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An electrochemical method for the extraction of precipitates from age-hardenable aluminium alloys

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An electrochemical method for the extraction of precipitates from age-hardenable aluminium alloys has been developed. Small anodic currents of $\sim 10\,\text{mA cm}^{-2}$ are applied to samples suspended in a methanolic electrolyte containing benzoic acid, oxine, and chloroform. An analysis of extractions made using different current densities shows that the principal function of the anodic current is to break down the aluminium oxide film. The method should have considerable application in the study of high strength aluminium alloys.

1. Introduction

Precipitated intermetallic compounds have long been of critical importance in determining the properties of a very large number of aluminium alloys. Because of the central role such precipitates play, the study of their structure and composition has widespread application in aluminium alloy metallurgy. In the past, the study of most aluminium alloy precipitates has of necessity been carried out primarily through the *in situ* X-ray methods first developed by Guinier [1] and by Preston [2]. It is possible to selectively remove $MnAl_6$ second phase particles by anodic dissolution of Al–Mn alloys in strong acids [3], but such acids are usually found to dissolve both matrix and precipitate constituents. More recently the electron microscope and extraction-replica methods for the study of isolated precipitate particles have been developed [4, 5]. These methods, however, cannot readily be used to produce the quantities of precipitates required for X-ray diffraction experiments or normal chemical analysis. X-ray, rather than electron microscope methods are needed, of course, if accurate lattice parameter measurements are to be made.

A variety of experimental procedures have been developed for the extraction of second phases from steels and nickel-based alloys. Many inclusions and intermetallic compounds, including simple and complex carbides, oxides, nitrides, and sulphides have been extracted from steels, for example, by the cold nitric acid method [6]. Separation of phases from nickel-based alloys has also been conducted for many years [7–11]. Carbide phases found in such alloys can be simply and quantitatively extracted because their bonding is sufficiently different from that of the f c c solid solution matrix, γ, and the ordered f c c precipitate, γ'. By using anodic dissolution techniques, separation of γ', whose composition, structure, and bonding are similar to the γ matrix, has been successfully accomplished.

Generally, galvanostatic or potentiostatic dissolution techniques have proven more satisfactory than simple chemical methods [12]. A recent anodic dissolution technique has been used, for example, to extract both precipitates and inclusions from a wide variety of steels with either low or high carbon content as well as with both low and high alloy content, including stainless steels [13]. This technique utilizes an NaCl–EDTA (ethylenediaminetetraacetic acid) solution as an electrolyte and current densities of approximately 50 mA cm^{-2} to quantitatively extract the second phases. No equivalent anodic or electrochemical methods appear to have been applied to the selective dissolution of aluminium alloys in organic media. Based on a chemical process proposed by Honda and Hirokawa [14], an electrochemical extraction method based on an organic medium specifically applicable to age-hardenable aluminium alloys has now been developed and applied quantitatively to an Al–4.1 wt% Cu alloy.

2. Experimental procedures.

A solution of benzoic acid, oxine (8-hydroxy quinoline), chloroform, and sodium hydroxide was reported by Honda and Hirokawa [14] to complex aluminium but not $CuAl_2$. In applying this solution to the selective dissolution of over-aged Al–4.1 wt% Cu samples, we have found the time required for dissolution to be variable, and times of up to several weeks can be required for significant amounts of dissolution. We have now found that the application of small (~10 mA cm^{-2}) anodic currents to aluminium alloys exposed to methanolic solutions of benzoic acid, oxine and chloroform alone, without sodium hydroxide, leads to the rapid (1 h) dissolution of 1 g samples of aged aluminium–copper alloy specimens.

A 300 ml volume of solution, sufficient to treat a 1 g sample, can be prepared by adding together sequentially, 15 g 8-hydroxy quinoline (5 w/v %), 60 g benzoic acid (20 w/v %), 60 ml chloroform (20 v/v %), and 165 ml methanol (55 w/v %). The application of an anodic current of approximately 10 mA cm^{-2} to the aluminium test sample, using a specimen of pure aluminium as the counter electrode, will lead to complete sample dissolution in approximately 1 h. Since the solution is highly combustible, care must be taken to avoid sparking.

Specimens of the high purity Al–4.1 wt% Cu alloy used in this study were solution heat-treated for 1 h at 500° C, water quenched, and then aged for 7.5 h at 300° C. These specimens were in strip form, 10 mm in width and 1 mm in thickness.

After dissolution of the sample, the 300 ml of solution are subjected to a centrifuge treatment at approximately 1000*g* for 10 min. The supernatant liquid is then decanted and the remaining liquid diluted with methanol and centrifuged again. This process is repeated several times, in order to prevent contamination with residual benzoic acid, before the sample is allowed to evaporate to dryness.

3. Results and discussion

In order to determine the possible effect of applied anodic current density on the extraction efficiency, a series of extractions were carried out at increasing current densities. Extractions were not carried to completion in order to prevent portions of alloy from dislodging from the sample. Approximately $\frac{1}{5}$ of each sample was dissolved in each case. In order to calculate the quantity of $CuAl_2$ which could theoretically be expected to be extracted during dissolution of the test sample, use has been made of the available solvus line and $CuAl_2$ phase limit data [15, 16]. These data, together with the extracted $CuAl_2$ and sample weights, can be used in a simple lever law calculation to determine the extraction efficiency. Since at 300° C the maximum solubility of Cu in Al is 0.35 wt % while the minimum copper concentration in $CuAl_2$ is 53.3 wt %, the fraction which consists of $CuAl_2$ of any mass of aged 4.1 wt % Cu alloy is given by

$$f_{CuAl_2} = \frac{4.1-0.35}{53.3-0.35} = 0.0708 = 7.08\% \quad (1)$$

This relation, together with the measured decrease in sample weight can then be used to determine the weight of available $CuAl_2$. An extraction efficiency of 100% would mean, of course, that all possible $CuAl_2$ was recovered. Debye–Scherrer X-ray photographs were used to confirm that the powder extracted was, in fact, $CuAl_2$.

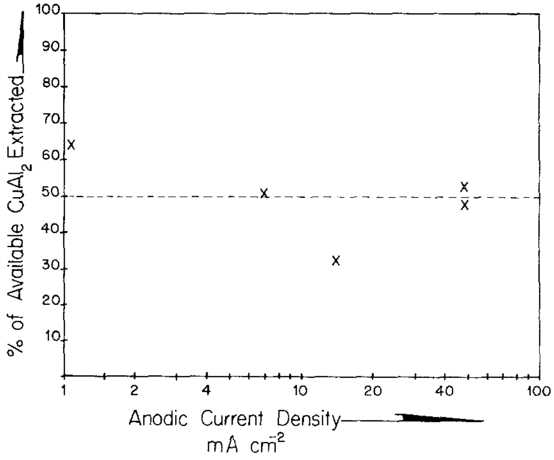

Figure 1 Extraction efficiency as a function of applied anodic current density.

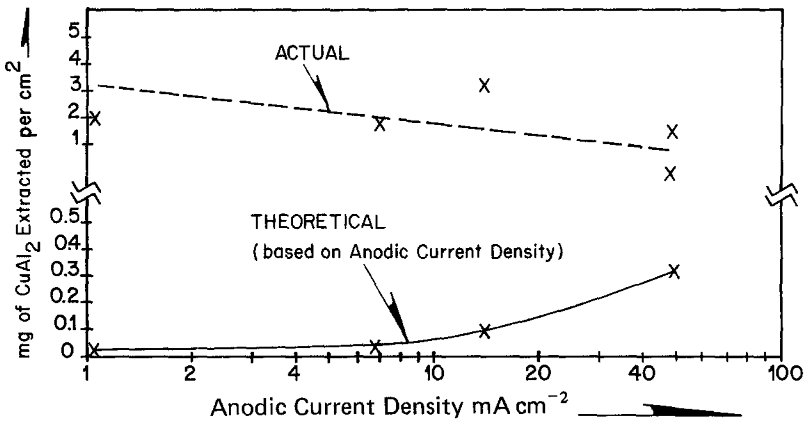

Figure 2 Amount of $CuAl_2$ per unit area of sample surface as a function of applied anodic current density.

Fig. 1 shows the extraction efficiency as a function of applied current density. Although there are relatively large differences from sample to sample, the differences do not appear to be systematic. From these data, it is reasonable to conclude that 50% of the available $CuAl_2$ precipitates can be extracted using any applied current density from approximately $1\,mA\,cm^{-2}$ to approximately $50\,mA\,cm^{-2}$. Indeed it is possible that a higher percentage might be extractable if dissolution was carried to completion because $CuAl_2$ particles adhere tenaciously to the surface of an incompletely dissolved sample. The appearance of these extracted precipitates is that of a black powder, similar to the appearance of substances such as platinum black or Raney nickel.

Fig. 2 is a comparison of the weight of the actual extracted $CuAl_2$ (expressed as mg/cm^2 of sample area), versus that which would be expected theoretically if the only cause of aluminium dissolution was the applied anodic current density. Assuming that Al dissolves as Al^{3+}, the maximum mass of Al that can be dissolved by the applied anodic current can be readily calculated from the total number of coulombs of charge passed. From the fraction of $CuAl_2$ present in the alloy calculated in Equation 1, it then follows that for every 92.92 g Al dissolved there should be 7.08 g $CuAl_2$ particles produced. As may be seen, the actual extracted $CuAl_2$ per unit area is approximately an order of magnitude higher than that calculated from the applied current. From this result it is reasonable to conclude that the primary function of the applied current is to break down the protective aluminium oxide film on the sample, following which simple chemical dissolution of the aluminium occurs.

This method is now being applied to commercial aluminium alloys and would appear to be a valuable metallurgical research tool in aluminium alloy development.

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