

Calculation Of The Interdiffusion Coefficient In The Cu–Zn Diffusion Couple

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Abstract. A quantitative analysis of multiphase diffusion in Cu-Zn diffusion couple is presented. The analysis is based in using the concentration profiles provided by electron micro-beam analyzer. From the dependence of the square of phase thickness from annealing time, the growth constant for each phase in each annealing temperature can be calculated. Knowing the growth constant of γ and ϵ phases one can calculate the activation energy and the diffusion coefficient of the above mentioned intermetallic phases.

Keywords: Diffusion, Interdiffusion coefficient, Activation energy; Plating technique, Optical microscopy; Electron micro-beam analyzer.

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INTRODUCTION

Diffusion between two metallic species is now a well recognized phenomenon and it is often accompanied by the formation of one or several intermetallic compounds. This phenomenon is generally described under the heading “multiphase diffusion”, which emphasizes the diffusion part of the whole process [1,4]. In a typical case pure metal A is bonded to pure metal B and diffusion is permitted at high temperature. Although both A and B atoms move, only one concentration profile, say of A, is established (the profile of B contains no new information). The resulting diffusion coefficient which is extracted from the profile is termed the interdiffusion coefficient [1,7,4].

In this work we have considered the diffusion in the infinite Cu – Zn couple produced by the plating technique. They were used four different annealing temperatures ranging from 250°C to 380°C. For each temperature they were used six different annealing times, ranging from 1 hour to 32 hours. The concentration profiles were determined by the use of the electron micro-beam analyzer. From the optical microscopy and the concentration profiles one can detect the presence of γ , ϵ and β phases according to the Cu – Zn phase diagram. Using the above mentioned concentration profiles we were able to do calculations only for γ and ϵ phases. The β phase was observed only at very high temperature and very long annealing times and it shows a reduced thickness.

EXPERIMENTAL

The base material was pure Copper and pure Zinc. The composition of the base material was determined by GD – OES.

To determine the appropriate filling material for the sample container two no annealed samples, were put in the sample container by filling those respectively with epoxy and tin. We were interested in finding an appropriate filling material, i.e. we did not want any diffusion to happen during the filling process. From the concentration profiles we noted that when the filling process was carried out using melted tin, the diffusion process has started. So the temperature reached during the filling process (or that of the melted tin) was high enough for the diffusion process to start, regardless of the time used to carry out the filling process. Using epoxy as a filling material we were able to get a sharp concentration profile with no intermetallic phase presented. From that point we decided to use epoxy as our filling material. One of the disadvantages of this filling material (with respect to tin) was that we will

use the carbon layer, needed for electron conduction during the measurement in the electron micro-beam analyzer. However, compared to tin, epoxy can offer very good possibilities for metallographic sample preparation [2].

The infinite Cu – Zn couple was produced by pressing two pieces of pure copper and pure zinc approximately 4cm² in size. To determine the appropriate force applied to the above mentioned pieces, we tried the forces: 200kN, 300kN and 320kN. From the concentration profiles of such samples (no annealing was applied) one can easily see that the results are almost the same. Therefore we think that the force applied to produce our samples (the infinite couple Cu-Zn) will have no effect in the diffusion process that we are going to study.

Annealing was carried out in thermal oven model: NABERTHERM Model L5 (30-3000°C).

We have used four different annealing temperatures: 250°C, 300°C, 350°C and 380°C. For each temperature the annealing times have been: 1h, 4h, 9h, 16h, 25h and 32h. After annealing, the samples were cooled very fast in cold water.

After the annealing, a layer of less than 1mm in thickness was mechanically cut off from the sample and the sample was put in the sample support by filling it with epoxy. After this process the sample was ready for metallographic preparation.

RESULTS AND DISCUSSIONS

Our optical microscope was model NEOPHOT 30, ZeisJena.

In the following we will show the pictures provided for two of our annealing times (respectively 16h and 25h) for the temperature 380°C:

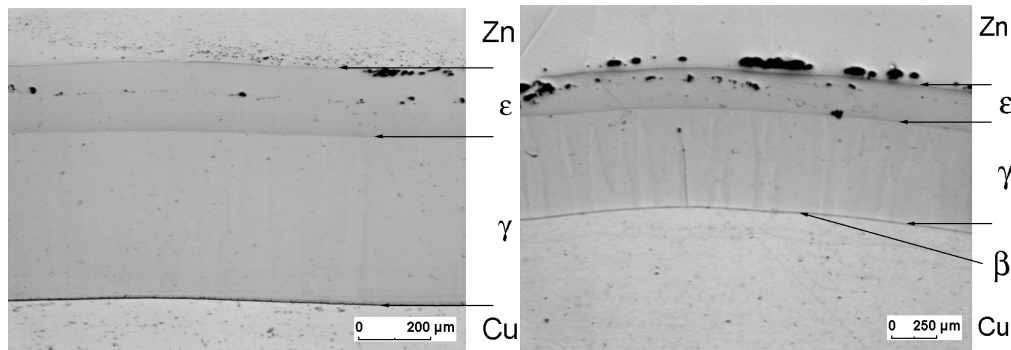


FIGURE 1. Obtained pictures from two samples at 380°C with different annealing times (16h and 25h).

The electron probe micro-analyzer was model JXA-8900. The measurement line has been perpendicular with the diffusion interface. There were used 200 – 1200 measurement points, 0.5 – 1 μm apart. In the following one can see the concentration profiles in weight percentage for the temperature 380°C.

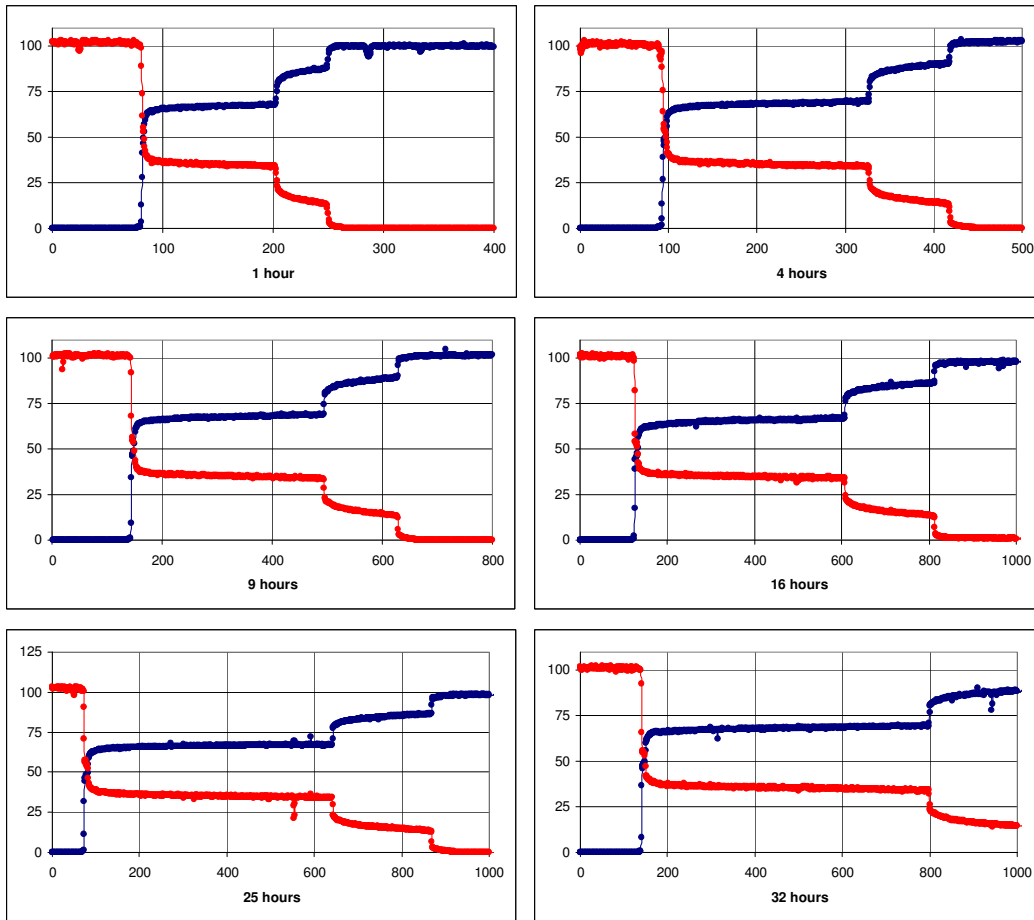


FIGURE 2. Concentration profiles at 380°C.

From the two pictures presented below one can see the presence of the expected phases according to the Cu-Zn phase diagram. (We have used an optical microscopy picture and the atomic map for two of our samples).

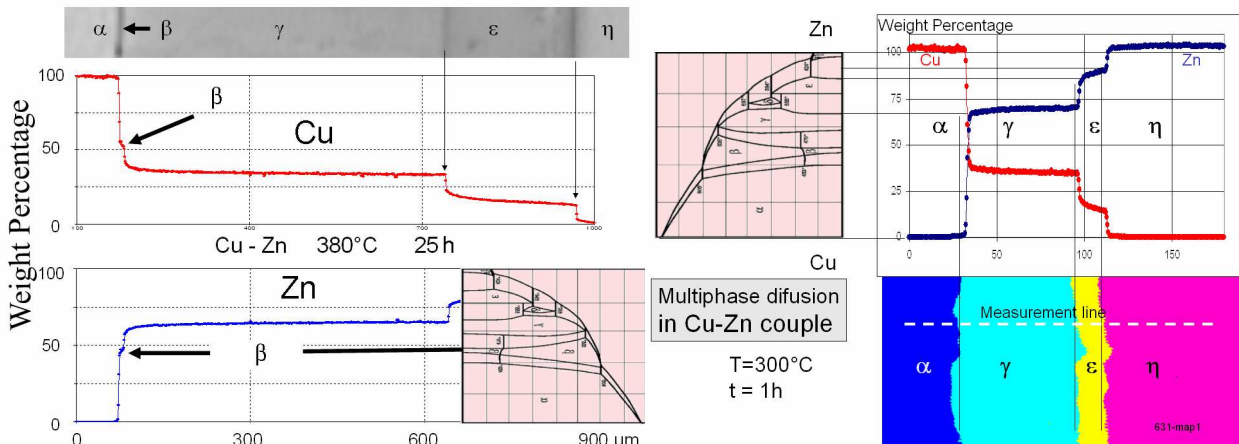


FIGURE 3. Graphical representation of the expected phases according to the Cu-Zn phase diagram.

The thickness of γ and ϵ phases were measured directly at the concentration profiles. From the data provided in such manner the dependence of the square of phase thickness from annealing time was studied. From the graphical

analysis of the experimental results it was observed a deviation from the parabolic law of phase growth ($\Delta x_i^2 = 2k_i \cdot t$) [3,5,6,8]. This was observed for the first two annealing times (1h and 4h). It may be explained as a lack of equilibrium state due to the very short annealing times. Anyway, we have reasons to believe that for very short annealing times the main role in the diffusion process is played by the chemical reactions. At this stage the phase growth law is a linear one [3]. By increasing the annealing time, the mass transport or atomic movements is the dominant factor in the diffusion process.

The next step was to determine the coefficient of phase growth for both phases in every used temperature. This was done by the use of regression analysis and the relation ($\Delta x_i^2 = 2k_i \cdot t$). The results are presented in the following tables:

TABLE a). The coefficients of phase growth.

| Temperature (K) | $k_\gamma \times 10^{-12}$ (m ² /s) | $k_\epsilon \times 10^{-12}$ (m ² /s) |
|-----------------|--|--|
| 523.2 | 622.8 | 12.4 |
| 573.2 | 1635.6 | 91.3 |
| 623.2 | 4079.8 | 399.2 |
| 653.2 | 6257.5 | 1150.6 |

The coefficient of phase growth k determines the speed of phase growth and therefore is proportional with the diffusion coefficient. From the well known form of dependence of the diffusion coefficient on temperature $D = D_0 \exp(-Q/RT)$ we get $k = k_0 \exp(-Q/RT)$. After the graphical analysis of the experimental results the calculated values are:

TABLE b). The activation energies for both phases.

| Q_γ (J/mol) | Q_ϵ (J/mol) |
|--------------------|----------------------|
| 5.1×10^4 | 9.7×10^4 |

The theoretical formulas used to calculate the diffusion coefficients are:

$$D_\gamma = k_\gamma \cdot \frac{1}{c-b} \cdot \frac{(b-a) \cdot (d-c)}{(b-a) + (d-c)} \quad \text{and} \quad D_\epsilon = k_\epsilon \cdot \frac{1}{e-d} \cdot \frac{(d-c) \cdot (f-e)}{(d-c) + (f-e)}$$

The meaning of the symbols used in the above formulas are:

TABLE c). Symbols used in the above formulas.

| Symbol | a | b | c | d | e | f |
|-------------|--------------------|--------------------|----------------------|----------------------|--------------------|--------------------|
| The meaning | $c_{\eta\epsilon}$ | $c_{\epsilon\eta}$ | $c_{\epsilon\gamma}$ | $c_{\gamma\epsilon}$ | $c_{\gamma\alpha}$ | $c_{\alpha\gamma}$ |

The above mentioned symbols were determined directly from the concentration profiles in the way that is shown in the following picture.

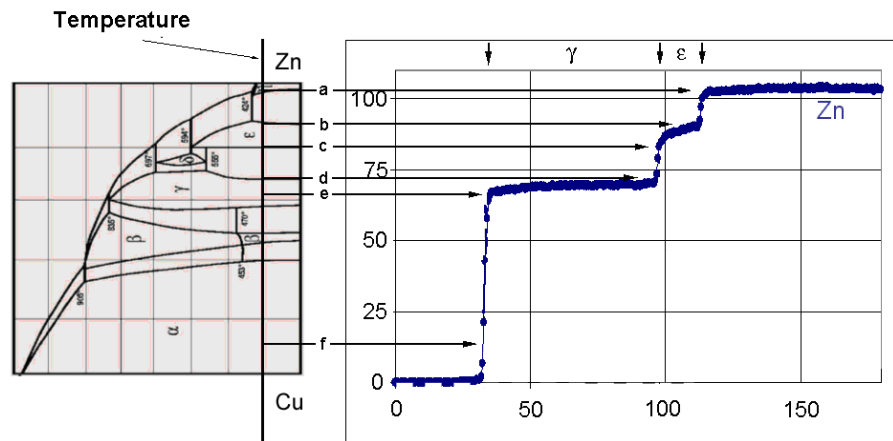


FIGURE 4. Getting the symbols used in our formulas by the concentration profiles.

The results are shown in the tables below:

TABLE d). The diffusion coefficients values.

| T (°C) | $D_{\gamma} \times 10^{-12}$ (m²/s) | $D_{\epsilon} \times 10^{-12}$ (m²/s) |
|---------------|--|--|
| 250 | 207.39 | 69.44 |
| 300 | 1445.87 | 304.30 |
| 350 | 1109.71 | 254.29 |
| 380 | 1432.97 | 896.32 |

SUMMARY AND CONCLUSIONS

During the study of the diffusion process in the Cu-Zn couple there were noted the presence of five phases. These are the expected ones according the Cu-Zn phase diagram (concerning the temperature range we have used).

During our experimental work we did not notice any phase boundary between solid solution α and η , respectively with Cu and Zn.

In the used temperature range the thick enough phases to do calculation are γ and ϵ phases.

For the high enough temperatures and the long enough annealing times we did notice the presence of the β phase. The absence of this phase for short annealing times is connected to the homogeneity of this phase.

By the use of the concentration profiles firstly we study the dependence of the square of phase thickness from the annealing time. It was shown that the law of phase growth is parabolic.

For very short annealing times we did notice a deviation from the parabolic law of phase growth. At this stage of the process there is no equilibrium state reached yet due to very short annealing times. We think that the dominant factors at this stage of the process are the chemical reactions happening at the interface between Cu and Zn atoms.

For the Cu-Zn diffusion couple we have calculated the coefficients of phase growth, their activation energies and corresponding diffusion coefficients for each of the annealing temperatures used.

In the future we will try to work at higher temperatures by using an appropriate geometry for the diffusion couple. This will enable us to do calculation even for β phase.

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