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The effect of microstructure on the anodic behaviour of Cu-Be-Ni-Zr alloy system

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The effect of heat treatment on the anodic behaviour of the Cu–Be–Ni–Zr alloy in 65% phosphoric acid has been investigated by the potentiostatic method. Different anode states obtained by quenching from temperatures of 900, 950 and 1000°C were examined under the microscope. It was found that the position and shape of the polarization curves, especially in the active and passive parts, are dependent upon the quenching temperature and colling rate. For pre-quenching temperatures up to 950°C, at which there are no appreciable changes in microstructure, the polarization curves are similar. For higher pre-quenching temperatures up to 1000 °C where substantial microstructural changes occur, the active part of the polarization curves becomes more negative, by almost 100 mV, while the passivation decreases.

1. Introduction

Recent investigations on binary and ternary alloys of the Cu–Be–Ni–Zr system have shown that anodic passivation occurs in phosphoric acid [1,2]. Parallel investigations of the polarization curves and microstructure revealed that the Cu_3Zr phase, which may also contain Ni or Be, is mainly responsible for passivation [1]. Similar behaviour was observed in the quaternary alloys of this system where the passivation is supposed to be caused by the intermetallic phase of complex chemical composition. For identification of the structure and composition, the intermetallic phase was separated out by anodic dissolution at constant potential. Since there is no published data on either the system or this intermetallic phase, it was necessary to determine the optimum conditions of heat treatment to get the alloy into an appropriate state for anodic dissolution.

During the anodic polarization experiments in phosphoric acid of samples heated at various temperatures, it has been noted that the polarization curves were affected by the temperature of prior heat treatments.

The results presented are intended to explain this behaviour by a comparison of the microstructure and polarization curves.

2. Materials and methods

The Cu–Be–Ni–Zr alloy* (Be+Ni+Zr less than 2%) was made from OFHC copper and Cu–Be, Cu–Ni and Cu–Zr master alloys by vacuum melting. After heating for 2 h at 900, 950 and 1000 °C, the samples were water-quenched. Prior to examination specimens were mechanically polished with diamond paste. The anodic behaviour was studied in 65% phosphoric acid using a PRT-500 L Tacussel potentiostat. The polarization curves with a potential change of 100 mV min^{-1} versus saturated sulphate electrode (SSE) were plotted on an X–Y recorder. These measurements and the etching of samples for metallographic examination were carried out as described elsewhere [3]; all were performed at room temperature.

Samples were etched for a specified time at constant potentials corresponding to the transpassive part of the polarization curve and then examined under a microscope.

The composition of the intermetallic phase inclusions was determined by electron probe microanalysis (SEM-2, AEI-Manchester). Quantitative determination of the inclusion composition was not possible because the area of the electron beam was greater than that of the inclusions. Be was determined by emission spectrophotometry.

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*Patented.

3. Results and discussion

The Cu–Be–Ni–Zr alloy in 65% phosphoric acid gives the polarization curves (Fig. 1) with the active, passive and transpassive transition [4,5].

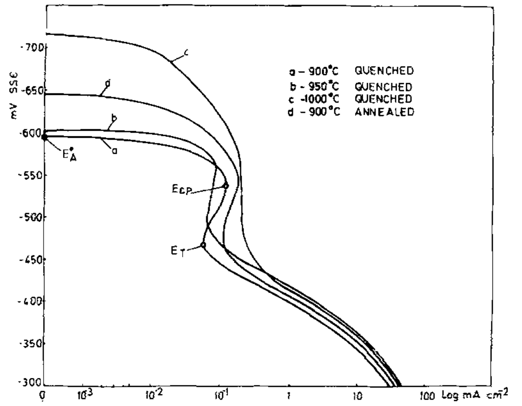

Fig. 1. Polarization curves of Cu–Be–Ni–Zr alloy.

The active part of the polarization curve of the samples quenched from 900 °C begins at the potential of $E^{\circ}_{A} = -595$ mV (Table 1). The increase of the potential leads to the passivation of the anode and to appearance of the passivation peak from $E_{cP} = -535$ mV to $E_T = -460$ mV, where more intensive anodic dissolution i.e., transpassive part of the curve begins.

Table 1. Polarization parameters

Pre-quenching temperature	E°_{A} (mV)	E_{cP} (mV)	i_{cP} (mA cm^{-2})	E_T (mV)	i_T (mA cm^{-2}
900°C	−595	−535	$1{\cdot}5 \times 10^{-1}$	−460	$5{\cdot}0 \times 10^{-2}$
950°C	−605	−560	$1{\cdot}0 \times 10^{-1}$	−475	$7{\cdot}0 \times 10^{-2}$
1000°C	−720	−600	$2{\cdot}0 \times 10^{-1}$	−450	$4{\cdot}0 \times 10^{-1}$

E°_{A} – Activation potential (the potential of anodic dissolution).
E_{cP} – Critical passivation potential.
E_T – Transpassivation potential.
i_{cP} – Critical passive current density.
i_T – Transpassive current density.

The increase of the quenching temperature to 950°C slightly shifts the active part of the polarization curve whilst the passivation potential is shifted towards more negative values. Passivation of the anode begins at $E_{cP} = -560$ mV and ends at about $E_T = -475$ mV. The passivation current charges insignificantly with increase of potential.

In contrast, quenching from 1000°C leads to a considerable change in the polarization curve, Fig. 1. First, the active part of the curve begins at $E^{\circ}_{A} = -720$ mV which is considerably more negative than in the previous two cases. Second, the alloy does not show typical passivation characteristics; that is, the current density does not show a tendency to decrease starting from $E_{cP} = -600$ mV as in the two previous cases, but slowly rises with increasing potential to about $E_T = -450$ mV. In the transpassive zone this begins to approach the two other curves.

For further analysis of the effect of the annealing temperature on the anodic behaviour, we shall make use of earlier [1] conclusions that the intermetallic phase is primarily responsible for passivation and that the alpha-solid solution determines the dissolution rate in the transpassive region. Thus, as far as the passivation process is concerned, the polarization curves will be very similar as long as the heat treatment procedure does not change the microstructure of the alloy.

Quenching from 900 and 950°C gives identical microstructures (Figs. 2 and 3) so the state of the anode is of a supersaturated copper solid solution with an intermetallic phase. Polarization curves obtained for these two quenching temperatures are very similar (Fig. 1), indicating a passivation process. The passivation film formation rate is higher than its dissolution rate up to the potential of $E_{cP} = -535$ mV, for 900°C (Table 1) where it reaches maximum. The critical passivation current density is about $i_{cP} = 1{\cdot}5 \times 10^{-1}$ mA cm^{-2}. At higher potentials, passive film continues to form and the current density decreases, reaching a minimum at about $i_T = 5{\cdot}0 \times 10^{-2}$ mA cm^{-2}. The polarization parameters for 950°C are very similar (Table 1).

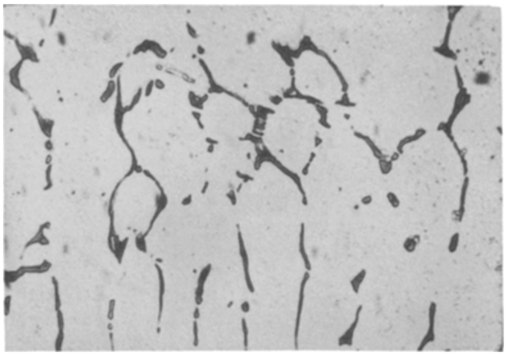

Fig. 2. Cu–Be–Ni–Zr alloy quenched from 900°C, etched at —370 mV, 10 s. × 500.

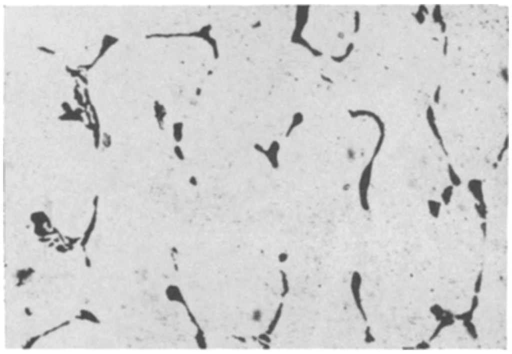

Fig. 3. Cu–Be–Ni–Zr alloy quenched from 950°C, etched at –370 mV, 30 s. × 500.

After quenching at 1000°C there is a complete change in the microstructure of this alloy (Figs. 4 and 5). The basic difference between the microstructure after quenching from 900 and 950°C (Figs. 2 and 3) and from 1000°C is that the intermetallic phase which is typical for temperatures below 950°C does not exist at 1000°C.

The anode state after quenching from 1000°C shows that the anodic part of the polarization curve begins at more negative potentials $E^0_A =$ —720 mV (Table 1) as in the case when Cu_3Zr is present in Cu–Zr binary system [2]. It seems that the form of the secondary phase in Figs. 4 and 5 is similar to that of the Cu_3Zr phase. In addition semiquantitative examination by electron probe microanalyzer show the second phase, which appears at 1000°C, contains less Zr and Ni as compared to the intermetallic phase stable at 900°C. One should, nevertheless, bear in mind the problems mentioned in Section 2.

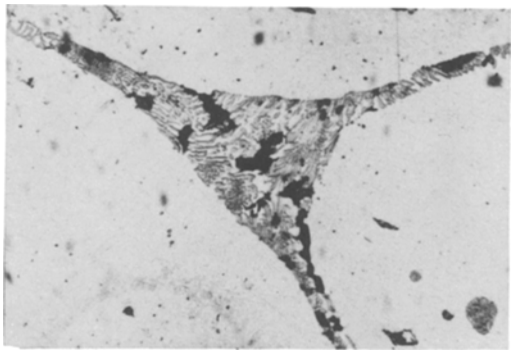

Fig. 4. Cu–Be–Ni–Zr alloy, quenched from 1000°C, etched at –370 mV, 25 s. × 500.

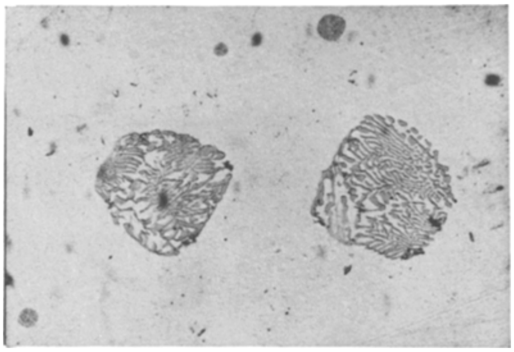

Fig. 5. Cu–Be–Ni–Zr alloy quenched from 1000°C, etched at –370 mV, 10 s. × 500.

The alloy microstructure after quenching from 1000°C could not be positively identified on the basis of the preliminary results. It is nevertheless apparent that alloy heated up to 950°C and at about 1000°C is brought into such a state that, although it remains a two-phase alloy in both cases, samples so treated behave electrochemically as two different alloys. The changes taking place in the range from 900 – 1000°C do not affect the transpassive part of the polarization curve. As has been found earlier [1], such behaviour can be explained by the fact that intensive dissolution of the copper matrix occurs in the regions more positive than —400 mV so the curves are identical in that part, regardless of the heat treatment procedure. These conclusions as to the behaviour of the alloy in the transpassive zone are confirmed by the Tafel slope values given in Table 2.

Table 2. Tafel's Constants

Pre-quenching temperature, °C	*a* V	*b*
900°C	–0·400	0·045
950°C	–0·420	0·050
1000°C	–0·420	0·050

The position and shape of the polarization curve after annealing at 900°C and furnace cooling constitutes further evidence in support of this conclusion. The shape of this curve is identical to that of the curve obtained after quenching from 900°C due to unchanged intermetallic phase (Fig. 6) even though a new dispersed phase is formed in the matrix which was not present in the alloy after quenching. As a consequence of the appearance of this finely dispersed phase, the whole polarization curve is shifted towards more negative potentials, i.e. more rapid dissolution of the alloy was observed.

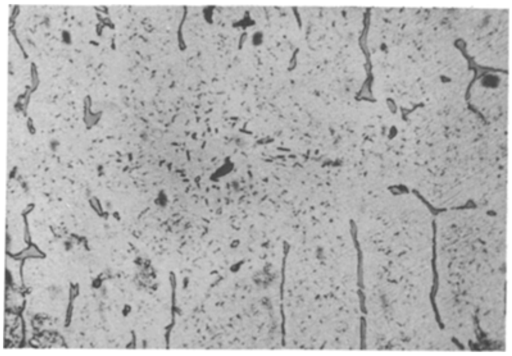

Fig. 6. Cu–Be–Ni–Zr alloy annealed at 900°C, etched at –370 mV, 10 s. × 500.

4. Conclusion

The influence of heat treatment on the anodic behaviour of the quaternary two-phase alloy has been investigated by the potentiostatic method. Comparative investigations of the microstructure and polarization curves have shown:

(1) The position and shape of the polarization curves considerably depend on the anode surface state.

(2) Change in the cooling rate from given temperatures (quenching versus furnace cooling) shifts the polarization curves considerably.

(3) The polarization curves indicate that a pre-quenching temperature between 900 and 950°C should be used as to achieve the appropriate state of the alloy. If a temperature of 950°C is exceeded, fundamental microstructural changes may occur which further lead to quite different anodic behaviour of the alloy, especially at lower current densities.

Acknowledgement

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