Stress corrosion cracking of copper-manganese alloys — effect of some chemical variables

U. K. CHATTERJEE, S. C. SIRCAR and T. BANERJEE

OCCURRENCE of stress corrosion cracking in binary copper-manganese alloys in the presence of ammonia has been first reported by Lahiri[1] where it has also been observed that Mattsson's solution[2] comprising $CuSO_4$, $5H_2O$ and $(NH_4)_2SO_4$ and ammonia, a very aggressive medium for stress corrosion cracking of brass, is very much effective in producing ready cracking in copper-manganese alloys. Copper-manganese system provides a wide range of solid solution ; in this respect it is comparable to the copper-zinc system, the stress corrosion studies of which have been carried out extensively. A few recent papers[3,4,5] deal with the electrochemical aspects of stress corrosion cracking of alpha brass in Mattsson's solution. In this context it will be of interest to study the behaviour of homogeneous copper-manganese alloys under the variable conditions of Mattsson's solution to get an insight into the mechanism of stress corrosion cracking.

Experimental procedure

Four alloys, designated as M_4, M_5, M_6 and M_7, were studied in the present investigation, the compositions of which are given in Table I. The tests were carried out with wire specimens of $0.025''$ dia. after an annealing at $500°C$ for 1 hour. Mattsson's solution containing 0.02 gm-atom/litre of Cu and 1 gm-mole/litre of NH_3 was used for the study of effect of solution pH, the latter being adjusted with the addition of NH_4OH solution. Solution of this composition had earlier been found to be more suitable for the purpose of control of pH after ageing, as the precipitation of basic copper sulphate is much reduced compared to a solution containing 0.05 gm-atom of Cu/litre. In all cases the solution was used after an ageing of 48 hours and the pH reported corresponds to the after-ageing state.

All the alloys were studied for the effect of solution pH on the cracking behaviour and the effect of copper concentration of the solution on cracking time was studied with the alloys M_4 and M_7.

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SYNOPSIS

Stress corrosion cracking tests of four homogeneous binary copper manganese alloys containing 7 to 23% manganese have been carried out using Mattsson's solution as the corrosive medium. Effect of variations in solution composition and pH on the cracking susceptibility has been studied in details. Change of potential during stress corrosion has been measured. The observed results have been discussed in the light of the chemical reactions involved and formation of surface film.
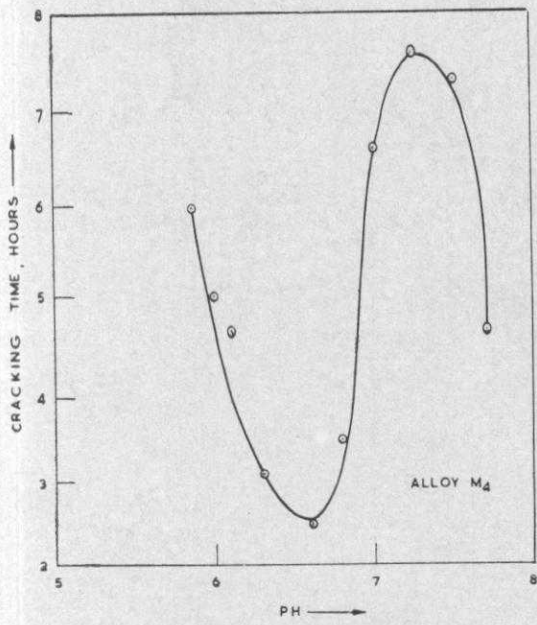
TABLE I Compositions of the alloys studied

| Alloy designation | Percentage composition (Wt.) | | Atomic % Alloy element |
	Cu	Mn	
M_4	91·62	7·06	8·10
M_5	85·07	13·91	15·75
M_6	82·45	15·81	17·60
M_7	76·78	22·86	25·35

Results

(a) Effect of pH

The effect of solution pH on the time of cracking has been shown in Figures 1 to 4. All of them show a similar trend of increasing susceptibility with an increase in pH in the initial range, attainment of a maximum susceptible range of pH, beyond which cracking time rises. At high pH values a second drop in cracking time is indicated. The maximum susceptible ranges of pH for the different alloys are as follows :
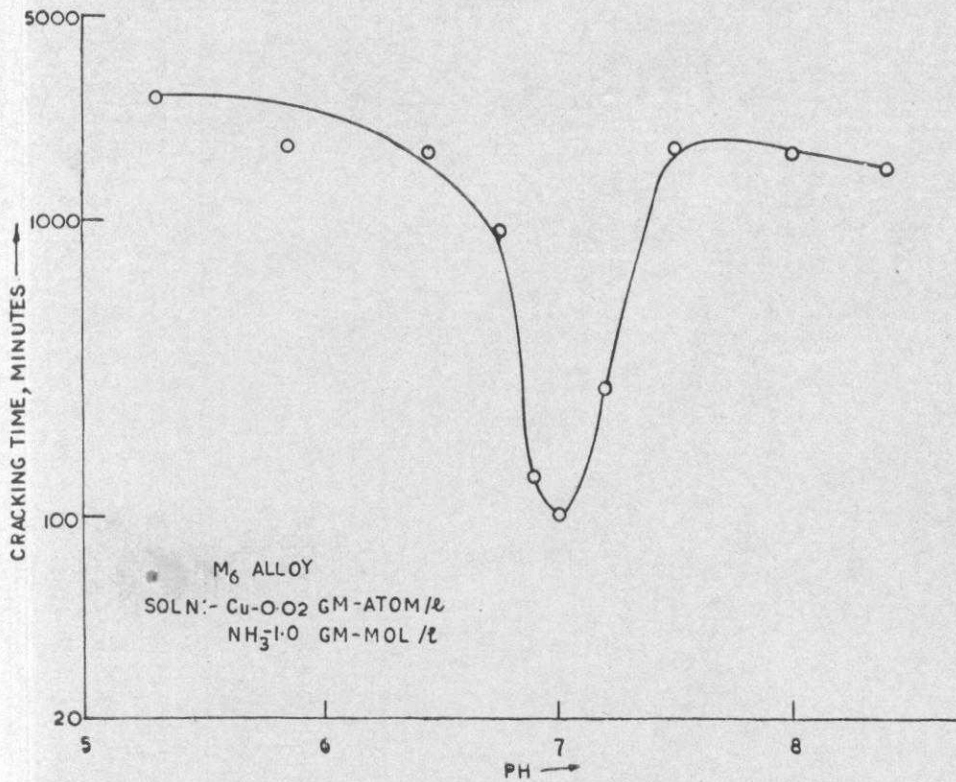
1 *Effect of pH on time of cracking of M₄ alloy*
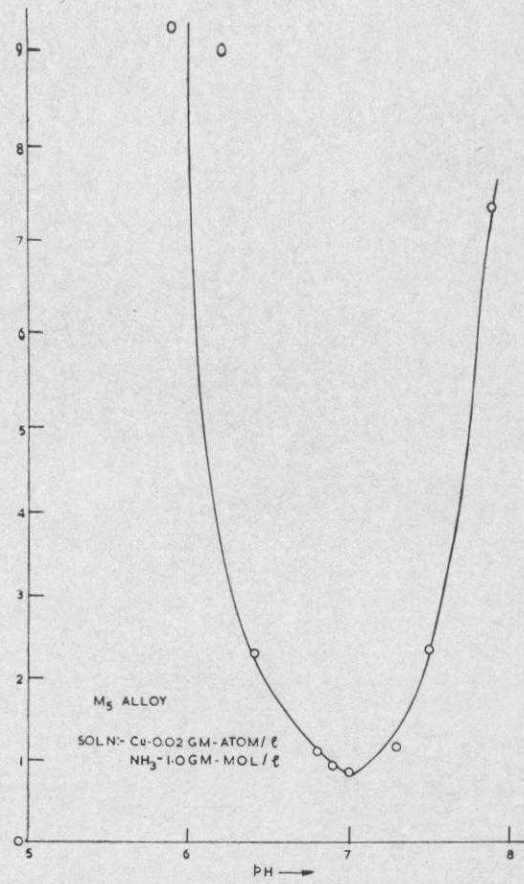
2 *Effect of pH on time of cracking of M₅ alloy*

3 *Effect of pH on time of cracking of M₆ alloy*

|		
M_4	...	6·3 to 6·9
M_5	...	6·8 to 7·2
M_6	...	6·8 to 7·2
M_7	...	5·8 to 6·7

It is to be noted that in the first three alloys with an increase in manganese content this maximum susceptible range shifts to the higher pH-values, with a progressive narrowing down of this range, and there is an increase in cracking time. In case of the alloy M_7, however, the maximum susceptible range shifts to the more acidic side, the range is widened and the overall cracking time shows a considerable decrease.

Film of varying thickness and colour was observed on the specimen surface at all pH values except for those tested at and above pH 8·0.

Microscopic examination of failed samples revealed that the mode of cracking was intergranular in alloy M_4, transgranular in alloys M_6 and M_7, while the alloy M_5 gave both inter and transgranular cracking depending on pH of test solution. At pH values below 7·7 transgranular cracking was observed in alloy M_5, while above pH 7·7 cracking was intergranular. At pH values higher than 8·0, alloys M_4, M_5 and M_6 did not show any crack, but the failed end showed tapering. The M_7, however, showed an extensive cracking at pH 8·0. Some typical cracks are shown in Fig. 5 to 10. Results of measurement of crack density and crack penetration are given in Table II.

(b) Effect of copper concentration in solution

Copper concentration in solution was varied from
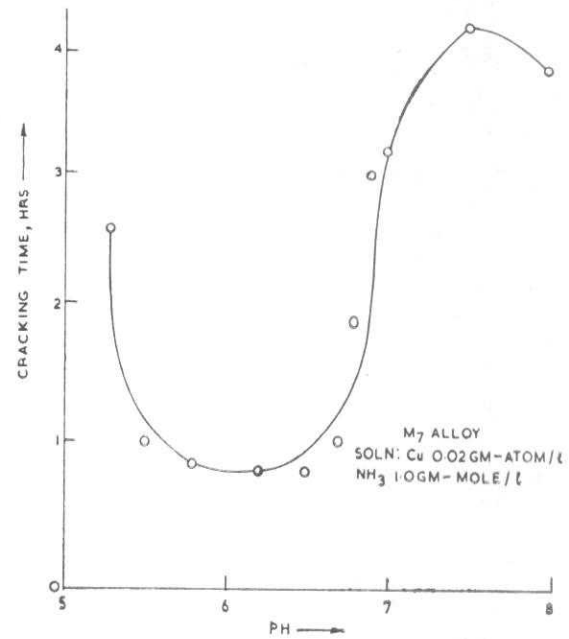
4 *Effect of pH on time of cracking of M_7 alloy*

0·002 to 0·05 gm-atom/litre. Test was confined to two alloys M_4 and M_7, representatives of alloys cracking in intergranular and transgranular fashion respectively. The effect on cracking time was found to be the same in both the cases ; a decrease in cracking time was observed with increase in copper concentration, however, the effect was more pronounced at lower concen-

TABLE II   Observations on cracks in copper-manganese alloys

Alloy	pH	Length of the specimen in which cracks observed, mm.	No. of cracks	Average penetration of cracks, mm.	Crack density mm^{-1}	Mode of cracking
M_4	5·6	0·35	5	0·015	14	Inter
	7·0	11	264	0·075	24	Inter
	7·8	13	350	0·058	27	Inter
M_5	5·7	2·5	63	0·094	25	Trans
	7·0	8	204	0·19	26	Trans
	7·7	6·6	72	0·067	11	Inter+trans (few)
M_6	5·3	16	392	0·133	27	Trans
	6·5	7	154	0·133	22	Trans
	7·4	2·5	19	0·05	3	Trans
M_7	5·5	9	200	0·125	22	Trans
	7·0	10·6	236	0·113	22	Trans
	8·5	10	254	0·094	25	Trans
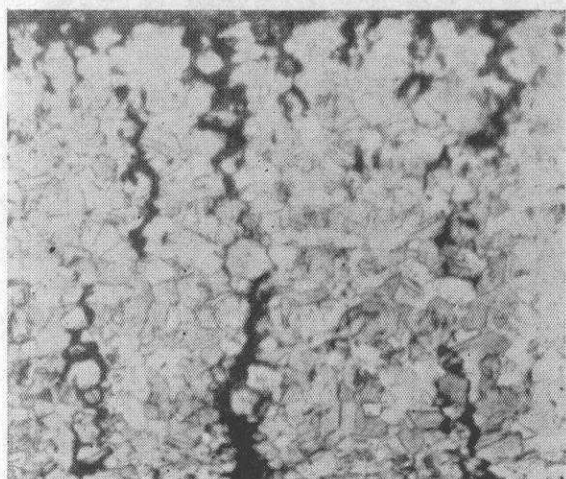
5 *Alloy* M₄, *pH* 6·6   ×450
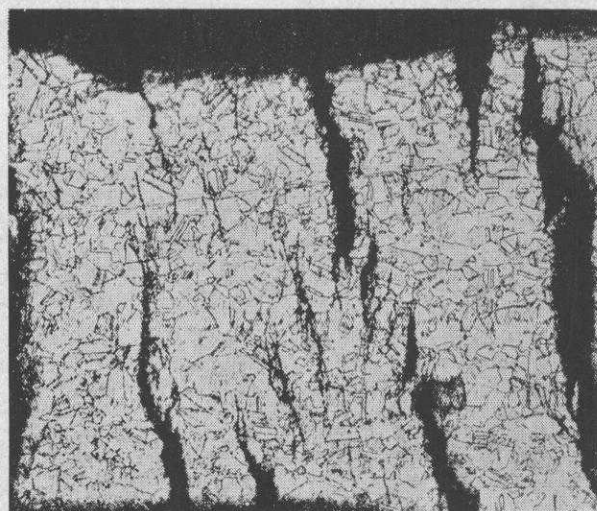
8 *Alloy* M₆, *pH* 6·5   ×240

6 *Alloy* M₅, *pH* 7·1   ×450
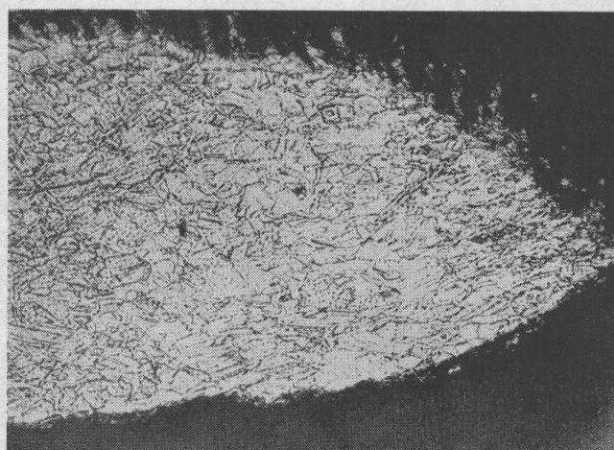
9 *Alloy* M₆, *pH* 8·0   ×240
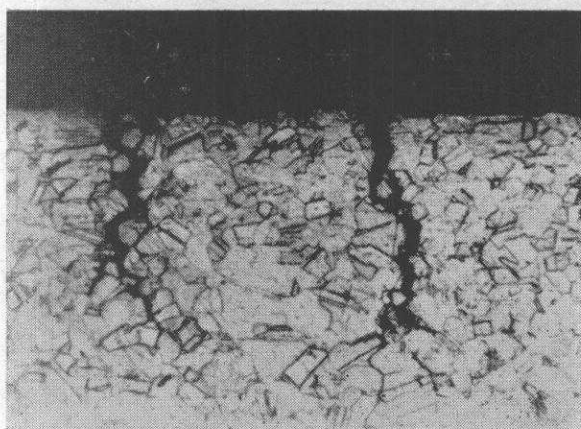
7 *Alloy* M₅, *pH* 7·7   ×450
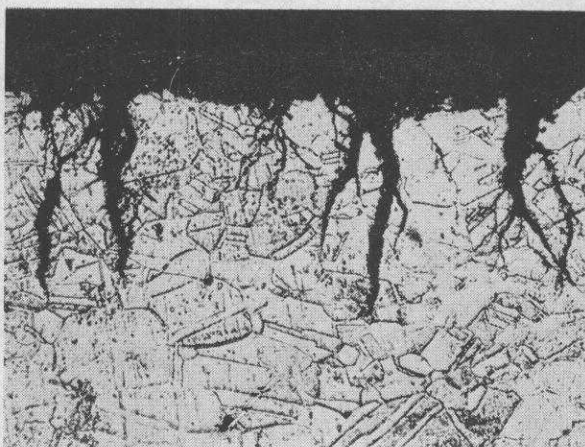
10 *Alloy* M₇, *pH* 8·5   ×450
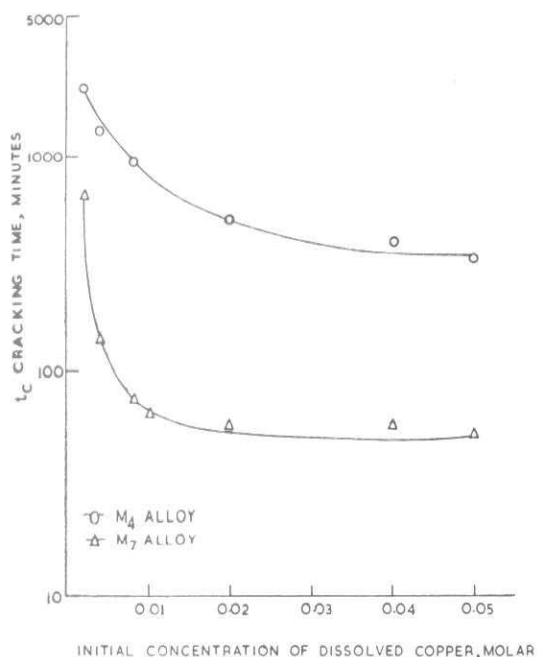
11 *Effect of solution composition on cracking time of copper manganese alloys*

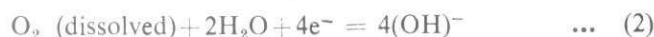trations of copper as can be seen from Fig. 11. Variation of copper concentration, however, was found to have no effect on the mode of cracking.

Discussion

Time of cracking in stress corrosion comprises time of crack initiation and time of crack propagation. Through the work of Hoar and Hines[6] it has been established that the major contribution to the total time of failure is by the time of crack initiation, and in the case of directly loaded specimens in tension in particular, once the crack is initiated propagation of the crack is rather a rapid process as the effective stress goes on increasing at every stage of propagation. Initiation of crack essentially takes place due to dissolution and in Mattsson's solution, it is associated with reaction of copper with aqueous ammonia in presence of air leading to the formation of copper (II) ammine complexes

$$Cu + nNH_3 + \tfrac{1}{2}O_2 + H_2O = Cu(NH_3)_n{}^{++} + 2(OH)^- \quad ... (1)$$
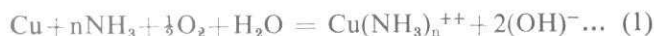
where the cathodic reaction is the reduction of O_2 :

$$O_2 \text{ (dissolved)} + 2H_2O + 4e^- = 4(OH)^- \qquad ... (2)$$

The number of ammonia ligands, n, may be from one to four and fractions thereof in the pH range of 5·0 to 8·0. According to Mattsson,[2] copper (II)-tetrammine plays the major role whereas Johnson and Leja[4] report that the most rapid cracking occurs in solution where n is about one to three. Nevertheless, copper (II)-ammine complex has a strong oxidising effect and in turn oxidises copper according to the reaction
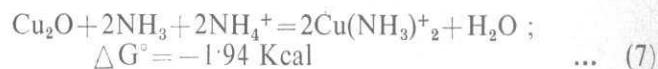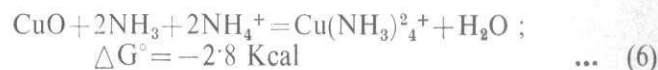
$$Cu(NH_3)_4{}^{2+} + Cu = 2\,Cu(NH_3)^+{}_2 \quad \triangle G^\circ$$
$$= -3·37 \text{ Kcal} \qquad ... (3)$$

This reaction continues as long as copper (II)–ammine exists in the solution. In the presence of oxygen, on the other hand, simultaneous oxidation from cuprous to cupric state occurs resulting in an increase in the concentration of copper (II)-ammine and the reaction thus becomes self-accelerating. In the pH range of 5·0—7·5 for a copper dipper into the solution, the initially available $Cu(NH_3)^{++}{}_2$ complex can lead to the formation of Cu_2O tarnish film given by the reaction

$$Cu + Cu(NH_3)^{++}{}_2 + H_2O = Cu_2O + 2NH^+{}_4 \quad \triangle G^\circ$$
$$= -8·71 \text{ Kcal} \qquad ... (4)$$
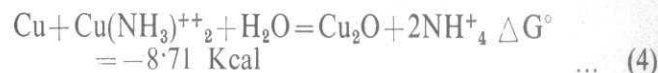
Formation of Cu_2O may proceed also by the reaction as suggested by Hoar and Booker[3]

$$2Cu + H_2O = Cu_2O + 2H^+ + 2e^- \quad \triangle G^\circ$$
$$= 32·53 \text{ Kcal} \qquad ... (5)$$
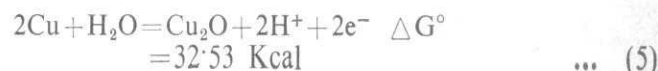
In excess of ammonia, dissolution of Cu_2O takes place according to the reactions

$$CuO + 2NH_3 + 2NH_4{}^+ = Cu(NH_3)^2{}_4{}^+ + H_2O ;$$
$$\triangle G^\circ = -2·8 \text{ Kcal} \qquad ... (6)$$

$$Cu_2O + 2NH_3 + 2NH_4{}^+ = 2Cu(NH_3)^+{}_2 + H_2O ;$$
$$\triangle G^\circ = -1·94 \text{ Kcal} \qquad ... (7)$$

$$Cu_2O + 4NH_3 + 2H^+ = 2\,Cu(NH_3)^+{}_2 + H_2O ;$$
$$\triangle G^\circ = -27·4 \text{ Kcal} \qquad ... (8)$$

In the potential-pH diagram for copper in ammonia solution, Mattsson[2] has reported the stability region of Cu_2O in the region pH 3·0-7·2, whereas Johnson and Leja[7] have shown this stability region to be above pH 10. The latter authors hold that the stability region of Cu_2O is brought down to below pH 7·0 as a result of additional reduction reactions due to presence of solute atoms. Whatever may be the proposition, black tarnish film of Cu_2O has been found to be associated in the pH range giving intense corrosion cracking and the role of such film in the cracking process has been amply established.[8] When alloying element is present along with copper, the dissolution reaction is favoured because of the following reaction :

$$Mn + 2Cu(NH_3)^{++}{}_2 = Mn^{++} + 2Cu(NH_3)^+{}_2 ;$$
$$\triangle G^\circ = -63·26 \text{ Kcal} \qquad ... (9)$$
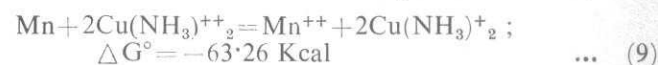
The importance of cupric-ammine complexes in the dissolution reactions, hence in the process of crack initiation, becomes obvious from the above discussion. In the present study the effect of copper concentration in solution on cracking time can be explained in these terms. An increase in copper content leads to an increase in the concentration of cupric-ammine complexes. This effect is obviously more prominent as the concentration increases from lower values. At higher concentration of copper, available ammonia becomes insufficient for formation of complexes, moreover, the concentration of complexes itself may reach a saturation value after which the cracking time obviously does not increase at the same rate.

12 *Potential/time curves at a pH of 5·6*

13 *Potential/time curves for different alloys during stress corrosion at a pH of 6·9*
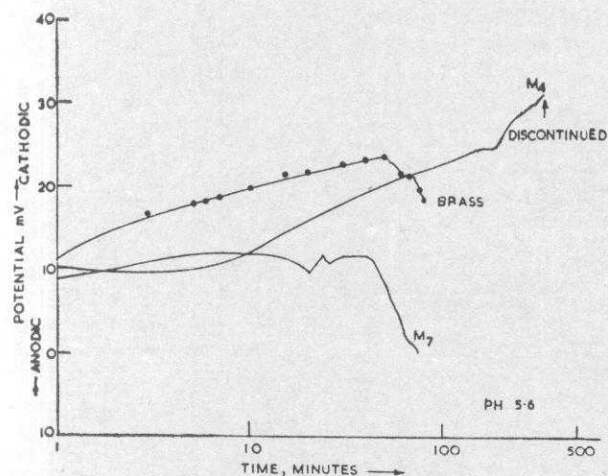
Effect of pH, however, cannot be explained in the simplified terms of ease of complex formation, as the effect itself is of complex nature. The variation in cracking time with change in pH shows minima in plots indicating a critical concentration of hodroxyl ions (OH^-_{cr}) which may bring about most suitable conditions for stress corrosion cracking. This idea may prove to be relevant from the following considerations :

1. At the critical concentration of hydroxyl ions ammonia ligands associated with copper, forming a cupro-ammine, may assume the most value leading to maximum dissolution.
2. Adsorption chracteristics of ions, responsible for cracking according to Uhlig's model[9], may vary with change in pH ; the adsorption is maximum at this critical value of pH.
3. A set of manganese hydroxides form as the pH is increased, and also Cu_2O. The morphology of these compounds forming film on the specimen surface determines the sites for chemical attack. At OH^-_{cr}, the most intense grain boundary attack is facilitated because of a particular film structure.

While sufficient data are not available in support of the first two propositions, the last one is partly supported by the potential studies made in the present investigation. These studies being carried out at pH values of 5·6, 6·9 and 8·5 show (Figs. 12–14) that there is a shift of potential to the nobler side in the first two cases, more being at 6·9, both qualitatively and quantitatively, and at pH 8·5 the shift is towards baser side where no film has been observed on the surface. The shift of potetnial towards nobler side is due to the formation of film on the surface which may be most effective for creating stress corrosion cracks at pH 6·6.

Based on the observed results and utilising the concept of critical concentration of hydroxyl ions, time of cracking has been found to be expressed quantitatively as a function of chemical variables by the following empirical relationship :[10]
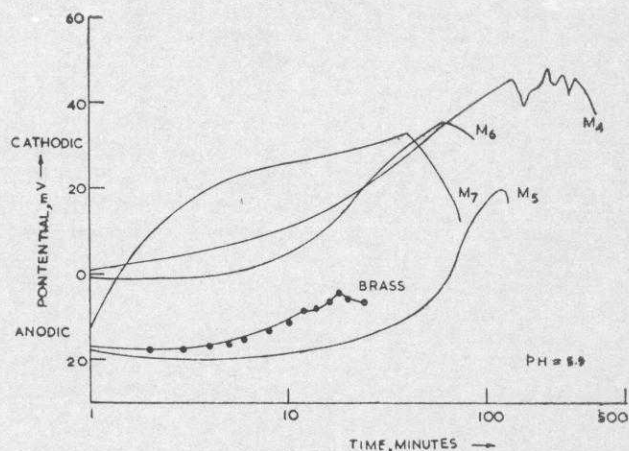
$$\frac{1}{t_c}=K_1(Cu)+K_2(Mn)+\frac{K_3}{K_4+(OH^-_{cr}-OH^-)^2}+K_5$$

where t_c=cracking time in hour,

K_1, K_2, K_3, K_4=constant terms associated with contributing factors given in the parentheses.
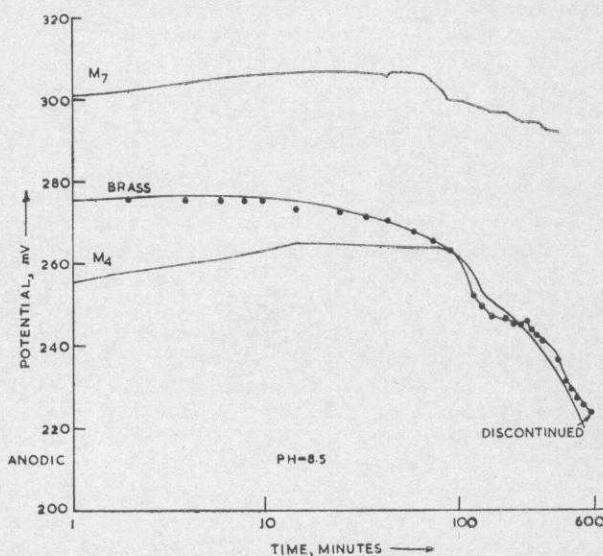
K_5 =contribution by other physical factors.

(Cu) =concentration of copper in solution expressed in gm atom per litre.

(Mn) =solute atom concentration in the alloy.

OH^- =concentration of hydroxyl ions in the solution at a particular pH.

OH^-_{cr}=critical concentration of hydroxyl ions for which the cracking time is minimum.

14 *Potential/time curves at a pH of 8·5*

The constant terms in the equation have been evaluated from the observed data by means of numerical and graphical calculations and it has been found that the calculated values correspond well to the observed cracking time and any deviation hardly falls beyond $\pm 20\%$ which is well within the allowable limit in the stress corrosion studies.

One important observation in the present study is the transition in cracking mode with increase in manganese content and also the pH-dependence of mode of cracking in the alloy M_5. Grain boundaries are essentially potential sites for preferential chemical attack with respect to grain body. Instability of grain boundaries in a chemical environment has been clearly demonstrated by Bakish and Robertson.[11] Segregation of solute atoms at grain boundary makes the latter more prone to chemical attack.[12] So, an initiation of crack at grain boundary and its propagation in an intergranular fashion by continuous electrochemical dissolution sustained by anodic depolarisation effect due to rapid yielding of crack tip[13] is not difficult to visualise.

While this is the situation for dilute alloys, in concentrated solid solutions a number of changes take place. The stacking fault energy of copper is lowered appreciably with the addition of zinc, aluminium,[14] manganese[1] and probably by other elements. Segregation is favoured at the widened stacking-faults in preference to the grain boundaries.[15] Dislocations often take a characteristic planer distribution which favours dissolution along restricted slip planes because of segregation at slip planes or at dislocations themselves. In some alloys appearance of short-range order may bring about local compositional variation inside the grains. Moreover, low stacking-fault energy and short-range order produce coarse slip in the alloy. Coarse slip is effective in causing intense local damage to surface films. All these lead to the possibility of greater chemical attack at reaction sites in the grain interior. Thus a transition in cracking mode from inter to transgranular may be expected with the addition of solute atoms as has been reported to take place in copper-aluminium alloys[16] and has been encountered in the present study in case of copper-manganese alloys at 16 atomic per cent manganese (alloy M_5).

It is interesting to note that in the alloy M_5 the transition in cracking mode has been observed to be influenced by pH of the solution. This alloy is of borderline composition where there is a tendency of equalisation of grain boundary and matrix potentials, difference in which provides the driving force for dissolution, and hence only a slight change in potential determines cracking mode. This slight variation is brought about by a variation in the pH of the solution. This explains the pH-dependence of cracking mode, a fact also observed by Mattsson[2] in case of copper-zinc alloy.

From alloy M_4 to alloy M_6, sites for chemical attack change from grain boundary to grain body. In this process, a balance of attack on both types of sites probably account for an accompanied increase in cracking time. In alloy M_7, however, the active sites are predominantly inside grain body where a transcrys-

talline failure is very much favoured, so in this particular case cracking time decreases to a considerable extent. The shift to more acidic range and the widening of susceptible range obviously suggest an ease of dissolution processes, but this needs further study for conclusive remarks.

Conclusion

Concentration of cupric ammonium complexes as well as of hydroxyl ions in the solution influences the cracking time of copper manganese alloys in Mattsson's solution. The former may be directly related to the dissolution reactions favouring initiation of cracks while the latter may be deemed to control the morphology of film formation on the specimen surface. Cracking proceeds as a result of electrochemical dissolution the driving force for which is the difference of potentials between the reactive sites and the surrounding matrix. The reactive sites are dependent on alloy composition, an increase in manganese content thus changes the cracking mode from inter to transgranular.

Acknowledgement

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Discussions

Mr V. P. Agarwal (Rourkela Steel Plant, Rourkela) : What is the effect of copper when present in traces in steel plates to be used for storage tanks for ammonia ?

Mr U. K. Chatterjee (Author) : From the viewpoint of stress corrosion cracking there seems to be hardly any effect.

Mr G. Rama Rao (I.O.C. Ltd., Barauni Refinery) : Will there be stress corrosion cracking in copper-nickel-aluminium alloys even in ammonia medium ? If so, to what degree compared to other copper alloys ?

Mr U. K. Chatterjee (Author) : Stress corrosion cracking is most likely to occur in copper-nickel-aluminium alloys even in ammonia medium. It can be assessed only on the basis of actual investigations.