Technical Section

HIGH-TEMPERATURE OXIDATION OF COPPER–MANGANESE ALLOYS

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ABSTRACT

Oxidation resistance of Copper-Manganese alloys containing 5, 10, 15 and 20 per cent Manganese increases with increase in Mn content. In Cu-20% Mn alloys, there is an initial linear oxidation representing a phase-boundary reaction and final parabolic oxidation governed by the Cu^+ ion diffusion through the scaling layer.

INTRODUCTION

Pure metals are rarely used as constructional materials. Oxidation of alloys and, particularly, methods to achieve improved oxidation resistance are, from a technological point of view, the most important aspect of high-temperature oxidation of metals. India has vast reserves of Manganese ores and therefore the utilization of manganese alloys has exceptional significance. Of these, the copper-manganese alloys has exceptional significance. Of these, the copper-manganese bronzes are finding wide use for the replacement of conventional brasses and bronzes for marine applications and as electrical resistors. Many of the physical and mechanical properties of copper-manganese alloys are found to be influenced considerably by prolonged annealing and heat-treatment at higher temperatures [1,2]. From these and other points of view, it becomes important to study the oxidation characteristics of copper-manganese alloys. Precise investigations into the internal and external oxidation of these alloys are also desirable since the appearance of internal oxidation (and the consequent dispersion strengthening with significant improvement in mechanical properties of alloys) could then be predicted with some certainty, which in turn would be very useful in dealing with the heat treatment and technological applications of these alloys.

The mechanism of alloy oxidation is quite complex and is controlled not only by the characteristics of the constituent metals but also by the nature of the oxides formed, their structure and solid solubility, the stability of the oxides in presence of the parent metal and the impurity elements, the transport processes in mixed oxides and alloy phases, oxide plasticity and creep, mechanical stresses in growing oxide scales, and adherence of scales to the alloy.

Copper and manganese form a continuous series of solid solutions with a minimum at 868°C with 30% Mn. At lower temperatures these might decompose into two phases. However it has been established that this decomposition is so sluggish that for all practical purposes it is assumed to be absent [1]. Under the experimental conditions copper can form CuO (under high oxygen pressures) and Cu_2O (in presence of copper or an oxygen partial pressure less than 4×10^{-5} atmospheres at 800°C) and manganese can form MnO, Mn_3O_4, Mn_2O_3, and MnO_2, depending upon the temperature and oxygen partial pressure (3-5). The mutual solid solubility of these oxides is only negligible.

Considerable work has been done on the oxidation of copper and copper alloys [6-8], but the published data on the oxidation of copper-manganese alloys [9-12] reveal conflicting conclusions. Rhines, Johnson and Anderson [11] have studied the internal oxidation of copper-manganese alloys containing 0.03 to 0.55 per cent manganese. Some work has also been done on the oxidation of Nickel-Manganese alloys [4,14,15]. It was felt that a thorough understanding of the oxidation

characteristics of Cu-Mn alloys would be helpful in the heat-treatment procedure for the alloys based on the Cu-Mn system; it would also throw more light on the mechanism of oxidation.

EXPERIMENTAL

Copper-manganese alloys were prepared from commercial copper and electrolytic manganese. Since electrolytic manganese contains considerable amounts of entrapped hydrogen (of the order of 200 ml/100 g.) prior degassing for about one hour at 500°C under vacuum was necessary, before its use for the alloy preparation. Copper was initially melted under borax flux in a salamander crucible and degassed manganese was added with continuous stirring with a graphite rod. The melt was poured at 1100°C into cast iron moulds Four alloys of the following nominal composition were selected for the study: Cu- 5% Mn, Cu-10% Mn, Cu-15% Mn, and Cu-20% Mn. The copper-20% manganese alloy on analysis was found to contain 80.7% copper.

For oxidation studies, alloy discs, 1.5 cms. in dia. and 1.5 cms. in height, having an apparent surface of about 10 sq. cm., polished on both sides, were prepared by standard metallurgical techniques. The rate of oxidation was followed by noting continuously the increase in weight with time of the alloy disc suspended from a precision balance. A thin mica sheet placed between the specimen and the platinum suspension wire avoids any interaction between them.The disc was in the centre of the even hot zone of the reaction tube inside a movable furnace arranged beneath the balance. In order to avoid any stray convection heating of the balance, the suspension wire passed through a small hold in a baffle consisting of a water-cooled plate much larger in area. A similar arrangement has been used for a variety of oxidation studies([10]). Temperature measurements were made with a Pt./Pt.-Rh thermocouple introduced into the furnace.

The temperature of the specimen in each experiment was raised with the assembly in a current of inert gas like nitrogen, and, at the required constant temperature nitrogen was replaced by a gas mixture of known oxygen partial pressure introduced through the bottom of the reaction tube. The gas leaves the system through the top nozzle guiding the suspension wire. In the present series of experiments $79N_2$-21_2 mixtures were used, which were made by randomly mixing dried and purified nitrogen and oxygen. A flow rate of 100 ml./min. was maintained; this was chosen as an optimum to meet the conflicting requirements of the necessity for a large flow rate to avoid the inward diffusion of air through the top nozzle where the suspension wire entered the reaction tube, and of a small flow rate to eliminate any

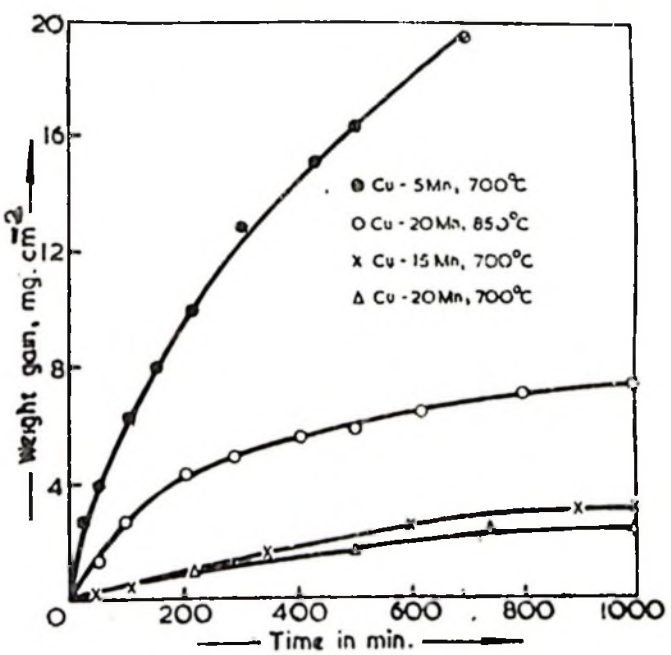


Fig. 1. Oxidation of Cu-Mu Alloys by air

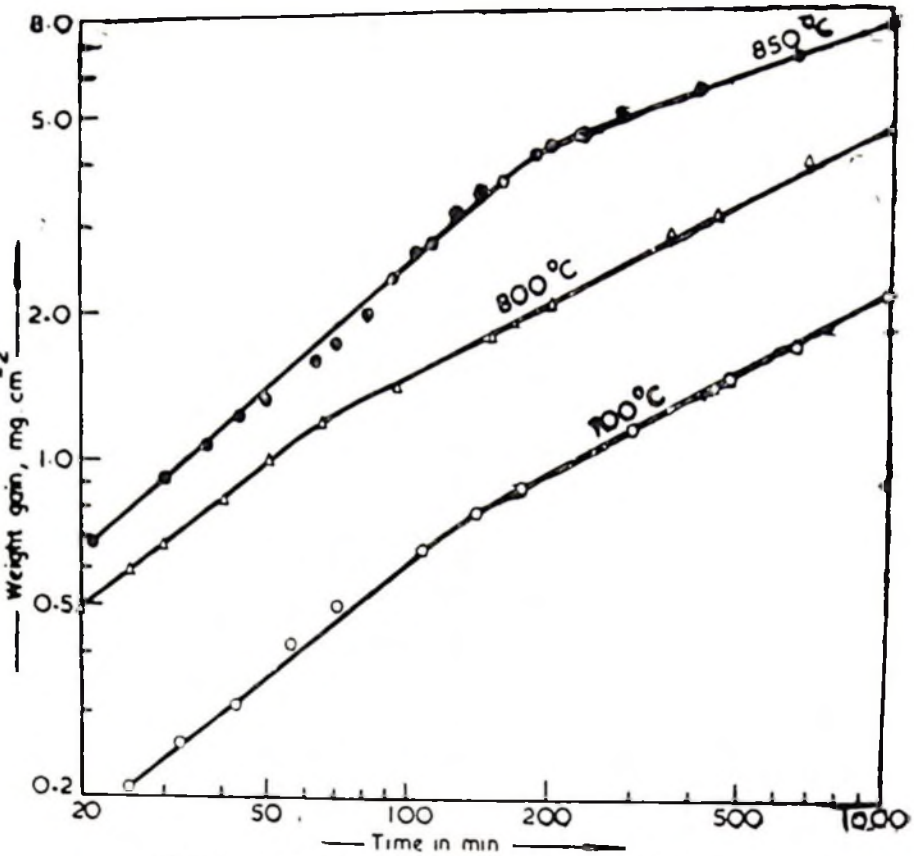


Fig. 2. Oxidation of Cu-20 Mn Alloys in air

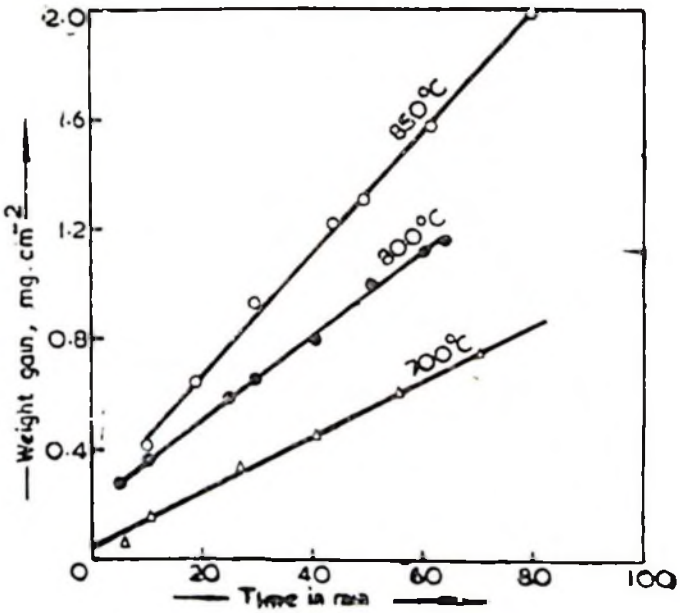


Fig. 3. Initial Linear Oxidation of Cu-20 Mn Alloys in air

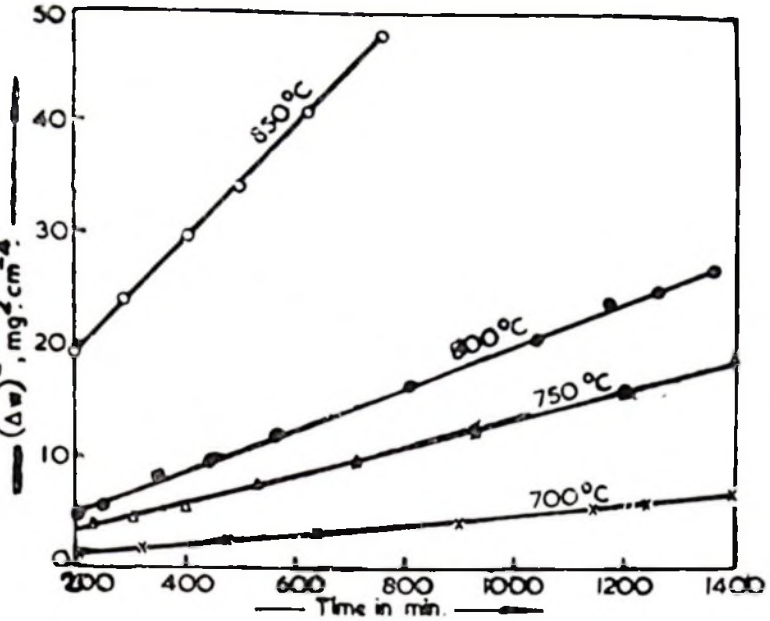


Fig. 4. Parabolic Oxidation of Cu-20 Mn Alloys

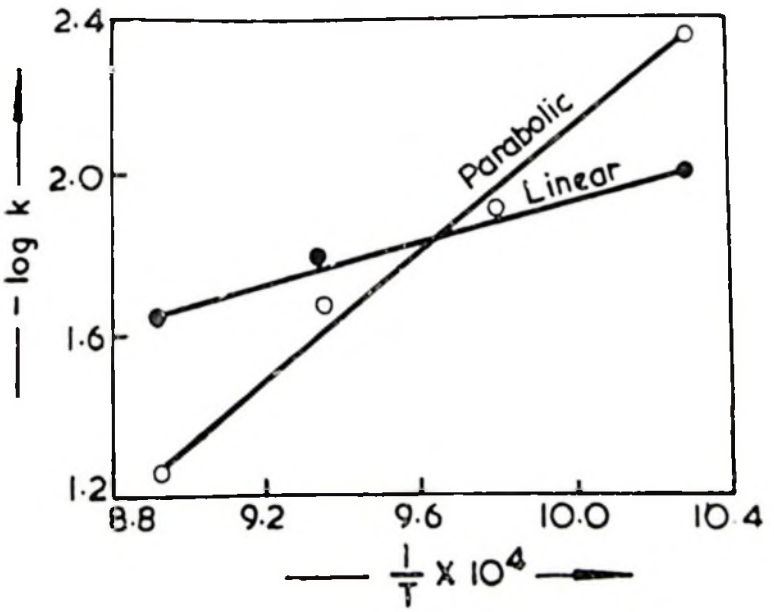


Fig. 5. Arrhenius Plots for Oxidation of Cu-20 Mn Alloys

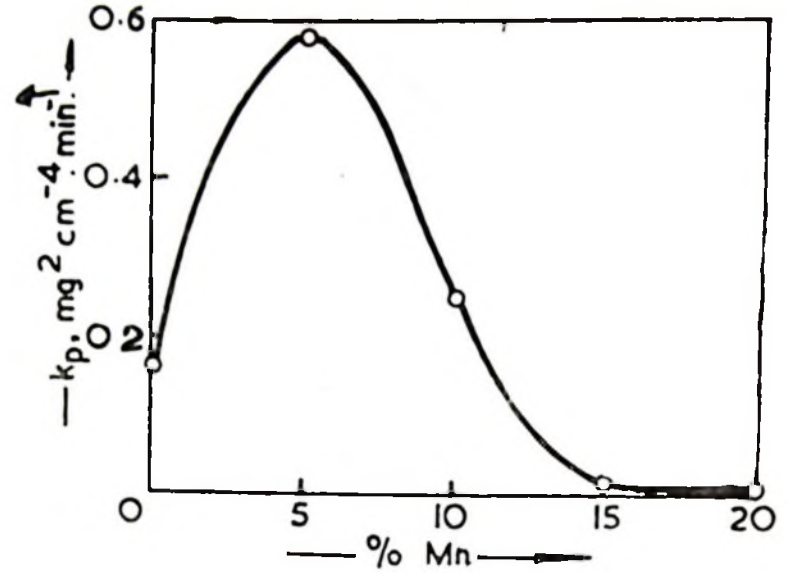


Fig. 6. Effect of Composition on the Oxidation of Cu-Mn Alloys at 700°C.

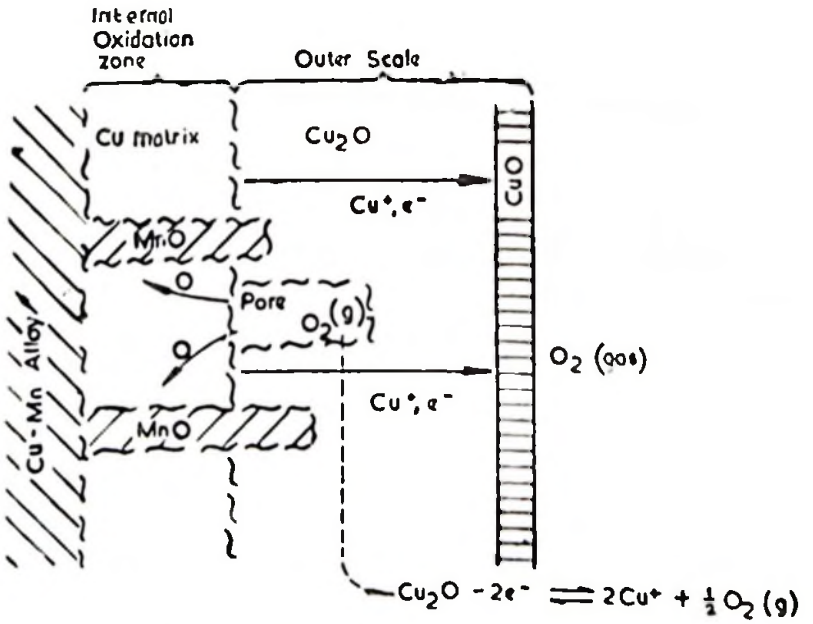


Fig. 7. Scheme of Cu-Mn Alloy Oxidation

buoyancy effects on the specimen which might upset smooth weight change observations. However, a range of 50-300 ml./min. had no significant effect on the reproducibility of results.

Upon conclusion of the weight gain measurements, the oxidized specimens were examined metallographically by standard techniques of mounting, sectioning, polishing and etching.

RESULTS AND DISCUSSION

The general behaviour of the oxidation of copper-manganese alloys is presented in Fig. 1. Increase in the manganese content of the alloy increases its oxidation resistance, although the Cu-5% Mn alloy oxidizes faster than pure copper.

In order to understand the kinetics and the operating mechanism of oxidation, the logarithm of weight gain per unit area, $\triangle w$, is plotted against the logarithm of time, t, for oxidation, in Fig. 2. It is evident from the distinct break in the curves that two mechanisms are operative. The slope of the curves for the initial oxidation region is close to unity (0.91, 0.85, 0.90), and in this case the oxidation is approximately governed by a linear rate law:

$$\triangle w = k.t + c \quad .. \quad .. \quad .. \quad (1)$$

where 'k' is the linear oxidation rate constant and 'c' is another constant. Fig. 3 presents the data on the initial linear oxidation of Cu-20% Mn alloys in air ($79N_2$-$21O_2$). The slope of the latter part of the oxidation curves in Fig. 2 is close to 0.5 (0.52, 0.50, 0.45, and 0.51), and this is the region governed by a parabolic rate law of oxidation:

$$\triangle w^2 = {}^kp.t \quad .. \quad .. \quad .. \quad (2)$$

where ${}^kp$ is the parabolic rate constant. For all the alloys studied there is a region of parabolic oxidation; data for Cu-20% Mn alloy are presented in Fig. 4.

Continued reaction of a metal or alloy exposed directly to oxygen is possible by countercurrent diffusion of metal and oxygen atoms (or ions and electrons) through grains, along grain boundaries or pores of an intermediate oxide layer at the metal-gas interface. The characteristics of this oxide layer (its defect structure, orientation, presence of cracks, pores, etc.) determine the mechanism of oxidation, while the kinetics of oxidation may be governed by diffusion processes and/or phase-boundary reactions. As a rule, high temperature parabolic oxidation signifies that a diffusion process is rate controlling. Such a process may include a uniform diffusion of one or both of the reactants through a growing compact scale (Wagner mechanism), or a uniform diffusion of gas into the metal. Since parabolic oxidation implies diffusion, the rate constant ${}^kp$ contains a diffusion constant and the activation energy for oxidation may then turn out to be that of the diffusion step. The rate constants for the linear as well as parabolic oxidation of copper and copper-manganese alloys in the range 700-850°C obey an Arrhenius relationship (Fig. 5), giving a value of 15,000 ± 3,000 cal/mole for the activation energy for the initia linear oxidation and 37,000 ± 2,000 cal/mole for the activation energy for the parabolic oxidation. This latter value agrees well with that for the high temperature oxidation of copper, *viz.*, 38,000 ± 2,000 cal/mole with the parabolic rate law.(6,7). Indeed, it is also necessary to compare this





value with the energy of activation for the diffusion of Cu+ ions through a Cu_2O layer, which is 37,000 cal/mole in the range 800-1000°C [17,18]. This remarkable closeness of the values may be partly fortuitous, but it certainly indicates the clear evidence for a preferred Cu+ ion diffusion through the scaling layer as the operating mechanism during the parabolic oxidation of copper and Cu-20% Mn alloys.

As can be seen from Fig. 2, the parabolic rate law is not obeyed at the beginning of the alloy oxidation, and this is understandable if one considers that in the first stage of the oxidation a predominant dissolution of oxygen and finally an oxide (*e.g.* Cu_2O) nucleation take place. Since the oxidation rate relationship is linear (Fig. 3), a surface or phase boundary process is rate controlling and this process has an apparent activation energy of about 15 kcal/mole (Fig. 5). This may involve for example, a steady-state reaction limited by the supply (chemisorption) of oxygen at the oxide surface, or a reaction governed by a steady-state formation of oxide at the metal/oxide interface. The linear rate law is applicable only to the point where the diffusion rate, which decreases with increasing layer thickness according to a parabolic rate law, becomes comparable with the rate of the phase boundary reaction. With further growth of a protective layer, the diffusion rate becomes the rate determining factor as can be seen from the pure parabolic rate law that begins to operate. With the available data in the present work, it is difficult to specify whether the rate-determining phase boundary process is at metal/oxide or oxide/gas interface. However Dell et al.[19] have shown that during the decomposition of nitrous oxide and simultaneous oxidation of copper sheets covered with Cu_2O, chemisorption is the rate determining step with an apparent activation energy of 20 Kcal/mole. in the temperature range 50-250°C. This is expected to be much smaller at higher temperatures (700-900°C as used in the present work) and may become comparable with the value of 15 Kcal/mole found for the initial linear oxidation. This leads to the indirect conclusion that the oxide/gas phase-boundary process, *viz.*, the chemisorption of oxygen is rate-determining during the intial oxidation of Cu-20% Mn alloys.

The parabolic rate constant at 700°C increases initially with manganese content upto about 5% and then decreases, even though the effect is only negligible in alloys containing more than 15% Mn (Fig. 6). Small amounts of manganese have been reported to decrease the oxidation resistance of copper and copper alloys [9,10]. In low-manganese alloys one would expect an initial spot-wise formation of Cu_2O (plus an outer skin of CuO) and manganese would diffuse into the alloy from the alloy/oxide interface. As oxidation proceeds, the concentration of manganese in the alloy will increase and the formation of manganese oxides will take place. Cu_2O is a p-type semiconductor and addition of small amounts of ions of higher valency (Mn^{2+} or Mn^{3+}) would result in the replacement of some of the Cu+ ions in the lattice, thus creating new cation defects. The rate of diffusion of cations would thus increase and so would the rate of oxidation, since it is a process essentially controlled by cation diffusion, as discussed earlier for the parabolic oxidation. With further increase in manganese content of the alloy, say in Cu-20% Mn alloy, conditions would be favourable for the formation of a composite scale of Cu_2O and MnO (or Mn_3O_4 etc.) having better oxidation resistance. The MnO scale grows according to either the displacement reaction:

$$Cu_2O + Mn^{2+} \rightleftarrows 2\,Cu^{+} + MnO \quad .. \quad (3)$$

in the scale, or the subscale reaction:

$$Cu_2O + Mn \rightleftarrows 2\,Cu + MnO \quad .. \quad (4)$$

both producing different layers in the oxide scale (plates 1 and 2). This is possible because of the large difference in the stability of these oxides[20] ($\Delta G°Cu_2O = 23.2$ Kcal at 700°C while $\Delta G°MnO = 75.0$ Kcal per mole). It has been reported that Cu-Mn alloys can be internally oxidized (13). Oxidation of Cu-20% Mn alloys in air would thus produce not only an external scaling layer on the alloy, which consist of Cu_2O with exterior thin layer of CuO, but also a subscale oxidation zone in the interior periphery of the alloy. This internal oxidation zone is due primarily to the solubility of oxygen in the alloy phase. If the rate of diffusion of oxygen in the scale/alloy interface becomes smaller than that in the alloy, the degree of internal oxidation should decrease and ultimately become negligible.

It is evident from plates 1 and 2 and the data presented earlier that the oxidation mechanism involves the formation of Cu_2O (plus an outer skin of CuO) layer and internal oxidation of manganese in the alloy periphery. As the growth of Cu_2O layer proceeds through outer migration of Cu+ ions via vacancies, one expects the development of porosity as a result of the accumulation of cation vacancies. This

would result in a two-zone Cu_2O layer—an outer compact Cu_2O layer (plus a skin of CuO), and an inner porous Cu_2O layer in which are also embedded particles of manganese oxides. This, in fact, is the general nature observed, even though the pores were visible on specimens only after prolonged oxidation. The pores will generally act as a solid-state diffusion barrier for the migration of Cu+ ions; but oxidation is sustained by transport of oxygen across the pores, the oxygen being formed through a decomposition of the oxide next to the pores:

$$Cu_2O \longrightarrow 2\,Cu^+ + 2e + 1/2\,O_2\,(g) \quad \ldots (5$$

This brings about continued internal oxidation and subscale formation. Such gas transport across pores through a dissociative scheme has been reported to be operating in the growth of FeO in iron alloys[21] and in the oxidation of Cu-Be and Ni-Cr alloys [6-8]. A schematic diagram for the mechanism of Cu-20% Mn alloy oxidation is given in Fig. 7. Internal oxidation and the resulting dispersion of fine oxide particles in the copper matrix strengthens the material; the hardness in the internal oxidation zone was found to be around 200 VHN while the normal hardness of the unoxidized part of the alloy is only about 90 VHN.

Thus, in contrast to the oxidation of pure copper, the mechanism of oxidation of Cu-Mn alloys is complex in the following respects: (*a*) low manganese alloy oxidation, where an oxide solid solution is preferentially formed, which can be described in terms of Wagner's scaling theory of lattice defects for heterotype mixed phases, (*b*) alloys for which, owing to differences in the free energies of formation of the individual oxides, the structure and growth of the scaling layer are determined by the competition between the diffusion processes in the alloy and in the scaling layer, and (*c*) oxygen solubility and internal oxidation of manganese, the less noble alloy partner.

SUMMARY

1. With minor additions of manganese, the oxidation rate of copper increases, while high-manganese alloys offer some resistance to oxidation due to the formation of composite scales.

2. The oxidation of Cu-20% Mn alloys obeys initially a linear rate law representing a phase-boundary reaction and finally a parabolic rate law implying a diffusion-controlled oxidation process.

3. The activation energy for the linear of Cu-20% Mn alloys is close to the energy of activation for chemisorption on the oxide, indicating the oxide-gas phase boundary reaction as the rate-controlling process.

4. The activation energy for the parabolic oxidation of Cu-20% Mn alloys is found to be close to the value for the oxidation of pure copper and for the diffusion of Cu+ ions throug Cu_2O. It is surmised that the onward diffusion of Cu+ ions controls the parabolic oxidation of these alloys.

5. The scaling layer consists of an outer skin of CuO, a compact layer of Cu_2O, a porous layer of Cu_2O in which are also embedded particles of manganese oxides and finally an internal oxidation zone.

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