The Diffusion Coefficients Of Cu And Zn In A-And H- Solid Solutions

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Abstract: In this work, the multiphase diffusion in the infinite couple Cu-Zn, was studied experimentally. The diffusion couples were prepared by platting technique. The samples were annealed in three different temperatures, which were taken below the melting temperature of Zn. For each temperature, there were used six different annealing times, ranging from 1h up to 32h. In the micrographs provided by light microscopy, it can be seen the formation of only two of the three intermetallic phases present in the Cu-Zn phase diagram, namely ε- and γ-phase. WDX EPMA analysis was used to obtain the concentration profiles of the diffusion layers. The diffusion coefficients of Cu and Zn in α- and η-solid solutions, are calculated using the solutions of second Fick’s law, for independent concentration case. Since the diffusion coefficients depends only on the temperature of annealing and not on the time of it, they must be the same for a given temperature. Therefore the diffusion coefficients were averaged for each temperature. Knowing the diffusion coefficients for each temperature, enables the calculation of the activation energies and the frequency factors as well.

Index Terms: Multiphase diffusion, Platting technique, Diffusion coefficients, Intermetallic phases, Activation energies, Frequency factor, EPMA.

1 INTRODUCTION

MULTIPHASE diffusion is a process where the diffusion on one or several chemical species, gives rise to the formation of intermetallic phases or compounds [1,2,5]. This phenomenon is also known as interdiffusion and it takes place in the presence of a chemical composition gradient [5]. Furthermore, it can be seen as a chemical reaction between the original species; by chemical reaction we mean the formation of one or more compounds composed of the two base material [3,5]. The multiphase diffusion enters into a wide range of other phenomena of concern to solid state physics and chemistry, metallurgy and materials science. It is often used for the determination of phase diagram of binary system and the production of useful intermetallics [5]. This is the reason for technological importance of multiphase diffusion. The interest on a fundamental level is just as great, for these processes often raise questions for which no appropriate answers yet exists [1,5]. In this work we have considered the multiphase diffusion in the infinite couple Cu/Zn, produced by platting technique. They were used three different annealing temperatures ranging from 300°C up to 380°C and for each temperature they were used six different annealing times, ranging from 1 hour up to 32 hours. The concentration profiles were determined by the use of the electron micro-beam analyzer [5]. From the light microscopy and the concentration profiles it can easily be seen the presence of ε- and γ-phase [8,9]. In doing calculations we were concerned in two terminal phases: α- and η-phase, which have the same crystal structures of the corresponding pure elements and presents a certain solid solubility range. α-phase crystalize in a f.c.c. lattice with a statistical distribution of elements and η-phase is a terminal solid solution of Cu in Zn with a compact hexagonal net [11,12].

The diffusion coefficients of Cu and Zn in α- and η-solid solutions respectively, were calculated from the solution of the second Fick’s law, for independent concentration case [1]. This approach was confirmed by the plot of the experimental values of \( \text{erf}^{-1}(1-2c/c_i) \) versus the diffusion layer thickness. The diffusion coefficients were averaged for every annealing temperature. From the relationship of lnD versus 1/T, which follows an Arrhenius form [1,2,3,5], we have calculated the activation energies and the frequency factor \( D_0 \).

2 EXPERIMENTAL

The base material was pure Copper and pure Zinc. The composition of the base material was determined by GD – OES. The infinite Cu – Zn couple was produced by pressing [1] against each other, two pieces of pure copper and pure zinc approximately 4cm2 in size. We have tried three different forces: 200kN, 300kN and 320kN and in each case the result was an unbroken sample. From the concentration profiles of the prepared samples with no annealing, we have seen that the results are the same. Therefore, we think the force used for preparing the samples have no effect in the diffusion process. The diffusion process is activated thermally. Therefore a great concern was about the mounting material for the annealed samples. As such a material was chosen epoxy, after firstly trying tin. The latter one was not appropriate, because the temperature reached during the mounting process (melting temperature of tin) was high enough for the diffusion process to start and this was confirmed by the concentration profiles provided by EPMA. Annealing was carried out in thermal oven model: NABERTHERM Model L5 (30-3000°C). We have used three different annealing temperatures: 300°C, 350°C and 380°C and for each temperature the times were 1h, 4h, 9h, 16h, 25h and 32h. After annealing, the samples were cooled very fast in cold water.

3 RESULTS AND DISCUSSIONS

In the following, we are presenting the micrographs obtained by light microscopy, for two of our samples. In both of them, one can easily see the presence of ε- and γ-phase, along with the mixed crystal zone on either side.
The concentration profiles were obtained by the use of WDX EPMA analysis. The electron probe micro-analyzer was model JXA-8900. The measurement line was perpendicular with the diffusion interface. There were used 200 – 1200 measurement points, 0.5 – 1 μm apart. Figure 2 shows two experimentally obtained concentration profiles. It can be seen (Figure 3, up) that a diffusion profile is also established in the mixed crystal zone. The diffusion coefficients of Cu and Zn in α- and η-solid solutions respectively, are calculated using the second Fick’s law, for independent concentration case. If the diffusion coefficient is independent of concentration, the second Fick’s law can be written as [1,5,6],

$$\frac{\partial C}{\partial t} = D \Delta C$$

It is a linear second-order partial differential equation for the concentration field C(x, y, z, t). If boundary and initial conditions are formulated, the solutions of this equation, can be written as [1,5,6],

$$1 - \frac{2c}{c_0} = \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right)$$

The diffusion coefficient of Zn in η-solid solution is calculated using the slope of the straight line, which represent the dependence of erf-1(1-2c/c0) versus x (Figure 3, down). The diffusion coefficients of Cu in α-solid solution are calculated in the same way. Since the diffusion coefficients depends only on the temperature and not on the time of the diffusion process, they must be the same for a given temperature. Therefore, the diffusion coefficients were averaged for each temperature [10]. The results are shown in Table 1.
The diffusion coefficient follows an Arrhenius relationship,

\[ D = D_0 \cdot \exp\left(\frac{-Q}{RT}\right) \]

By getting the logarithms of both sides of the above equation, we end up in a linear equation. The graphical representation of such an equation is shown in Figure 4.

From the above mentioned Arrhenius relationship, we have calculated the corresponding activation energies and the frequency factors. The results are shown in Table 2.

**4 SUMMARY AND CONCLUSIONS**

During the experimental study of the multiphase diffusion in the Cu-Zn couple produced by plating technique, we were able to detect the presence of ε- and γ-phase according to the Cu-Zn phase diagram; this was done by the use of light microscopy and EPMA; in our calculations we were concerned in the two terminal phases, namely α- and η-solid solutions. From the EPMA results, it was seen that a diffusion profile was also established in these mixed crystal zones as well; The diffusion coefficients of Cu and Zn in α- and η-solid solutions respectively, were calculated using the solution of second Fick’s law, for the independent concentration case. The assumption that the corresponding diffusion coefficients are independent from the concentration was proven experimentally. The reported diffusion coefficients are averaged values for each temperature. The Arrhenius relationship between the diffusion coefficients and the temperature of annealing, enables the calculation of the corresponding activation energies and the frequency factor.

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**REFERENCES**


