JOURNAL OF APPLIED ELECTROCHEMISTRY 11 (1981) 299–303

Selective anodic dissolution of phases in copper-based alloys in citric acid solution

A. MANCE, A. MIHAJLOVIĆ

Institute of Nuclear Sciences 'Boris Kidrič', Department of Materials Science, Vinča-Beograd, Yugoslavia

Received 30 June 1980

The anodic behaviour of as-cast and homogenized binary copper-based alloys with Zr, Cr, Al, Si and Sn in 50% citric acid solution has been studied by the potentiostatic method. At positive potentials all as-cast and homogenized alloys with low additions of alloying elements behave in a manner similar to that of copper. However, there is an essential difference between the polarization curves for copper with 8% Al and those for copper. The differentiation ratio of dissolution rates and optimum values of dissolution potentials were calculated using the data for as-cast alloys. The highest differentiation ratio was found for the Cu–8%Al alloy. On the basis of calculated potentials, a number of experiments were performed in order to separate the phases.

1. Introduction

The dissolution potential of a particular phase in a heterogeneous alloy can be determined on the basis of the dissolution rate differentiation ratio. However, bearing in mind the difficulties in the determination of separate polarization curves for each phase present in alloy, the equation for the dissolution rate differentiation ratio was modified to obtain the optimum dissolution potential from the dissolution rate ratio expressed as current densities at a given potential for the basic metal and its alloy [1]. Therefore, the modified Pražak's equation [2] for copper alloys, i.e., for the systems investigated here, is $D_M = (i_{Cu}/i_A)_E$, where D_M is the differentiation ratio for the matrix, and i_{Cu} and i_A are dissolution rates for copper and alloy, respectively.

Previous investigation [3] of a complex copper system has shown the possibility of applying the modified equation to determine the dissolution potential of the matrix in other simple copper alloys. The results of investigations of Cu–1%Zr, Cu–1%Cr, Cu–2%Cr, Cu–4%Al, Cu–8%Al, Cu–2%Si and Cu–8%Sn alloys are presented in this paper.

2. Materials and experimental techniques

The alloys Cu–1%Zr, Cu–1%Cr, Cu–2%Cr, Cu–4%Al, Cu–8%Al, Cu–2%Si and Cu–8%Sn were made from OFHC copper and Cu–Zr, Cu–Cr, Cu–Al, Cu–Si and Cu–Sn master alloys by melting in an electroresistant vacuum furnace and casting into metallic moulds. Investigations were performed on samples in the as-cast and homogenized (equilibrium) states. The specimens were annealed at different temperatures and for different time intervals (Table 1), depending on the type of the alloy, and then furnace cooled. Prior to each experiment the specimens were ground and polished with diamond pastes. Potentiodynamic polarization measurements, etching of samples for metallographic experiments and dissolution of as-cast samples were carried out with an electronic PRT 500-L 'Tacussel' potentiostat. The curves were plotted on an X–Y recorder while the potential was automatically increased at a speed of $dE/dt = 100\,mV\,min^{-1}$. The working potential was measured with respect to a saturated sulphate

Table 1. Thermal treatment of copper alloys

Alloys	*Annealing temperature* (°C)	*Annealing time* (h)
Cu–1%Zr	900	1
Cu–1%Cr	950	3
Cu–2%Cr	950	3
Cu–4%Al	800	5
Cu–8%Al	800	5
Cu–2%Si	840	5
Cu–8%Sn	680	3

0021–891X/81/030299–05$02.50/0

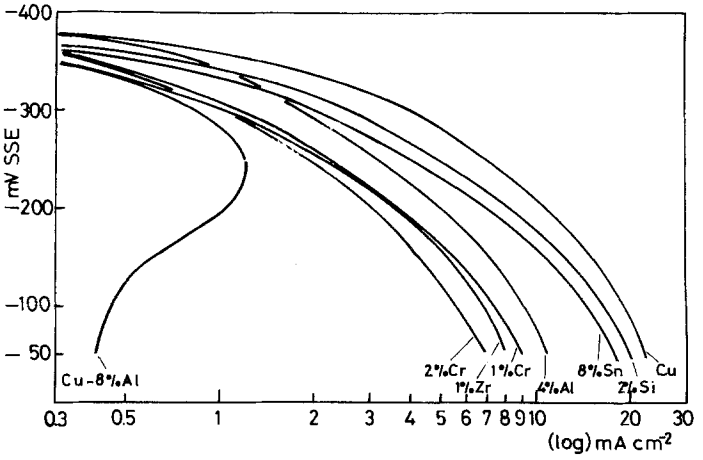


Fig. 1. Polarization curves for copper and the alloys.

electrode (SSE); 50% citric acid solution was used as the electrolyte.

3. Results and discussion

The polarization curves for copper and the as-cast alloys, presented in Fig. 1, all have similar shapes with the exception of Cu–8%Al, for which the curve is different in both shape and position. The position of the curves for the alloys depend on both the kind and quantity of alloying elements. The additions cause shifting of the polarization curves towards lower current densities at the same potential values. The dissolution rate differentiation ratio as a function of the potential was calculated from the data obtained for the polarization curves for copper and the as-cast alloys by applying the modified equation for D_M.

D_M curves are presented, together with the microstructures, for the as-cast alloys in Figs. 2–8. The alloys are classified into three groups: the first group, Cu–1%Zr, Cu–1%Cr and Cu–2%Cr, consists of those alloys with low solubility of alloying elements in solid solution which do not change microstructure during homogenization; the second group, Cu–4%Al, Cu–2%Si and Cu–8%Sn, contains those alloys in which a second phase appears due to the solidification conditions. Complete dissolution of alloying elements takes place in these alloys after homogenization. The third group is represented by Cu–8%Al, in which anodic dissolution is reduced to a minimum, irrespective of the state of the alloy.

D_M curves and the corresponding microstructures for the first group of alloys are given in Figs. 2, 3 and 4. The maximum D_M was observed at about −250 mV for all three alloys. As has already been stated, homogenization of these alloys does not change their microstructure. Due to the low solubility of Zr and Cr in copper, Cu_3Zr and Cr were precipitated from the copper matrix. After homogenization the alloys remain unchanged i.e., heterogeneous, since the phases present in the as-cast state are still present in the copper matrix.

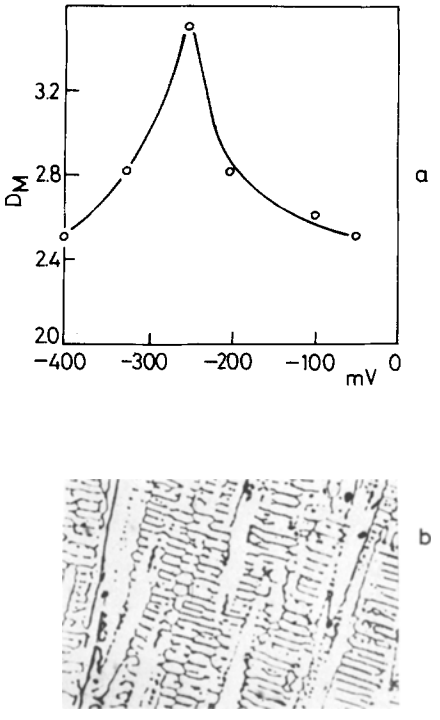
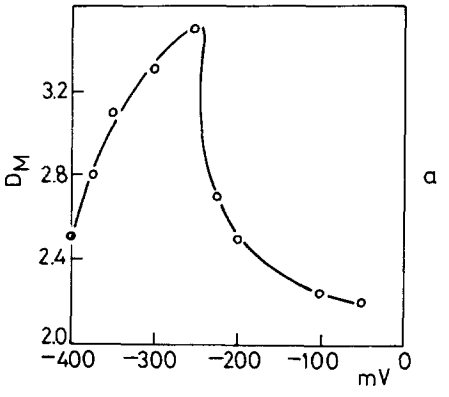


Fig. 2. (a) D_M curve for Cu–1%Zr alloy. (b) Microstructure of this alloy, 110×.



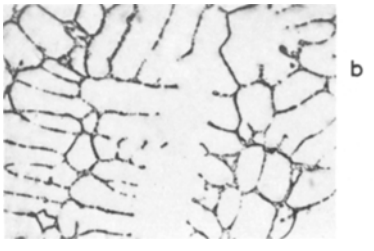
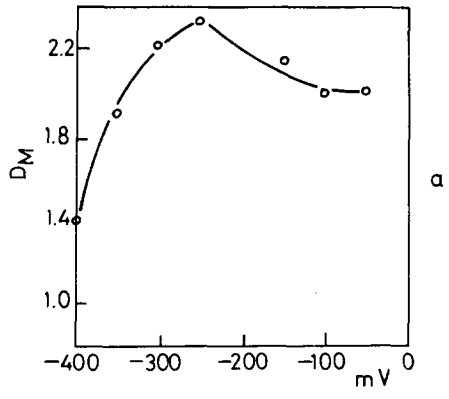


Fig. 3. (a) D_M curve for Cu–1%Cr alloy. (b) Microstructure of this alloy, 110×.



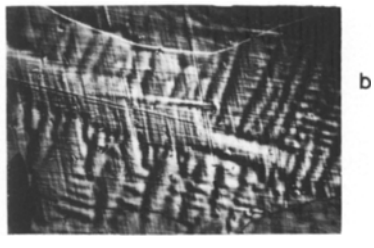
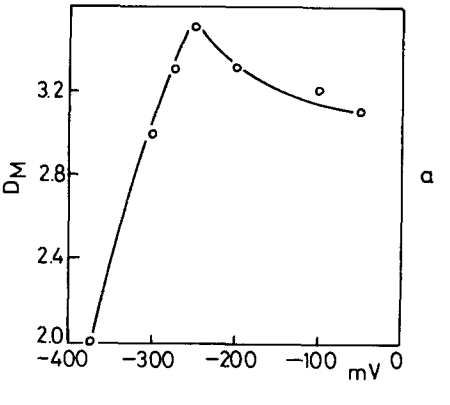


Fig. 5. (a) D_M curve for Cu–4%Al alloy. (b) Microstructure of this alloy, 110×.



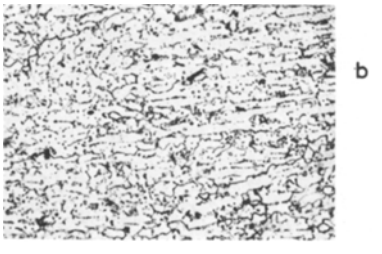
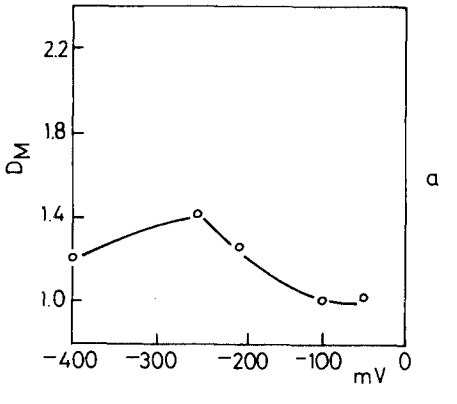


Fig. 4. (a) D_M curve for Cu–2%Cr alloy. (b) Microstructure of this alloy, 110×.



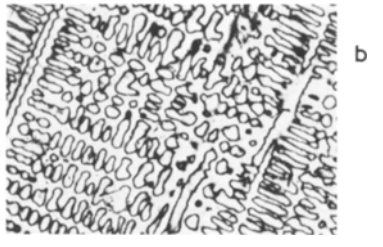


Fig. 6. (a) D_M curve for Cu–2%Si alloy. (b) Microstructure of this alloy, 110×.

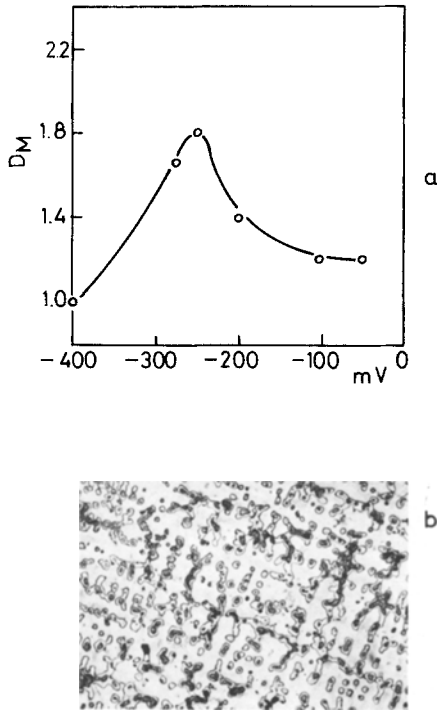


Fig. 7. (a) D_M curve for Cu–8%Si alloy. (b) Microstructure of this alloy, 110×.

Therefore, dissolution of the copper solid solution [4], can be achieved at a potential of −250 mV irrespective of the state of the alloy, while the solid residue of the second phase is obtained after dissolution of the matrix. We wish to point out that the polarization curves of these alloys for the as-cast and homogenized states are practically identical.

In the second group of alloys, non-equilibrium phases in a typical dendritic arrangement appear, due to the solidification conditions. The D_M curves and microstructures of Cu–4%Al, Cu–2%Si and Cu–8%Sn as-cast alloys are given in Figs. 5, 6 and 7, respectively. The polarization curves of these alloys are also close to that of copper (Fig. 1). Although the maxima of the D_M curves are less explicit, the optimum potential of dissolution is still at about −250 mV. After homogenization of these alloys the polarization curves shift towards higher current densities, as can be seen in Fig. 8 for Cu–4%Al. They are therefore closer to the curve for copper, indicating single-phase structure with electrochemical behaviour similar to that of copper. The microstructures of the homogenized alloys Cu–4%Al, Cu–2%Si and Cu–8%Sn, presented in Figs. 9a–c, respectively, show almost complete dissolution of the alloying additions in the copper matrix after homogenization.

Unlike the first group, where the state of the alloys is not essential for determination of the dissolution potential, in the second group separation of phases by selective dissolution of the copper matrix is possible only in the as-cast state, as a single phase alloy is obtained by homogenization. The same applies for the alloys containing alloying elements in which the second phases appear under non-equilibrium solidification conditions. Since copper alloys contain amounts of Al, Si and Sn in the solid solution which depend on the degree of achieved homogenization, their anodic behaviour should be investigated in greater detail in order to determine dissolution potentials more precisely.

The third group of alloys, which show low anodic dissolution under our experimental con-

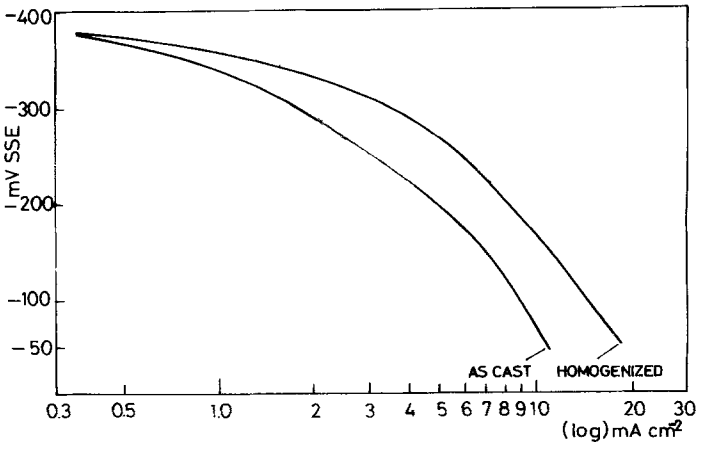


Fig. 8. Polarization curves for the Cu–4%Al alloy.

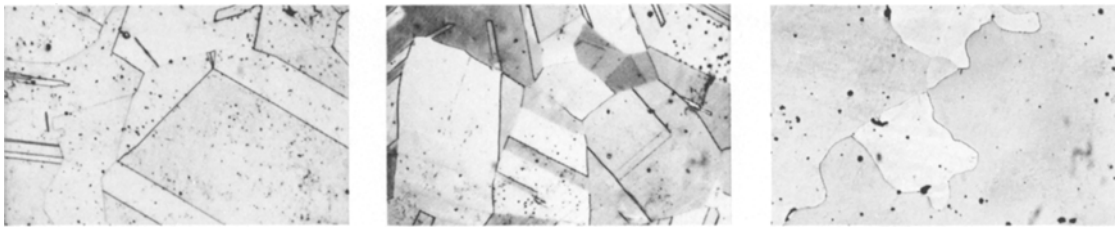


Fig. 9. Homogenized state of the alloys, 110×. Left, Cu–4%Al; middle, Cu–2%Si, right, Cu–8%Sn.

ditions, is represented by Cu–8%Al. As can be seen in Fig. 10, which presents the D_M curve and microstructure of this alloy, there is no maximum in the curve, as ought to be expected from the anodic behaviour shown in Fig. 1. After homogenization the alloy becomes single phase due to complete dissolution of Al in the copper matrix. However, the polarization curve in the homogenized state only insignificantly changes the shape and position as compared to the as-cast state. Absence of intensive anodic dissolution of the copper matrix because of high content of Al shows that the electrolyte used in this experiment cannot be used for separation of phases of this alloy in the investigated range of potentials.

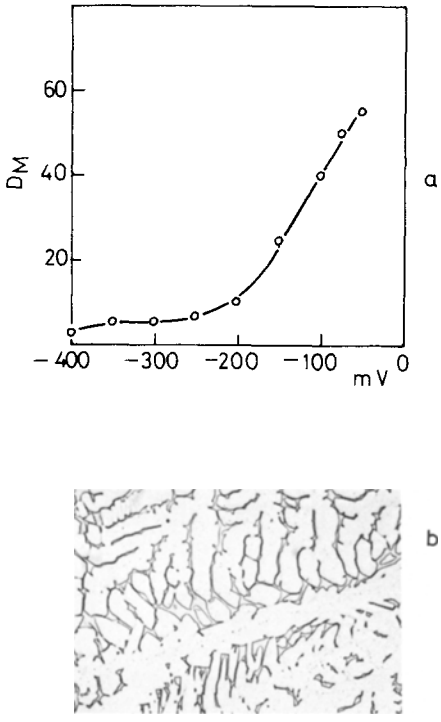


Fig. 10 (a) D_M curve for Cu–8%Al alloy. (b) Microstructure of this alloy, 110×.

4. Conclusions

Two-phase copper alloys, containing Zr, Cr, Al, Si and Sn, have been investigated in the heterogeneous, as-cast state. From the microstructure and anodic behaviour in the as-cast state and after homogenization, it can be concluded that:

(a) The method of selective anodic dissolution in 50% citric acid solution can be used for the determination of the optimum dissolution potential D_M by applying the modified Pražak's equation.

(b) For all the investigated alloys, except Cu–8%Al, the copper matrix dissolution potential is about −250 mV versus SSE.

(c) Cu–8%Al does not dissolve anodically under the experimental conditions used in this paper. D_M values increase with increasing potential.

Acknowledgement

Financial support for these investigations by NSF USA Grant GF-31057 is greatly appreciated. This research was supported in part by grants from the Serbian Research Funds, Yugoslavia.

References

[1] A. Mance and A. Mihajlović, *4th Yugoslav Symposium on Electrochemistry, Dubrovnik*, June (1975).

[2] V. Cihal and M. Pražak, *J. Iron Steel Inst.* **193** (1959) 360.

[3] A. Mance and A. Mihajlović, *J. Appl. Electrochem.* **11** (1981) 205.

[4] A. Mihajlović, A. Mance and V. Perović, 'Microstructural Science', Vol. 1, Elsevier, New York (1974) p. 259.