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The anodic behaviour of copper-based alloys in phosphoric acid

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The anodic behaviour of as-cast and homogenized binary copper-based alloys with Zr, Cr, Si, Sn and Al in 65% phosphoric acid was studied by a potentiostatic method. The biggest difference in the anodic behaviour between as-cast and homogenized samples was found for Cu–8% Sn and Cu–8% Al alloys.

1. Introduction

Previous investigations of the anodic behaviour of binary copper-based alloys with 1% Zr (all in wt%), 1% Cr, 2% Si, 4% Al, 8% Al and 8% Sn in 50 vol% citric acid [1] have shown that in the as-cast and homogenized states these alloys with low additions of alloying elements behave in a similar way to pure copper. From the data obtained from the polarization curves and microstructures the alloys were classified into three groups.

To the first group belong alloys with a low solubility of the second element in solid solution and which are two-phase regardless of the state of the alloy. After dissolution of the copper matrix in citric acid at a constant potential a solid residue of the second phase is obtained. The polarization curves of typical members of this group, Cu–1% Zr, Cu–1% Cr, and Cu–2% Cr alloys in as-cast and homogenized states, are practically identical.

To the second group belong the alloys Cu–4% Al, Cu–2% Si and Cu–8% Sn which contain non-equilibrium phases due to the solidification conditions. After homogenization, the polarization curves of these alloys approach the curve for copper, indicating similar electrochemical behaviour. Examination of the microstructure of alloys after homogenization showed that the alloying additions were dissolved in the copper matrix.

The third group of alloys, which were the most resistant to dissolution under the experimental conditions, is represented by Cu–8% Al. The polarization curve of the homogenized state only changes slightly in shape and position compared to the as-cast state, i.e. anodic dissolution is minimal irrespective of the state of the alloy. Significant changes in the shape and position of polarization curves with the structural state have been reported earlier for complex copper alloys [2].

The results of investigations on binary Cu–1% Zr, Cu–2% Cr, Cu–2% Si, Cu–8% Sn and Cu–8% Al alloys in 65 vol% phosphoric acid are presented in this paper.

2. Materials and methods

The Cu–1% Zr, Cu–2% Cr, Cu–2% Si, Cu–8% Sn and Cu–8% Al alloys were made from OFHC (oxygen-free high conductivity) copper and Cu–Zr, Cu–Cr, Cu–Si, Cu–Sn and Cu–Al master alloys, by melting in a vacuum furnace and casting into a metallic mould. Investigations were performed on samples in the as-cast and homogenized (equilibrium) state. The specimens were heated at different temperatures and for different time intervals, depending on the type of alloy, and the furnace was then cooled. The data are given in Table 1. Prior to each experiment, specimens were ground and polished with diamond pastes. Electrochemical measurements and etching of samples for metallographic experiments were carried with an electronic 'Tacussel' potentiostat. 65 vol% phosphoric acid was used as the electrolyte. The potentiodynamic curves were plotted on to an X–Y recorder using a potential scan rate of 100 mV min^{-1}. The working potential was

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Table 1. Heat treatment of alloys

Alloys	*Heating temperature* (° C)	*Holding time* (h)
Cu–1% Zr	900	1
Cu–2% Cr	950	3
Cu–2% Si	840	24
Cu–8% Sn	680	24
Cu–8% Al	800	24

measured with respect to the saturated Hg_2SO_4 electrode (SSE).

For microstructural investigations, the specimens were etched potentiostatically for defined times at a constant potential of – 250 mV (SSE) chosen on the basis of previously reported polarization curves [3].

3. Results and discussions

The polarization curves and microstructure of unalloyed copper are given in Fig. 1. The alloys with low additions of alloying elements have polarization curves which are all similar in shape and position, i.e. Cu–1% Zr (Fig. 2), Cu–2% Cr (Fig. 3) and Cu–2% Si (Fig. 4) and to that of copper. After homogenization, 1% Zr and 2% Cr alloys remain two-phase, because the solubility of Zr and Cr in copper is low and consequently only the small change in polarization curves after homogenization was to be expected, particularly for Cu–1% Zr alloy. A slightly larger change after homogenization observed in the case of the Cu–2% Cr alloy results from a larger difference in the Cr content of the alpha-solid solution between the as-cast and homogenized state.

The as-cast alloy with 2% Si has a certain amount of retained second phase (Fig. 4) so it could be considered as two-phase. However, because the amount of this phase is very low, it seems more appropriate that the structure given in Fig. 4, showing the dendrites of alpha-solid solution, be regarded as single-phase. After homogenization, the large recrystallized alpha-grains are formed. Since in both states the alpha-phase exists and the only difference is in the phase morphology, the negligible difference in polarization curves is to be expected (Fig. 4).

The other two alloys, Cu–8% Sn (Fig. 5) and Cu–8% Al (Fig. 6) give polarization curves which differ from that of copper due to high concentrations of alloying elements. The addition of 8% Sn or 8% Al changes the polarization curves so that at a potential of about – 300 mV, the alloys in the as-cast state have current density about 70 mA cm^{-2}. For the same potential the unalloyed copper sustains a current density of about 150 mA cm^{-2}. Both alloys are heterogeneous in the as-cast state and become single-phase (alpha-solid solution) after homogenization. The polarization curve of the alloy with 8% Sn after heating at 680° C is shifted toward more positive potentials by 300 mV. It is interesting to note that the polarization curves of both alloys in the homogenized state have two passivation peaks: at potentials of – 350 and – 250 mV. The lower peak is close to that which

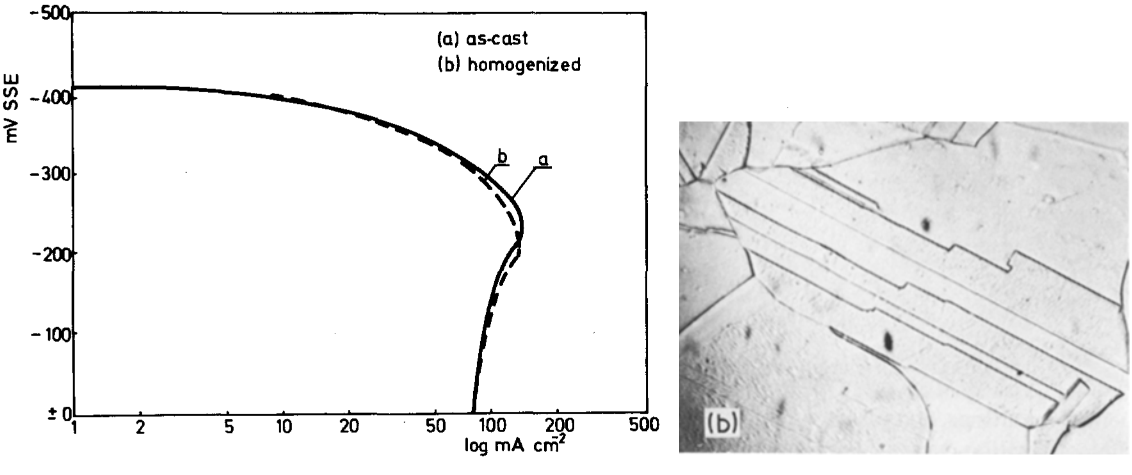

Fig. 1. Polarization curves and microstructure (X430) of unalloyed copper.

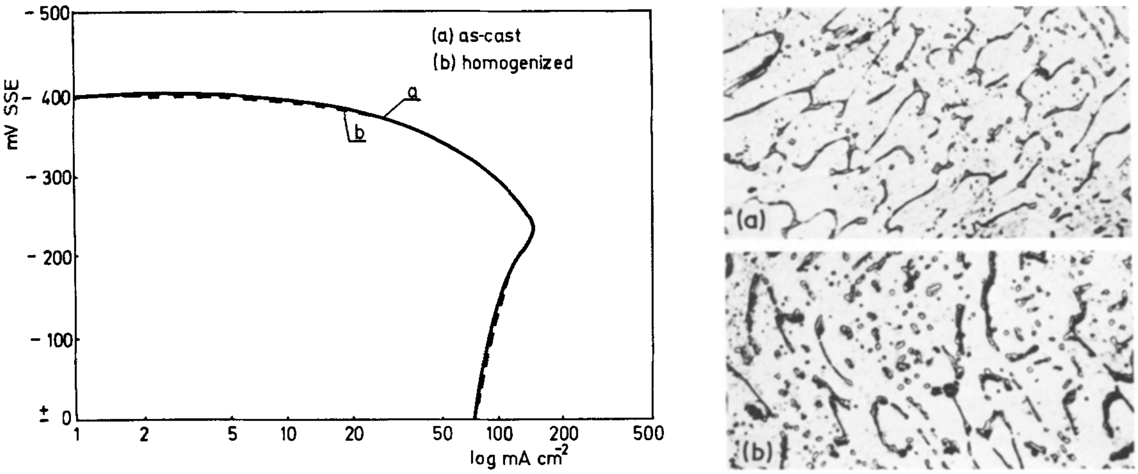

Fig. 2. Polarization curves and microstructures (X192) of Cu–1% Zr alloy.

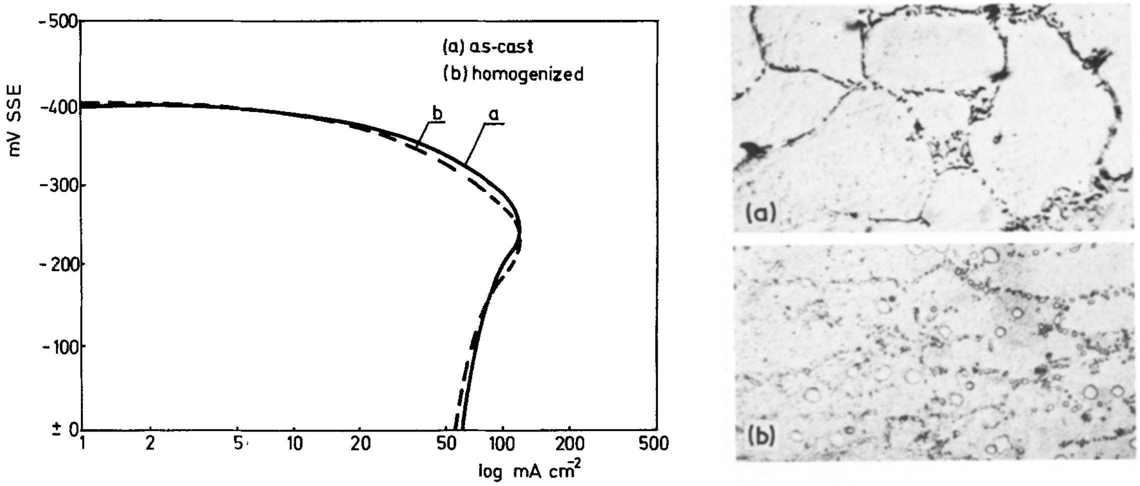

Fig. 3. Polarization curves and microstructures (X540) of Cu–2% Cr alloy.

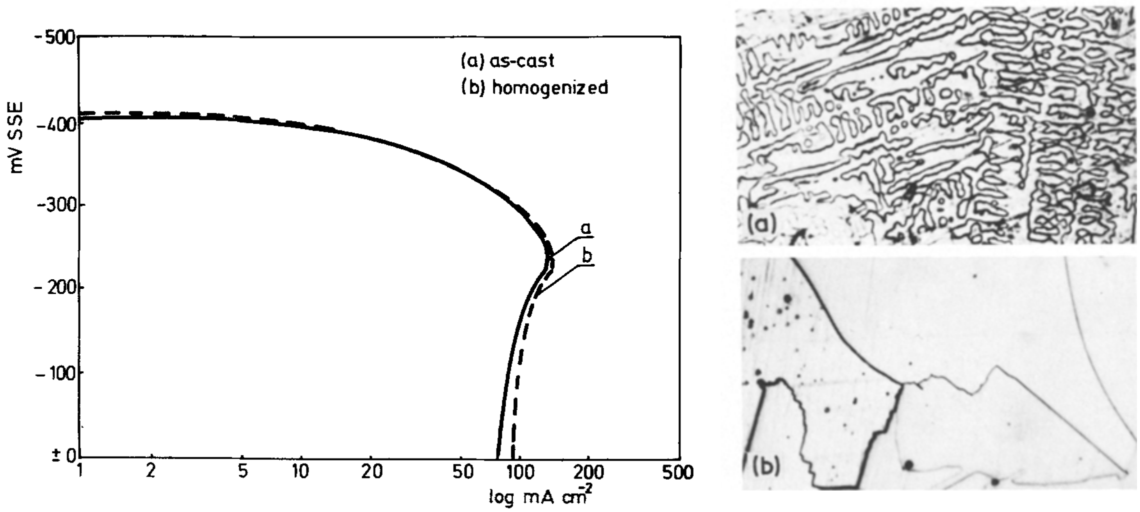

Fig. 4. Polarization curves and microstructures (X96) of Cu–2% Si alloy.

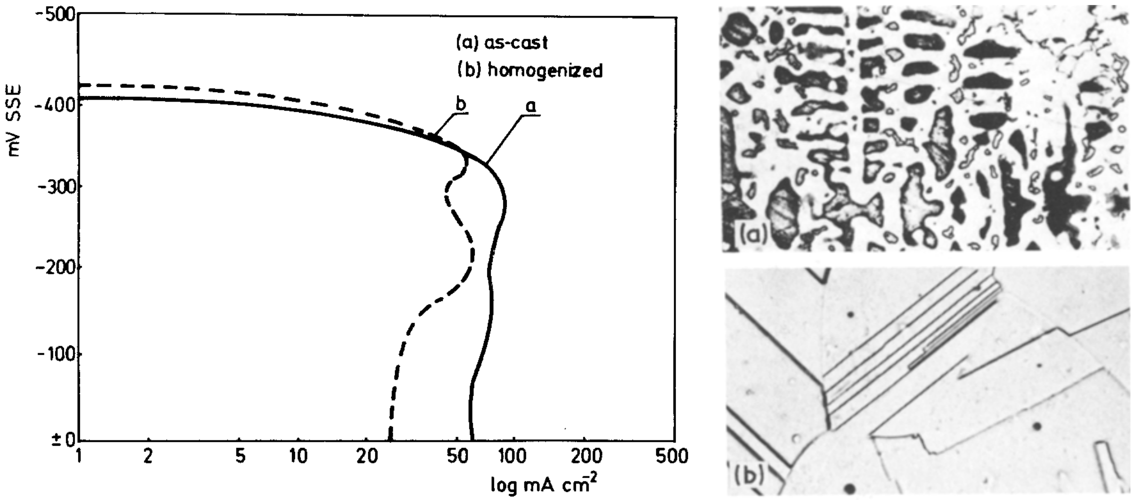

Fig. 5. Polarization curves and microstructures (×192) of Cu–8% Sn alloy

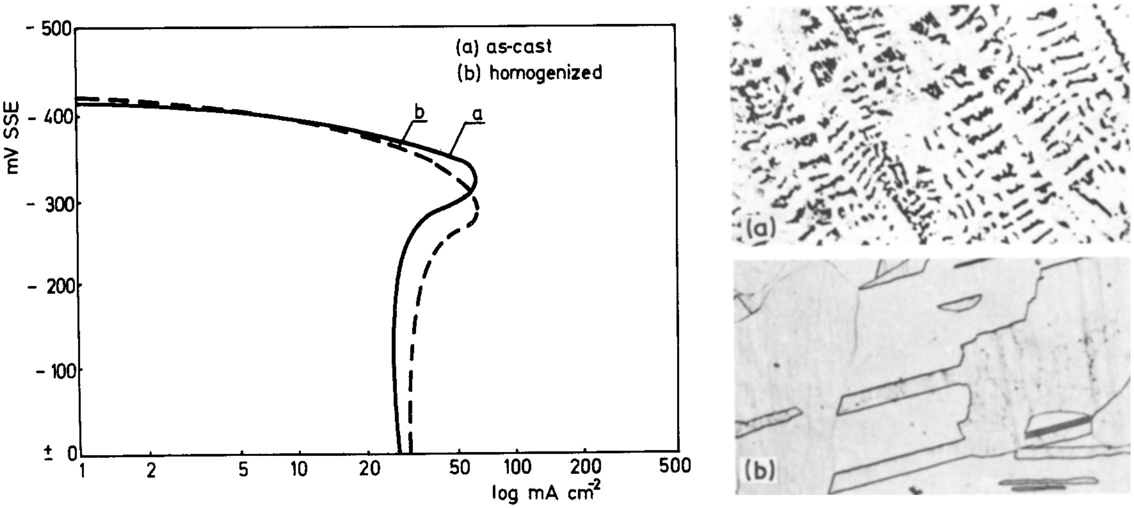

Fig. 6. Polarization curves and microstructures (×96) of Cu–8% Al alloy.

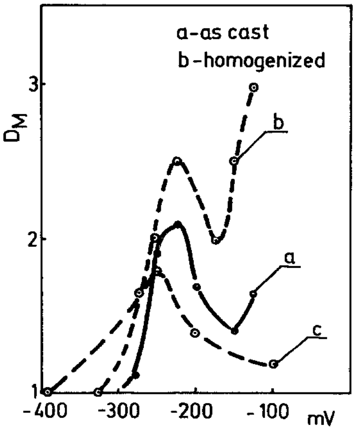

Fig. 7. D_M curves of Cu–8% Sn alloy.

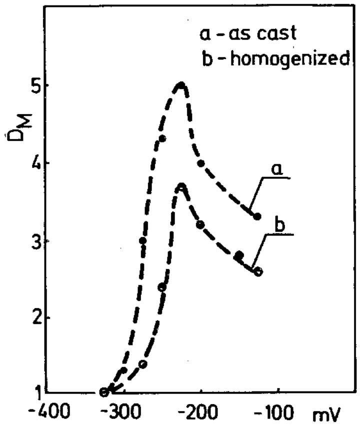

Fig. 8. D_M curves of Cu–8% Al alloy.

appears for unalloyed copper, so it seems that it is the consequence of the reaction of the solid solution with the electrolyte. The existence of two passivation peaks particularly for Cu–8% Sn indicates that the alloys did not achieve complete solid solution. The spherical inclusions in Fig. 5 are probably the incompletely dissolved second phase. It is likely that the upper passivation peak is due to the reaction between electrolyte and second phase.

The Cu–8% Al alloy shows passivations typically in the potential range − 400 to − 200 mV in both the as-cast and homogenized state. The passivation peak is probably the result of the formation of a passive layer which contains Al_2O_3. As distinguished from the other alloys the annealed state has a slightly higher current density in the potential range from − 300 to 0 mV. This lower corrosion resistance of annealed Cu–Al alloys is known. It may be argued that if after homogenization the γ_2-phase was retained in the structure, the corrosion resistance decreased because γ_2-phase is cathodic in character with respect to the alpha-matrix.

An earlier paper [1] reported the application of the modified equation $D_M = (i_{Cu}/i_L)_E$, where D_M is the differential ratio for the matrix (Cu) and i_{Cu} and i_L are dissolution rates for copper and for the alloy, respectively, expressed as the current densities at the potential E. This equation may be used to determine the optimal dissolution potential of a copper matrix in citric acid for a complex heterogeneous copper alloy. This method is also applied to the Cu–8% Sn alloy. By anodic dissolution at constant potental, − 250 mV, the complete dissolution of the matrix is achieved while the second phase remains as a solid residue. The D_M versus E curve for this alloy in citric acid is given in Fig. 7, curve c.

For the same alloy in the as-cast and homogenized state examined in 65% phosphoric acid (Fig. 7, curves a and b), the relationships are curves with two peaks. The examination of the change of microstructure with potential at different points on the polarization curve, indicates that in the case of phosphoric acid the D_M–E curves reflect the selective passivation process of the Cu–8% Sn alloy. In the potential range from − 400 to about − 325 mV phosphoric acid reacts with the anode and forms a passive layer initially on the second phase. As the potential is made more positive to about − 200 mV the passive layer covers the matrix. With further increase of the potential above − 200 mV the simultaneous dissolution of both phases begins.

The D_M–E curves for Cu–8% Al (Fig. 8, curves a and b) show the same behaviour. The curves have only one peak that indicates passivation after the dissolution of the single-phase anode.

4. Conclusions

Homogenization of heterogeneous as-cast binary copper-based alloys with low Cr and Zr additions only changes slightly the polarization curves in 65% phosphoric acid although the homogenization brings about slight changes of microstructure particularly in the Cu–Cr alloy.

Cu–2% Si alloy is single-phase in both the as-cast and homogenized state. The change of morphology of the alpha-solid solution during homogenization slightly changes the polarization curves.

The biggest difference in anodic behaviour between the non-equilibrium (as-cast) and equilibrium (homogenized) states was found for the Cu–8% Sn alloy. Although the difference between these two structural states in the Cu–8% Al alloy is the same as in the Cu–8% Sn alloy, small differences in the anodic behaviour of the as-cast and homogenized states of the Cu–8% Al alloy could be a consequence of the formation of passive layer rich in Al_2O_3. The decrease of corrosion resistance of the Cu–8% Al after homogenization is probably the result of a retained γ_2-phase.

Acknowledgement

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