $H_2SO_4$ AT 35°C.

In this circuit since only a small area (2 mm²) is exposed to the acid attack the A.P.B. diagram is not

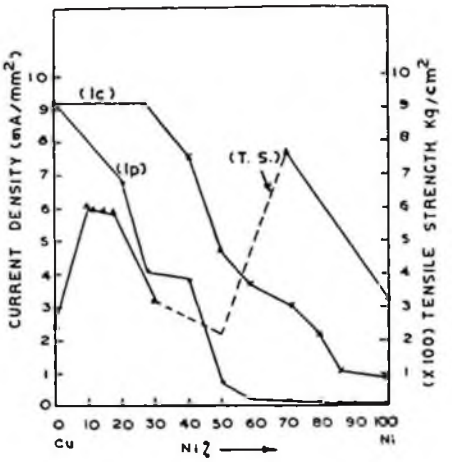



FIG. 6 – EFFECT OF Ni% ON CORROSION BEHAVIOUR (Ic & Ip) AND TENSILE STRENGTH OF Cu – Ni ALLOYS

affected by the side reactions such as pitting etc. The A.P.B. diagrams obtained for the alloys in 0.5% $H_2SO_4$ at 35°C are shown in Fig. 5 (A) and 5 (B). The values of, $E_{po}$, $I_c$ and $I_p$, obtained from these diagrams have been plotted against the chemical composition of the alloy in Figs. 6 & 7.

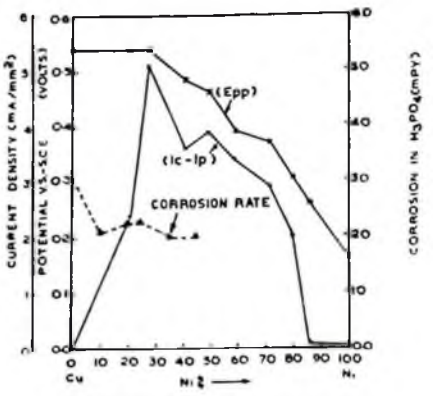



FIG. 7- EFFECT OF Ni% ON Epp, (Ic - Ip) AND CORROSION RATE OF Cu-Ni ALLOYS IN DILUTE AERATED $H_3PO_4$ (@ 4%) AT 20°C

The $I_c$ (critical current density) and $I_p$ (current density at passivation) has been plotted in Fig.6. against % Ni. $I_c$ remains constant up to 28% Ni and then it decreases as the Ni percentage is increased. The $I_p$ decreases from the very beginning as the Ni percentage is increased, but it has an arrest at 28 to 40% Ni. In general, both these curves show a change in the slope of the curve at 30, 50 and 70% Ni. The third curve shown in this figure represents the change in tensile strength of some Cu-Ni alloys (flat product) with increasing percentage of Ni[3]. The trend of the curve very closely follows the $I_c$ curve up to 30% Ni ; beyond this, data have not been available up to 70% Ni, which shows maximum tensile strength. There may occur another maximum in the tensile strength at 50% Ni.

The change in $E_{pp}$ (Primary Passive Potential) with the increase in Ni percentage is shown in Fig. 7. A constant $E_{pp}$ is seen up to 30% Ni (0.540 volts S.C.E.) and beyond this it gradually decreases with Ni% (0.160 volts at 100% Ni). The second curve shows the $(I_c-I_p)$ values as obtained from Fig. 6. This difference between the critical current and the passivation current indicates the passivation efficiency of these alloys since the decrease in the current is mainly due to the nature of the oxide film formed on the surface of the metal. It can be seen from this figure that both the $E_{pp}$ as well as $(I_c-I_p)$ curves show the characteristic changes in their slope at 30%, 50% and 70% Ni. It is interesting to note that the commonly used Cu-Ni alloys have 70-30 and 30-70 composition respectively. The corrosion behaviour of some of the Cu-Ni alloys in aerated phosphoric acid[3] (8.4%) at 20°C is also shown in Fig. 7, and the slope of this curve tallies with that of the $(I_c-I_p)$ curve.

The corrosion behaviour of Cu-Ni alloys in NaOH and $NH_4OH$ solutions have been studied by Hopkinson[4]. The corrosion tests in NaOH show a gain in weight whereas the corrosion in $NH_4OH$ media shows a loss, because the corrosion product formed in $NH_4OH$ solution is soluble in ammonium hydroxide. The results of Hopkinson also show a characteristic change in slope at about 30, 50 and 70% Ni.

## Discussion

Since Cu-Ni alloys form a complete series of solid solution, the corrosion behaviour as well as the mechanical properties should have been expected to behave in a manner similar to that of pure metal, and show a linear change from copper to nickel. But due to the disordering and heterogeneity introduced at the atomic level the mechanical properties as well as chemical behaviour of these alloys very much deviate from the ideality, and although these properties can be correlated to each other qualitatively the specific values of corrosion rate change with the chemical composition of the alloy. While the tensile strength of these alloys initially increases with %Ni, which introduces heterogeneity in the structure, the corrosion rate at first remains constant and then starts decreasing. When the Ni percentage is increased beyond 10% the tensile strength starts decreasing up to 30% Ni. In nickel-rich alloys, the tensile strength and corrosion rate show an identical behaviour. The change in electrode potential as well as corrosion behaviour of Cu-Ni and Ni-Co systems as recorded by Landau and Oldach[5] are in good agreement with the present discussion. Ni-Co alloys also form a complete series of solid solution.

While explaining the passivation mechanism of Cu-Ni alloys in $H_2SO_4$ solution Goel[1] has argued that the $E_{pp}$ value for Ni-rich alloy observed (-0.086V) during the test is in close agreement with the calculated potential required for the formation of NiO (-0.108V), which is followed by the formation of $Ni_2O_3$ and $Ni_3O_4$. He has further explained that when a Cu-Ni alloy is in contact with stagnant 0.5M $H_2SO_4$ solution the metal gets dissolved in the acid shifting the pH of the solution, just in contact with the metal surface, to a higher value approaching 6.

At this pH as is evident from the Pourbaix diagram (Fig. 4) nickel oxides are formed on the surface which impart passivation.

The marked change in the corrosion characteristics of alloys containing 30 to 35% Ni can be attributed to the change in the lattice parameter of the alloy, which shows a 0.11% decrease[6] and an associated increase in the density of the alloy. This contraction in lattice and increase in the density may be responsible for the formation of a dense adherent passivating film on the metal surface leading to better polarization behaviour, and hence the improved corrosion resistance. Osterwald and Uhlig[7] have pointed out that 40% Ni alloy is said to be corresponding to a critical atomic configuration. While alloys having more Ni contain electron vacancies in the d-band, typical of transition metals, and exhibit passivity, the alloys containing less Ni in common with Cu, correspond to an essentially filled d-band of energy level and hence are active. This explanation is plausible only if we consider the metallic solid solution to behave like an ionic solution. Although ionic conductivity has been detected in certain alloys in molten state the theory of ionic structure of liquid metals and alloys is not yet confirmed.

Osterwald and Uhlig[7] have concluded that the $E_{pp}$ of Cu–Ni alloys shows a linear relationship and increases with the pH of the solution,

$$E \text{ (volts } H_2 \text{ scale)} = -0.125 + 0.059 \text{ pH}$$

The have also concluded that the $I_c$ decreases with pH and it is given by the relationship :

$$\log I_c = \lambda \text{pH} + \log K$$

where $\lambda = 0.^{-}6$ and $K = 27$ Ma/cm$^2$.

## Conclusion

In Cu–Ni alloys the corrosion is improved in general with the addition of Ni and Cu in each other up to about 30%. The two most suitable alloys are those containing 30-35% Ni and 70% Ni in copper which are in conformity with the prevalent compositions. The mechanism of corrosion of these alloys in $H_2SO_4$ solution changes with the Ni content of the alloy. While in copper-rich alloys, copper imparts immunity at lower pH, passivation is attained by a galvanic action where Ni gets preferentially dissolved and helps in the formation of an oxide layer as the pH in the vicinity of the alloy surface increases beyond 6. In high Ni alloys, nickel gets passivated to form nickel oxide layer on the surface and thus it imparts corrosion resistance, and copper acts only as a filler material to reduce the cost of the alloy. It also improves the mechanical properties of the Ni-rich alloy. The corrosion resistance of Cu–Ni alloys in alkaline solution is very good and under this condition both copper and nickel form their respective coherent oxide films, so much so, in NaOH solution these alloys show an increase in weight.

In general it can be said that corrosion is a structure sensitive property which is very much affected by the atomic structure of the alloy, its microstructure as predicted from the phase diagram, as well as the history of prior treatment. The results quoted in this paper, show that while controlled heterogeneity in alloys improve the mechanical properties, it may, even on atomic scale, retard the corrosion resistance of the alloy in general. Hence a correlated and systematic study of the effect of alloying elements on the matallurgical and corrosion behaviour of alloys is essential for the alloy design and development.

**Acknowledgement**

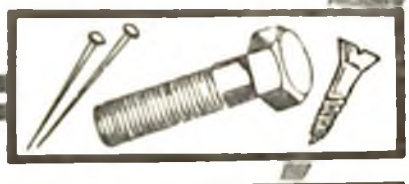
The author wishes to thank Professor K. I. Vasu, Department of Metallurgy, Indian Institute of Science, Bangalore and presently Jubilee Fellow at the Department of Metallurgical Engineering, Institute of Technology, B.H.U., Varanasi, for his valuable discussions during the preparation of this paper.

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