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Electrochemical separation of phases in a copper alloy containing beryllium, nickel and zirconium

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To determine the chemical composition of phases in a heterogeneous Cu–Be–Ni–Zr alloy, a 50% citric acid solution was used to permit selective electrochemical dissolution of the copper matrix from the second phase. Using the potentiostatic method it was found that quantitative dissolution of the copper matrix could be achieved at −250 mV (versus SSE). The method described for the separation of the copper matrix from the second phase could also be successfully applied to other heterogeneous copper alloys.

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1. Introduction

Many multicomponent alloys exist as complex and heterogeneous mixtures of intermetallic phases because of reaction of the alloying elements with the basic metal and also because of their mutual reaction. Copper is known as an element which tends to form complex, heterogeneous alloys, such as the Cu–Be–Ni–Zr alloy investigated in the present work. On the basis of preliminary metallographic investigations it was assumed that this alloy is composed of a copper-based solid solution with unknown concentrations of alloying elements and a second, so-called, intermetallic phase with composition and properties so far undescribed in the literature [1, 2].

In order to determine the number of phases, and their chemical and other characteristics, it was first necessary to separate them electrochemically. In the present work we used the metallographic method for identification of the phases, the potentiostatic method for recording polarization curves and for selective dissolution, and X-ray diffraction analysis, electron microprobe and analytical micromethods for the determination of the chemical composition of the phases.

2. Materials and experimental techniques

The alloy Cu–0.8%Be–3%Ni–2%Zr was prepared from OFHC copper and Cu–Be, Cu–Ni and Cu–Zr master alloy by melting in an electroresistant vacuum furnace and casting in a metallic mould. Investigation was performed on samples homogenized by annealing for 2 hours at 950° C and furnace cooled. Prior to each experiment the samples were ground and polished on diamond pastes. An electronic 'Tacussel' potentiostat was used to record polarization curves, to etch the samples for metallographic experiments and to control the potential for selective dissolution of the alloy at a constant potential. Polarization curves for the alloys were recorded in 50% citric acid and in 65% phosphoric acid solutions at a potential scan rate of 100 mV min^{-1}. The selective dissolution of the alloy at a constant potential was performed in 50% citric acid solution with intensive stirring. The working electrode potential was measured versus a saturated sulphate electrode (SSE) [3].

For microstructural investigation the samples were etched for a specified time at the potentials determined on the basis of the polarization curves [4], and then examined under a microscope.

3. Results and discussion

The quaternary Cu–Be–Ni–Zr alloy, whose microstructure is shown in Fig. 1, is a heterogeneous alloy which has a copper solid solution (white matrix) and a network of a second phase. The polarization curve obtained in 50% citric acid solution (Fig. 2) indicates the absence of passivation, compared with the polarization curve

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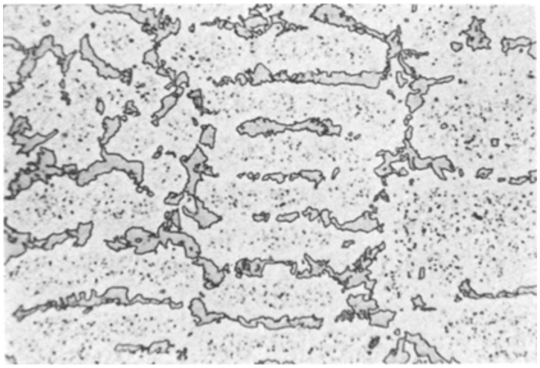

Fig. 1. Microstructure of Cu–Be–Ni–Zr alloy after etching in citric acid, 425 ×.

obtained in phosphoric acid. The anodic behaviour of Cu–Be–Ni–Zr alloy in phosphoric acid has been described earlier [4]. It has been found that in phosphoric acid at potentials more positive than − 400 mV (SSE) anodic dissolution of both the copper matrix and the intermetallic phase takes place. In contrast, in citric acid the intermetallic phase does not dissolve, but the copper matrix does. Such selectivity makes it possible to dissolve only the copper matrix by anodic dissolution at a controlled potential, and thus to separate the intermetallic phase for further examination [5] (Fig. 3).

It has been found by carrying out the alloy dissolution at different potentials along the polarization curves in 50% citric acid that the best selectivities are achieved in the potential region between − 300 mV and − 200 mV. In order to determine the dissolution potential of the alloy the usual method of intersection of two tangents in the region of the change of the curve direction was applied [6]. In this case, the tangents intersect at a potential of approximately − 250 mV. The value of the dissolution potential was obtained from several polarization curves and a deviation of ± 20 mV was found. In addition the optimum dissolution potential of a heterogeneous alloy can be calculated from the dissolution differential ratio D_M of the phases at a given potential using Stern's equation [7]. Since polarization curves of the two phases required by Stern's equation were not available, i.e., those of the copper solid solution and intermetallic phase, the values for copper and for Cu–Be–Ni–Zr alloy were employed since:

(a) The Cu–Be–Ni–Zr alloy belongs to the group of so-called dilute alloys, as it contains relatively low concentrations of the alloying elements Be, Ni and Zr. Also, only a small amount of Zr can be dissolved in the copper solid solution. This was assumed to indicate that a

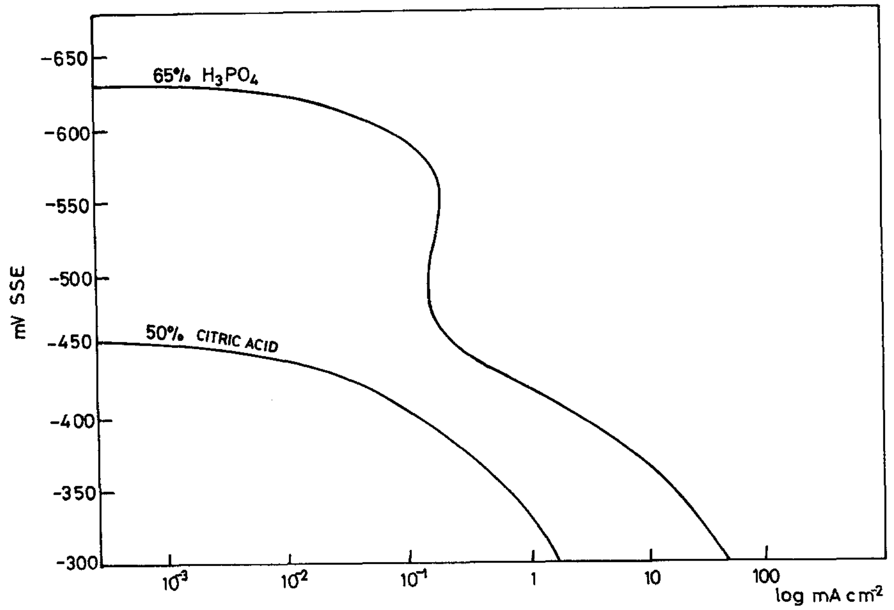

Fig. 2. Polarization curves for the Cu–Be–Ni–Zr alloy in 65% phosphoric acid and 50% citric acid.

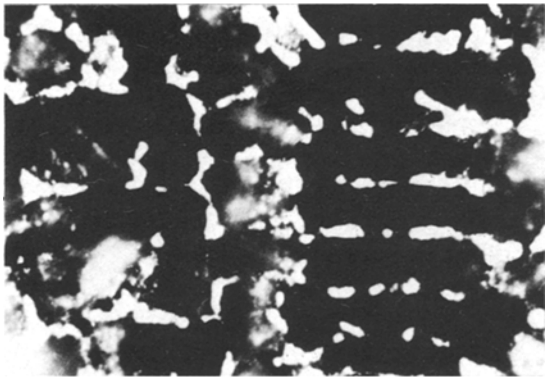

Fig. 3. Microstructure of Cu–Be–Ni–Zr alloy after 100 hours of anodic dissolution in citric acid, 425 ×.

diluted copper solid solution in citric acid may behave in a similar way to copper.

(b) As has been proved earlier [5], the difference between the polarization curves of the quaternary alloy and copper is due only to the presence of the intermetallic phase. Therefore, the dissolution rates expressed in Stern's equation as current densities for the phases could, in this case, be referred to the copper and the alloy dissolution rates, i_{Cu} and i_{A} respectively, i.e. $D_{\mathrm{M}} = (i_{\mathrm{Cu}}/i_{\mathrm{A}})_{\mathrm{E}}$. By applying this modified equation we have obtained a curve with peak D_{M} value at − 250 mV where the optimum selective dissolution of the copper matrix can be expected. This potential of − 250 mV is in agreement with the one obtained graphically.

Three samples were dissolved at a potential of − 250 mV. The anode was weighed at the beginning and at the end of the dissolution. About 7% of a sponge residue consisting of the undissolved, intermetallic phase was found for each of the three samples. X-ray diffraction analysis showed no free copper nor other elements or their oxides in the sponge residue, but only the lines of the intermetallic phase (Fig. 4) [3]. This is in agreement with the results obtained by diffraction analysis of the Cu–Be–Ni–Zr alloy. The diffractogram in Fig. 5 shows that besides copper (200) and (111) lines, the alloy in the equilibrium state shows also weak lines of a second (intermetallic) phase at 2θ values of about 38.5° and 44.5°.

After selective dissolution of the samples at a potential of − 250 mV, the electrolyte was chemically analysed to determine its composition. The concentration of all the four elements was determined using analytical micromethods [8, 9] to be Cu 97.5%, Ni 1.5%, Zr 0.012% and Be 0.79%. The intermetallic phase obtained as a sponge residue after quantitative electrolytical dissolution of the copper matrix was examined by the electron microprobe method. The average amounts of Cu, Ni and Zr found in the sponge residue were 56.5%, 15.0% and 26.0% respectively. Beryllium was determined by the emission spectrographic method.

In order to confirm the results obtained with the microprobe, chemical analysis of an average sample of the three specimens of the intermetallic

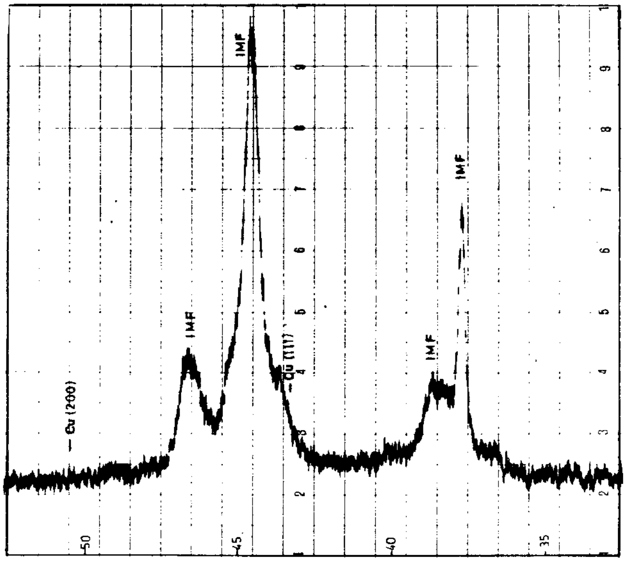

Fig. 4. X-ray diffractogram of intermetallic phase.

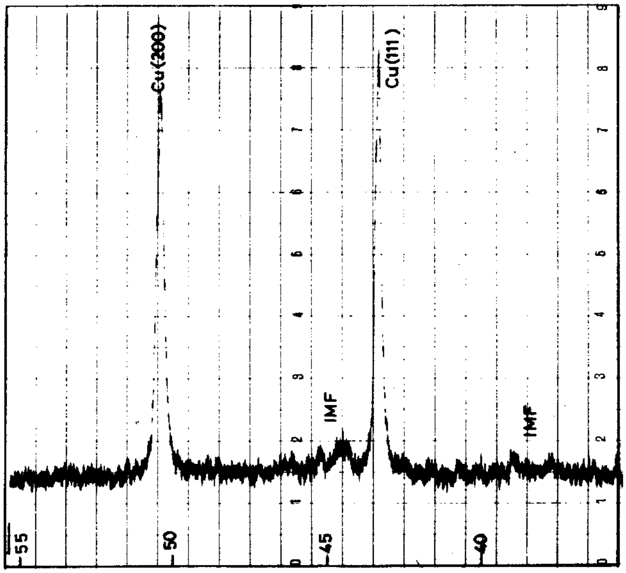

Fig. 5. X-ray diffractogram of Cu–Be–Ni–Zr alloy.

phase sponge was performed using standard analytical methods. The values obtained were: Cu 58.0%, Ni 14.0%, Zr 25.0% and Be 2.5%. The results of both methods are in good agreement and one can conclude that the average chemical composition of the intermetallic phase is Cu 56.6%, Ni 15.2%, Zr 25.8% and Be 2.2%.

In order to test the reliability of the method of selective dissolution, we have synthesized and examined the intermetallic phase. The electrochemical behaviour, chemical composition and X-ray data of synthesized intermetallic phase were in good agreement with those obtained previously by analysing the sponge residue after selective dissolution of the alloy.

The modified expression (D_M) for the determination of the optimum potential for selective, quantitative separation of the phases has also been applied successfully to some other copper alloys, such as Cu–Zr, Cu–Cr, Cu–Sn and Cu–Al.

4. Conclusions

A 50% citric acid solution can be used for the selective anodic dissolution of two-phase copper alloys. In contrast to phosphoric acid, citric acid solution can be use to reveal the microstructure of some copper alloys. After separation of the phases by anodic dissolution in citric acid, the following composition of the solution has been found: Cu 97.5%, Ni 1.5%, Zr 0.012% and Be 0.79%; this represents the composition of the copper matrix.

The sponge residue, i.e., the intermetallic phase, was investigated by X-ray diffraction and was found not to contain free copper from the matrix, i.e., the phases were separated. The intermetallic phase was chemically analysed and the following composition found: Cu 56.6%, Ni 15.2%, Zr 25.8% and Be 2.2%. The same method of determination of D_M for selective separation of phases could be applied successfully to other two-phase copper alloys.

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References

[1] A. Mihajlović, S. Malčić and O. Nešić, *J. Inst. Metals* **99** (1971) 19.
[2] A. Mihajlović, M. Jovanović and O. Nešić, *Metals Technol.* (1979) 190.
[3] A. Mance, *Paper presented at the 4th Yugoslav Symposium of Electrochemistry, Dubrovnik,* June (1975) 417.
[4] A. Mihajlović and A. Mance, *Metallogr.* 9 (1976)71.
[5] A. Mihajlović, A. Mance and V. Perocić, 'Microstructural Science', Vol. 1, Elsevier, New York (1974) 259.
[6] A. Mance, *J. Nucl. Mater.* **31** (1969) 252.
[7] M. Stern, *Corrosion* 14 (1958) 329.
[8] M. Kliska–Matić and M. Marinković, *Glasnik H.D., Beograd* **38** (1973) 357
[9] A. Muk and J. D. Pokidycheva, *Glasnik H.D., Beograd* **44** (1979) 665.