

Kinetics of formation of diffusion layer at the electrolytic deposition of aluminium on copper base from molten electrolyte

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Formation of diffusion layers in the system Cu—Al was investigated in the temperature range 200—400°C. Temperature dependence of kinetics of formation of the diffusion layer can be formally described by interdiffusion coefficient $D = 0.17 \exp(-15\,600\text{ K}/T)$. When the layer of alloy at the Cu—Al interphase is thinner than ca. 3 μm , then its growth is faster than it corresponds to a process governed by diffusion.

Изучалась кинетика диффузии в системе медь—алюминий в температурном интервале 200—400°C. Для температурной зависимости коэффициента диффузии найдено соотношение $D = 0,17 \exp(-15\,600\text{ K}/T)$. Было найдено, что скорость образования тонких интерметаллических слоев (меньше 3 мкм) на медных подложках быстрее, чем соответствует диффузионному режиму отложения.

Electrolytic deposition of aluminium from molten mixture NaCl—KCl—AlCl₃ on steel or copper bases enables to prepare aluminium layers with good anticorrosive properties. The process is carried out at elevated temperatures, which positively influences kinetics of formation of diffusion layer. This layer assures good adhesivity of the deposited coatings to substrate metal. Therefore knowledge of kinetics of growth of diffusion or intermetallic layers plays an important role in the determination of optimum operational parameters of electrolytic deposition of metals from molten electrolytes.

Recently we published two papers dealing with electrolytic deposition of aluminium from molten NaCl—KCl—AlCl₃ mixture on steel, copper or steel copper-plated substrates [1, 2]. We found that kinetics of deposition of coherent aluminium coatings depends remarkably on the first stage of formation of new phase on the surface of base metal. Since the deposition of aluminium is carried out at temperatures about 200°C, it is not possible to explain mechanism of formation of the new phase by a model derived for the formation of nuclei on an inert surface. At 200°C it is not possible to neglect the reaction between the deposited and base metal. Till now only data on diffusion in the system Cu—Al at temperatures over 400°C have been published [3—6]. Extrapolation of these data to 180°C, that is to

the temperature at which aluminium is deposited, indicates that the thickness of growth of intermetallic or diffusion layers should be after 1 h about 1 μm . However, the experimentally found thickness of the diffusion layer at conditions of electrolytic deposition of aluminium (180°C, 10 min) is 2 μm and after 1 h of heating at 200°C about 4 μm .

This work is devoted to investigation of growth of diffusion layer in the system Cu—Al in temperature interval 200—400°C at conditions close to electrolytic deposition of aluminium.

Experimental

Samples for investigation of diffusion were prepared by electrolytic deposition of aluminium on copper plate from the electrolyte containing (in mass %) 70% AlCl_3 + 15% NaCl + 15% KCl . The electrolysis was carried out at 180°C for 10—60 min with cathodic current density 3 A dm^{-2} . Aluminium rod (99.99% Al, \varnothing 4 mm) served as an anode. Anodic current density was 2 A dm^{-2} . Thickness of the deposited aluminium layer was determined gravimetrically, by means of an X-ray microprobe JXA-5A and by the method of anodic dissolution of aluminium [7]. Advantage of the method used is that it allows to prepare samples with an excellent adhesivity of both deposited and base metals, which favourably influences reproducibility of diffusion experiments. It is important especially at shorter time of diffusion (up to several hours). The samples were heated for 1—100 h at chosen temperature in order to obtain diffusion layers several micrometers thick. Distribution of concentration of aluminium and copper in the diffusion layer was determined by means of the X-ray microprobe. Quantitative point analysis with step 1 μm was used.

If the thickness of diffusion layer is less than *ca.* 3 μm , results of an X-ray microprobe are not reliable. We found that in this case it is useful to determine the thickness of diffusion layer from the material balance of the electrolytically deposited aluminium. The method of anodic dissolution of aluminium allows to determine thickness of pure aluminium. As we know the total amount of deposited aluminium we can calculate the amount of aluminium which reacted with copper. It should be mentioned that the anodic dissolution of the diffusion layer Cu—Al gave bad reproducibility and therefore it was not possible to apply the same method of investigation as in the case of the system Fe—Al [7].

Results and discussion

The interdiffusion coefficients were determined by the Boltzmann—Matano method [8]. It was found that the growth of diffusion layer can be described at temperatures lower than 300°C and time interval shorter than 100 h by a formal concentration dependent interdiffusion coefficient. At these conditions the X-ray microprobe could not distinguish individual intermetallic phases. However, their presence influences the formal interdiffusion coefficient. These phases are at given

time of experiment remarkable only at higher temperatures, approximately from 400°C. Temperature dependence of such interdiffusion coefficient can be described by an Arrhenius relationship

$$D = 0.17 \exp(-15\,600 \text{ K}/T) \quad (1)$$

At 300°C, the value of the interdiffusion coefficient in concentration range 100—37 mole % Al equals $2.3 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$. In the concentration range 37—0 mole % Al the interdiffusion coefficient decreases linearly from this value to $5 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$. The observed concentration dependence of interdiffusion coefficient is apparently formal and it originates from that we did not observe individual intermetallic phases.

The formal description of concentration dependence of interdiffusion coefficient is suitable for a comparison of calculated and experimentally determined distribution of aluminium in diffusion layer. It enables to determine the thickness of diffusion layer at conditions close to deposition of aluminium.

If the diffusion coefficient is constant then for the case of infinite diffusion it holds

$$c(x, t) = 0.5 \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (2)$$

where x is the distance, t is time of diffusion and erfc is the error function complement.

When the diffusion coefficient is a function of concentration, situation is somewhat more complicated. In this case it is possible to use a method of digital simulation of diffusion [8]. In our case when the diffusion coefficient is either constant or linearly dependent on concentration we shall use for digital simulation of diffusion the following finite difference equation

$$c_x^{t+\Delta t} = c_x^t + \left[\frac{t}{(\Delta x)^2}\right] \left[D(c_x^t) \cdot (c_{x+\Delta x}^t - 2c_x^t - c_{x-\Delta x}^t) + \left(\frac{dD}{dc}\right)_{c=c_x^t} (c_{x+\Delta x}^t - c_x^t)(c_x^t - c_{x-\Delta x}^t) \right] \quad (3)$$

Derivation of this equation is presented in [9] where it was used for solution of electrochemical problems. Eqn (3) allows to calculate concentration $c_x^{t+\Delta t}$ at point x in time $t + \Delta t$ if we know distribution of concentration in time t . At the beginning of calculation we know distribution of concentration at time $t = 0$. Then we can calculate concentration in time intervals Δt , $2\Delta t$, $3\Delta t$, etc. at points Δx , $2\Delta x$, $3\Delta x$, etc. Stability of solution depends on the fulfillment of condition

$$D\Delta t/(\Delta x)^2 \leq 0.5 \quad (4)$$

In Fig. 1 an experimental distribution $c/c_0 = f(x)$ is compared with that calculated using digital simulation of diffusion. (c is the amount of aluminium in unit volume

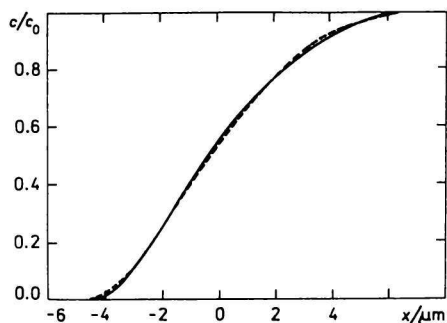


Fig. 1. Relative concentration of aluminium in the diffusion layer as a function of distance from the Matano plane.

Temperature 300°C, time 62 h.

— Experimental distribution of relative Al concentration; - - - calculated distribution of Al concentration.

of the system Cu—Al; c_0 is the same quantity for pure aluminium.) The presented experimental data were obtained for temperature 300°C and time 62 h. It follows that the model of concentration dependent interdiffusion coefficient describes the distribution of aluminium in copper very well.

In Fig. 2 comparison of our formal interdiffusion coefficient and literature data on interdiffusion coefficients in solid solution of copper in aluminium is presented. It follows that both sets of data are in a good agreement. It suggests that it would be possible to extrapolate these data to the temperature of electrolysis and to estimate the thickness of diffusion layer.

While the growth of diffusion layer at 300°C can be explained by diffusion mechanism, situation at 200°C is different. The interdiffusion coefficient obtained by extrapolation from temperature interval 300—600°C to 200°C equals $8 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$. Assuming that the solid solution Cu—Al grows by a diffusion mechanism then the Cu—Al layer should be after 95 h 1.35 μm thick. However, the observed thickness of this layer is $3.65 \pm 0.25 \mu\text{m}$. This value was obtained using the method of anodic dissolution. The X-ray microprobe gives 4 μm . Even after 1 h thickness of the diffusion layer is 1.25 μm . The difference between experimentally determined and calculated thickness indicates that the beginning

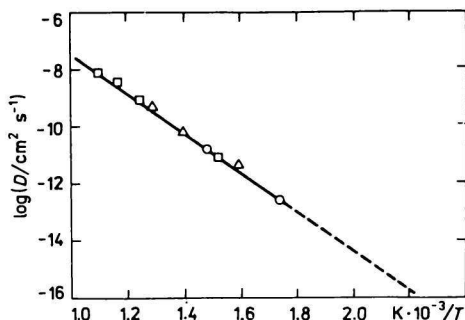


Fig. 2. Temperature dependence of the interdiffusion coefficient in solid solution of copper in aluminium.

Δ According to [4]; □ according to [5]; ○ this paper.

stage of formation of Cu—Al solid solution at electrolytic deposition of aluminium on a copper base is not governed by diffusion. No such behaviour was observed in the case of the system Fe—Al [10]. According to *Geguzin* [11] this phenomenon, *viz.* the existence of another than diffusion transport of substance, is a general law in the case of thin diffusion layers which do not reach a certain limit thickness. In the case of the system Cu—Al this limit thickness seems to be about 1 μm . A fast initial growth of solid solution in the system Cu—Al can explain why the first stage of electrocrystallization at the electrodeposition of aluminium on copper base differs remarkably from formation of crystal nuclei on steel plates [2].

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