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THE GROWTH OF BETA PHASE IN THE GAMMA-BRASS–COPPER DIFFUSION COUPLE

RAST BETA FAZE V DIFUZIJSKEM PARU GAMA MEDENINA – BAKER

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In this work we make a quantitative investigation of the growth of the β-phase in the γ-brass/copper diffusion couple. The diffusion couple was produced by electrolysis. The analysis of multiphase diffusion in the γ-brass/copper system was based on using the concentration-depth profiles provided by electron micro-beam analyzer. The growth constant of the β-phase for each of the used temperatures was calculated from the time dependency of the β-phase thickness. Using the Matano method it was possible to calculate the interdiffusion coefficient of Zn in the β-phase. The activation energy for the diffusion of Zn in the β-phase was also determined.

Keywords: γ-brass-copper system, growth of intermetallics, multiphase diffusion, interdiffusion coefficients, activation energy

V delu je prikazana kvantitativna preiskava rasti β-faze v difuzijskem paru γ-medenina-baker. Difuzijski par je bil izdelan z elektrolizo. Analiza difuzije v večfaznem difuzijskem sistemu γ-medenina-baker temelji na uporabi profilov koncentracija-globina, dobljenih z elektronskim mikroanalizatorjem. Konstanta rasti β-faze pri vsaki od uporabljenih temperatur je bila izračunana iz časovne odvisnosti debeline β-faze. Z uporabo Matano metode je bilo mogoče izračunati koeficiente nasprotnosmerne difuzije Zn v β-fazi. Določena je bila tudi aktivacijska energija za difuzijo Zn v β-fazi.

Ključne besede: system γ-medenina-baker, rast intermetalnih zlitin, difuzija v večfaznem sistemu, koeficienti nasprotnosmerne difuzije, aktivacijska energija

1 INTRODUCTION

The phenomenon of diffusion between two metallic species, which is followed by the formation of one or more intermetallics, is known as multiphase diffusion or interdiffusion.[1–3] Multiphase diffusion could be as well looked at as a chemical reaction between the original species, and this is why it can be referred to as chemical diffusion.[1]

An experiment on multiphase diffusion consists in the study of a concentration-depth profile, known also as the diffusion profile, by examining a polished cross-section of the diffusion sample.[4] This profile is most often established on a transverse section by electron-probe microanalysis (EPMA). The diffusion profile is then used to extract the corresponding diffusion coefficients by comparison with the corresponding solution of Fick's second law and the most common method used is the Matano method.[1,2]

An experimental diffusion profile has the form of a series of curved segments, with concentration discontinuities at every interface. These concentration drops correspond to the intersection of an isotherm with the phase boundaries of the phase diagram. If the phase diagram of the selected system contains intermetallics, it is expected that the multiphase diffusion will give rise to the formation of these intermetallic layers.[5] In practice, certain phases are sometimes missing from the diffusion zone or the composition of the phases can differ from those indicated on the phase diagram. Sometimes, extra phases also appear.[5,6] Although in most cases parabolic growth kinetics are observed, other kinetics can be observed as well.[7]

This paper originated from a study of multiphase diffusion in the Cu/Zn diffusion couple.[8] Although many works have been carried out for multiphase diffusion on different binary systems, there are no systematic results found in the literature for this system. Referring to the Cu-Zn phase diagram[9], there are four intermetallic phases, i.e., β-phase, γ-phase, δ-phase and ε-phase. So one can expect the formation of four stacked intermetallics in the diffusion zone.[6,7] (It should be noted that unlike the other phases, δ-phase is stable over a limited temperature range going from 558 °C up to 700 °C.) One of the major difficulties in the investigation of the multiphase diffusion between copper and zinc is that there is a great difference in the melting temperatures of the diffusing species. So, for the growth of zinc-rich phases (γ- and ε-phase) low annealing temperatures must be used, while for the growth of the copper-rich phase (β-phase) higher temperatures are needed. Consequently, the problem cannot be solved by a simple combination of copper against zinc. In the experimental study mentioned above[8], the β-phase was observed at a relatively high

temperature (380 °C) and a relatively long annealing time (25 h) and it showed a reduced thickness. In order to have a well developed layer of the β-phase, longer annealing times are needed and this will result in an extended thickness of the fastest growing phase, γ-phase.[8] So for the production of an infinite diffusion couple by a plating technique, the starting dimensions of the Cu and Zn samples must be considerable and this will limit the possibility of having a stable diffusion couple.[10]

In this work the diffusion couple was produced by electroplating copper in γ-brass. Annealing was performed in four different temperatures ranging from 500 °C to 650 °C and for each temperature we used six different annealing times, ranging from 1h to 14 h. The concentration-depth profiles were determined by the use of EPMA. The presence of β-phase was detected by optical microscopy and EPMA. From the time dependency of the phase thickness, we have calculated the growth constant of the β-phase. Knowing the growth constant of β-phase and applying Matano analysis, we have calculated the interdiffusion coefficient of the fastest diffusing element, zinc.[8,11] Using the Arrhenius relationship of the diffusion coefficient from temperature, we have calculated the activation energies for diffusion in β-phase.[12,13]

2 MATERIALS AND EXPERIMENTAL PART

The base material was γ-brass and the melting of it was done in a middle-frequency induction furnace with a crucible. Casting took place in a cast-iron mould. The content of the produced γ-brass was investigated by GDOES and X-Ray and the results are: 31.34 % of amount fractions of Cu and 68.52 % of amount fractions of Zn and 0.14 % of amount fractions of Fe.

γ-brass is a brittle intermetallic and prior to electrolysis the γ-brass sample was subject to a heat treatment at 650 °C for about 8 h. This was necessary for removing any residual stresses or internal stresses[14] and thus facilitating the mechanical cut of the sample. After the heat treatment the homogeneity of the γ-brass sample was verified by EPMA.

The γ-brass samples were cut by a diamond cut-off wheel in plane cylindrical slices of 5 mm in thickness and nearly 30 mm in diameter. A fine grinding was sufficient for the copper atoms to be deposited in the γ-brass sample during the electrolysis. The used copper electrolyte contained 40 g/L copper and 160 g sulphuric acid (H_2SO_4). The temperature was 65 °C and the current was 0.2 A. The deposition process took place for about 30 h. By the light microscopy it was observed a deposited layer of copper with a thickness of more than 1 mm.

Annealing was carried out in thermal oven NABERTHERM Model L5 (30 °C–3000 °C). The temperatures were 500 °C, 550 °C, 600 °C and 650 °C and for each temperature there were used five to six different annealing times, ranging from 1 h to 14 h. Just after the annealing, each sample was cooled very quickly in cold water.

3 RESULTS AND DISCUSSION

After diffusion annealing the samples were polished perpendicularly to the diffusion zone and then they were

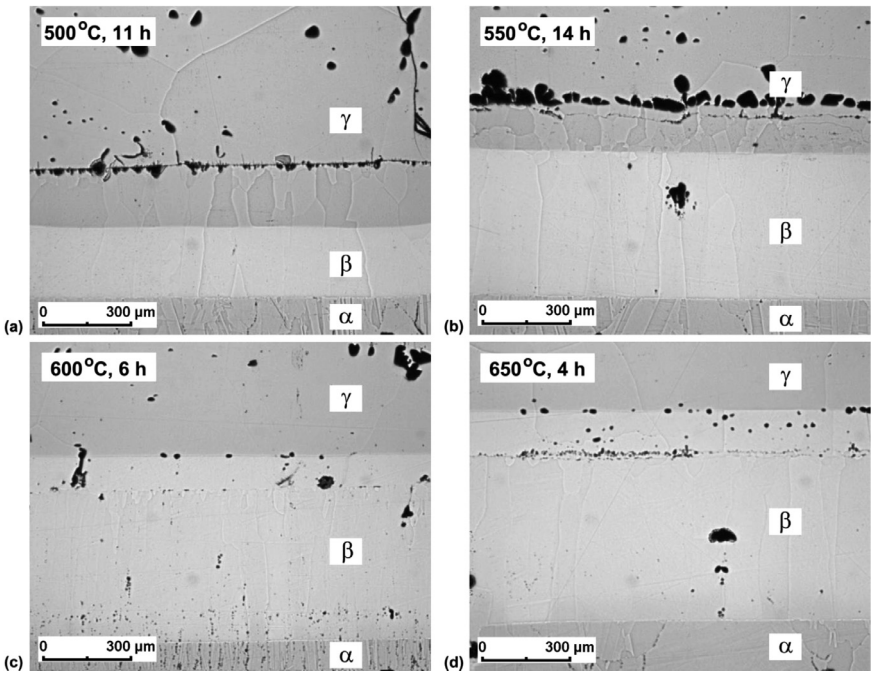

Figure 1: Optical micrographs of the diffusion zone at annealing temperature: a) 500 °C, b) 550 °C, c) 600 °C and d) 650 °C
Slika 1: Mikrostruktura difuzijskega področja pri temperaturi žarjenja: a) 500 °C, b) 550 °C, c) 600 °C in d) 650 °C

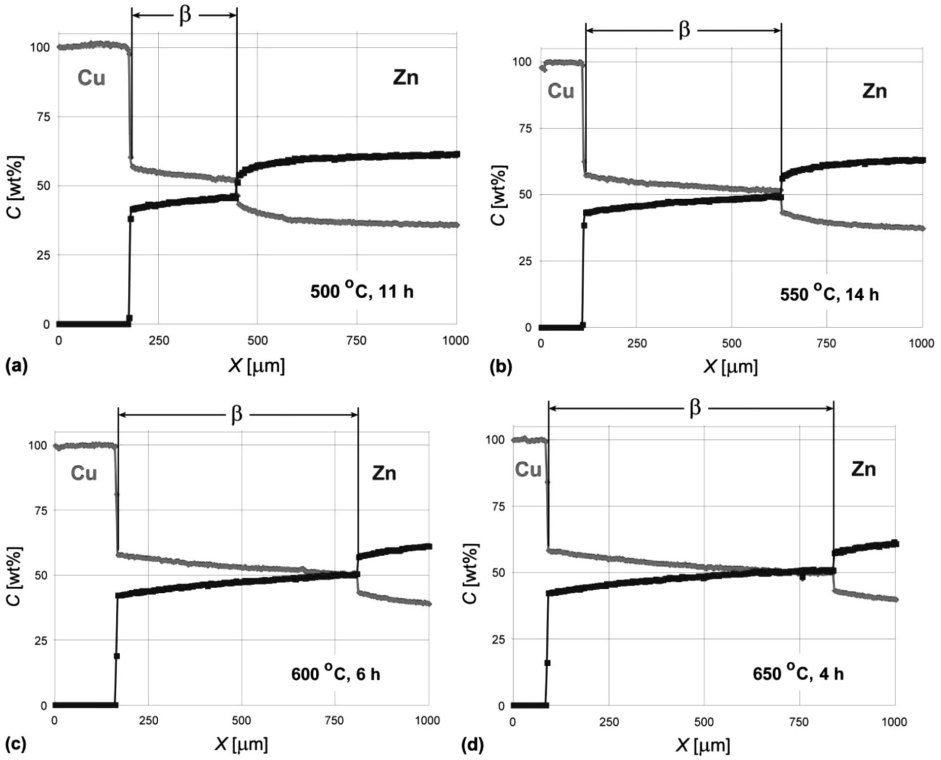

Figure 2: Concentration-depth profile across the diffusion zone at annealing temperature: a) 500 °C, b) 550 °C, c) 600 °C and d) 650 °C
Slika 2: Profil koncentracije v globino preko področja difuzije pri temperaturi žarjenja: a) 500 °C, b) 550 °C, c) 600 °C in d) 650 °C

investigated by light microscopy. **Figure 1** shows the typical optical micrographs of the diffusion zone for each of the annealing temperatures. From the micrographs shown one can see the presence of a well-defined layer of β-phase. The thickness of the β-phase is increasing with temperature, as well as with time (**Figure 1a–1d**). The presence of β-phase was detected by EPMA-WDX analysis.

The concentration-depth profiles across the diffusion zone were determined by the use of EPMA-WDX analysis, operated in step-scan-mode (20 kV, 100 nA, Δx = 1 μm). Depending on the thickness of the β-phase, the measurements were conducted for 600 up to 1200 data points. The concentration-depth profiles of the same samples shown in the above optical micrographs are presented in **Figure 2**.

In β-phase field the concentration of Cu continuously increases while that of Zn continuously decreases. As shown in the optical micrographs, from the presented concentration-depth profiles one can easily see that β-phase is becoming thicker with increasing temperature (**Figure 2a–2d**), as well as with time.

In **Figure 3** we propose a schematic diagram that illustrates the presence of β-phase in the diffusion zone, according to Cu-Zn phase diagram. On the right-hand side of the selected concentration-depth profile, a 90° rotated phase diagram is zoomed out in the same scale. The β-phase field of the concentration-depth profile corresponds to that of the phase diagram. Below the same concentration-depth profile, an X-ray atomic map of the same sample is placed. This phase distribution image was provided by EPMA. (As we have already mentioned, the presence of β-phase in the diffusion zone was detected by EPMA-WDX analysis.)

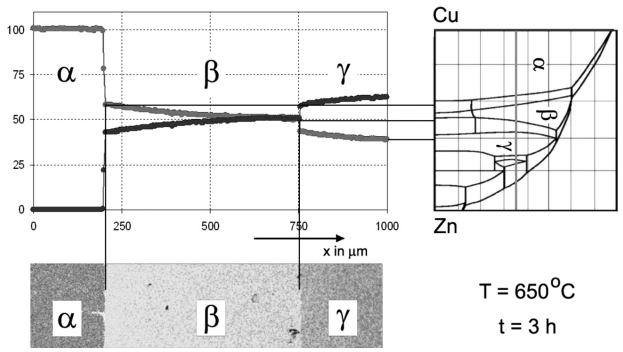

Figure 3: A schematic diagram illustrating the presence of β-phase in the diffusion zone.
Slika 3: Shematski diagram, ki kaže prisotnost β-faze v področju difuzije

3.1 Time dependency of the β-phase thickness

Figure 4 shows the plots of the square of the β-phase thickness versus diffusion time for each annealing temperature according to Equation (1):[1,2]

$$X_i^2 = 2k_i t \quad (1)$$

where X is the thickness of the i-phase region, k_i is the phase growth constant and t is the diffusion time. The

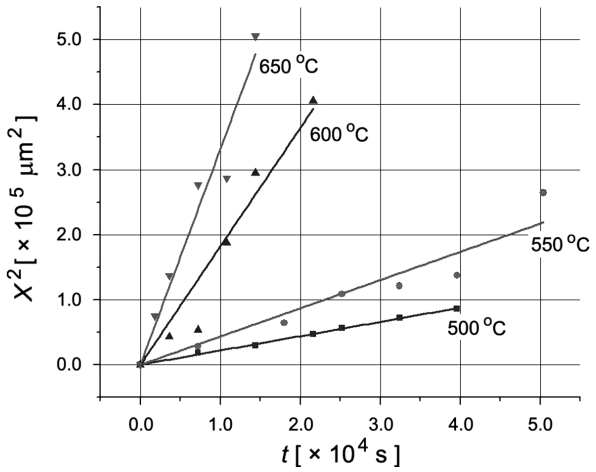

Figure 4: The plots of the square of the β-phase thickness versus diffusion time, for each temperature

Slika 4: Diagram kvadratov debeline β-phase pri navedenih temperaturah, v odvisnosti od časa difuzije

average layer thicknesses of the β-phase were measured directly in the EPMA concentration-depth profiles.

Parabolic growth and no incubation period were observed for all the temperatures used. It means that during the whole intermixing process local thermodynamic equilibrium is maintained and the layer growth is diffusion controlled.[15]

The growth constants for the β-phase, which were determined from the slope of the plots in **Figure 4**, are presented in **Table 1**.

Table 1: The growth constants for the β-phase at each temperature

Tabela 1: Konstante rasti β-faze pri navedeni temperaturi

Temperature (°C)	k(β) (m²/s)
500	1.10×10^{-12}
550	2.17×10^{-12}
600	9.11×10^{-12}
650	1.66×10^{-11}

From the values reported in **Table 1** we can see that the phase-growth constants are increasing with temperature. The phase-growth constants have a complex meaning and they depend on the diffusivity in the layers, as well as on the concentration gradients on both sides of the interface and on solubility limits of the phases.[15]

As with the diffusion coefficients, the temperature dependence of the phase growth constants follows an Arrhenius relationship.[1,2]

$$k = k_0 \exp\left(-\frac{Q}{RT}\right) \qquad (2)$$

Referring to Equation (2), from the slope and intercept of the plot of ln(k) versus 1/T, shown in **Figure 5**, we have calculated the activation energy Q, for the growth of the β-phase and the constant k_0 for the β-phase. The calculated values are reported in **Table 2**.

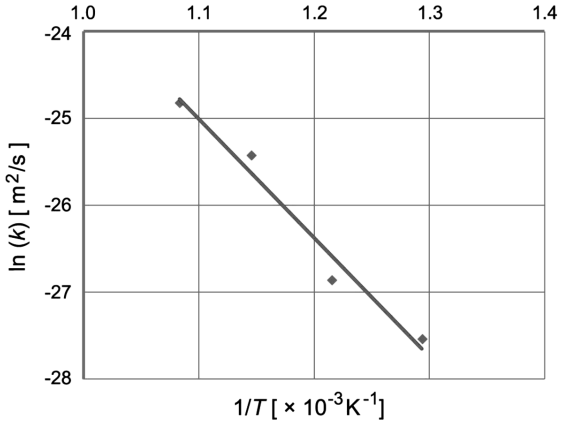

Figure 5: The plot of ln(k) versus 1/T

Slika 5: Odvisnost med ln(k) in 1/T

Table 2: The value of the activation energy for the growth of β-phase and that of the constant k_0

Tabela 2: Vrednost aktivacijske energije rasti β-faze in vrednost konstante k_0

Intermetallics	Q (J/mol)	k_0 (m²/s)
β-phase	11.34×10^4	4.55×10^{-5}

3.2 The diffusion coefficients of Zn in the β-phase

The diffusion coefficient of the fastest diffusion element, which in the case of our system is zinc,[8] was determined by employing the Matano method. The diffusion coefficients were calculated according to Equation (3):[7]

$$D_\beta = k_\beta \cdot \frac{1}{c_{\beta,\alpha} - c_{\beta,\gamma}} \cdot \frac{(c_{\beta,\gamma} - c_{\gamma,\beta}) \cdot (c_{\alpha,\beta} - c_{\beta,\alpha})}{(c_{\beta,\gamma} - c_{\gamma,\beta}) + (c_{\alpha,\beta} - c_{\beta,\alpha})} \qquad (3)$$

The symbols used in Equation 3 were extracted from the corresponding concentration-depth profiles, as illustrated schematically in **Figure 6**. The calculated diffusion coefficients are reported in **Table 3**.

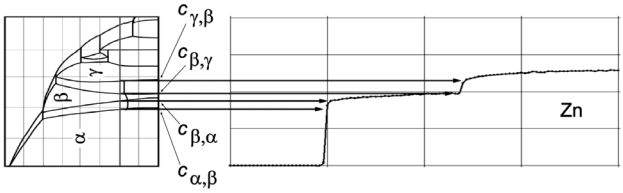

Figure 6: A schematic illustration of the meaning of the symbols used in Equation 3

Slika 6: Shematski prikaz pomena simbolov, uporabljenih v enačbi 3

Table 3: The diffusion coefficients of zinc in the β-phase

Tabela 3: Koeficienti difuzije cinka v β-fazi

Temperature (°C)	D^{Zn}_β (m²/s)
500	8.47×10^{-13}
550	1.54×10^{-12}
600	3.30×10^{-12}
650	4.43×10^{-12}

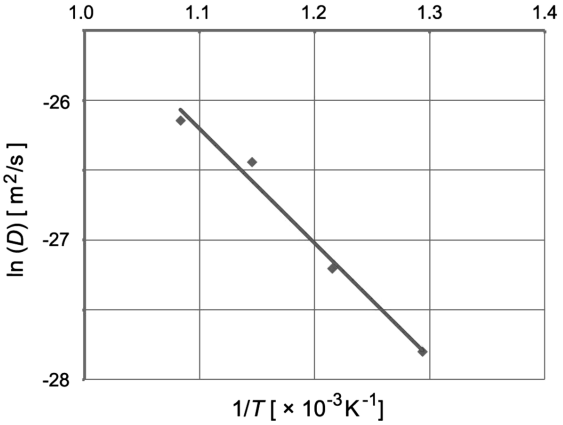

Figure 7: The plot of ln(*D*) versus 1/*T*
Slika 7: Odvisnost med ln(*D*) in 1/*T*

Table 4: The activation energy for the diffusion of zinc in β-phase and the corresponding frequency factor
Tabela 4: Aktivacijska energija za difuzijo cinka v β-fazi in odgovarjajoč frekvenčni faktor

Intermetallics	$Q^{Zn}{}_{\beta}$ (J/mol)	D_0 (m^2/s)
β-phase	6.82×10^4	3.47×10^{-8}

3.3 The activation energy for the diffusion of zinc

The temperature dependence of the diffusion coefficients follows an Arrhenius relationship.[1,2]

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad (4)$$

Table 4 shows the activation energy for the diffusion of zinc in β-phase $Q^{Zn}{}_{\beta}$, and the corresponding frequency factor D_0, which are calculated respectively from the slope and intercept of the plot of ln(*D*) versus 1/*T* shown in **Figure 7**.

4 CONCLUSIONS

The γ-brass/copper diffusion couple produced by electrolysis can be used successfully in multiphase diffusion studies. After an isothermal diffusion annealing at four different temperatures, for five to six different annealing times, the growth of β-phase was observed in the diffusion zone. A single-phase domain was examined by light microscopy and the presence of β-phase was identified by EPMA-WDX analysis. The compositions of the β-phase did not differ from those indicated on the phase diagram.

The phase-growth constants for each temperature were determined by the time dependency of the β-phase thickness and the calculated values are presented in **Table 5**. Using the least-square fit to the experimental data a parabolic growth rate was observed. From the temperature dependency of the corresponding phase-growth constants, the activation energy characterizing the growth of β-phase was determined and its value is $Q = 11.34 \times 10^4$ J/mol. (The corresponding constant is $k_0 = 4.55 \times 10^{-5}$ m^2/s.)

Using the EPMA concentration-depth profiles and employing the Matano method, we have calculated the interdiffusion coefficients; these values are presented in **Table 5**. The activation energy of zinc in the β-phase was also determined and its calculated value is $Q^{Zn}{}_{\beta} = 6.82 \times 10^4$ J/mol. (The corresponding frequency factor is $D_0 = 3.47 \times 10^{-8}$ m^2/s.)

Table 5: The growth constants for the β-phase and the diffusion coefficients of zinc in the β-phase
Tabela 5: Konstante rasti β-faze in difuzijski koeficienti cinka v β-fazi

Temperature (°C)	k(β) (m^2/s)	$D^{Zn}{}_{\beta}$ (m^2/s)
500	1.10×10^{-12}	8.47×10^{-13}
550	2.17×10^{-12}	1.54×10^{-12}
600	9.11×10^{-12}	3.30×10^{-12}
650	1.66×10^{-11}	4.43×10^{-12}

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