INTERDIFFUSION IN THE MG-RICH AND AL-RICH SOLID SOLUTIONS OF THE MG-AL BINARY ALLOY

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ABSTRACT

The interdiffusion in the Mg-rich and Al-rich solid solution of Mg-Al couple was investigated using a conventional diffusion couple experiment. The diffusion couple was prepared by pressing a magnesium cylinder into a cylindrical hole of aluminum. The samples were annealed in three different temperatures and for each temperature there were used six different annealing times.

The light microscopy and EPMA examination confirmed that the developed diffusion layers after the annealing were thick enough to analyze the diffusion parameters.

By examining the concentration profiles provided by EPMA, it was seen the composition dependence of the interdiffusion coefficients were negligible in the α- and δ-solid solutions. Therefore the interdiffusion coefficients of Mg and Al respectively in α- and δ-solid solutions, were calculated using the solutions of second Fick's law, for independent concentration case, where a diffusion couple comprised of a pair of semi-infinite solids was considered. Since the interdiffusion coefficients were regarded as constants within the range of selected temperature and composition, they were averaged for each temperature. Using the provided values of the diffusion coefficients for each temperature, we were able to calculate the activation energies for the growth of each phase.

Keywords: *Interdiffusion, Boltzmann-Matano Analysis, Interdiffusion Coefficients, Activation energies, EPMA.*

INTRODUCTION

Aluminum and magnesium are lightweight metals, and they both have a moderately low melting temperature. Over the years magnesium alloys have been developed mainly in connection with the aerospace industry. The large scale development and application of Mg-Al alloys have been encouraged by the demand for lightweight and environment friendly materials in the automotive industry [1,2,3,4]. Furthermore, the Mg-Al alloys with high contents of aluminum offer a good combination of mechanical properties and corrosion resistance and therefore these alloys have been used in defense, metallurgical and manufacturing industries as well [1,2]. Being more recyclable and less costly to produce, these alloys have replaced engineering plastics for many applications [2].

Interdiffusion is a process which takes place in the presence of a chemical composition gradient which results in the formation of intermetallic phases or compounds [5,6,7,8,]. It plays a critical role into a lot of phenomena concerning solid state physics, metallurgy and materials science. An atomistic understanding of diffusion in intermetallics is more complex than that of diffusion in metallic elements [11]. The interest on interdiffusion is on a fundamental level as well, because this process run with a lot of questions for which no appropriate answers yet exists [8,9,11,12]. Interdiffusion is commonly used for the production of useful intermetallics [10,11] and that is why it is of a great importance from a technological perspective.

During a diffusion anneal a concentration profile develops over a certain range in the diffusion zone. This profile can be measured on a cross section of the diffusion zone by electron microprobe analysis. Such a profile can then be used to calculate the diffusion parameters [8,10,11].

In this work we have considered the interdiffusion in the infinite couple Mg/Al, produced by pressing a magnesium cylinder into a cylindrical hole of aluminum. Diffusion annealing was performed in three different temperatures, 320^{o}C, 350^{o}C and 380^{o}C, which are well below the melting temperatures of magnesium and aluminum. For each temperature, diffusion annealing was performed for six different times starting from 1h up to 36h.

The results presented in this paper are those concerning two terminal phases: α- and δ-solid solutions, which have the same crystal structures as the corresponding pure elements and present a certain solid solubility range.

The diffusion coefficients of Mg and Al in α- and δ-solid solutions respectively, were calculated from the solution of the second Fick's law, for independent concentration case [5,8]. The reported values of the corresponding diffusion coefficient are averaged values for each annealing temperature [12].

The plot of *lnD* versus 1/*T*, which follows an Arrhenius form [5,6,7,8], is used to calculate the corresponding activation energies.

MATERIALS AND METHODS

The base materials for producing the Mg-Al diffusion couple were pure aluminum and pure magnesium and their composition was checked by GD-OES. The production of an infinite diffusion couple comprised by this two elements, is problematic due to the rapid oxidation of aluminum and therefore we have tested two different methods.

The first method consists in pressing a magnesium cylinder into a cylindrical hole of aluminum. The outer diameter of the magnesium cylinder was 8.00mm and the inner diameter of the aluminum cylindrical hole was 7.95mm. In order to facilitate the pressing process, the magnesium cylinder was cooled in liquid nitrogen.

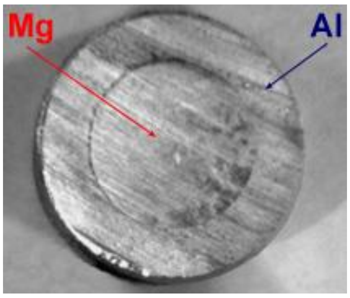

Figure 1. The diffusion couple was prepared by pressing a Magnesium cylinder into a cylindrical hole of Aluminum.

The second method is the very well known pressing technique. It consists in pressing two metallic plates against each other. Firstly aluminum was sputtered over the magnesium plate and then an aluminum plate was pressed against it.

A careful examination by light microscopy made us believe that the sample produced by the first method (Figure 1), offered a better interface and for that reason we decided to go on with this technique in preparing our diffusion couples. Furthermore, two different forces were tested for pressing the magnesium cylinder into the cylindrical hole of aluminum, 200N and 350N. In both cases the resulting samples showed very good adhesion and they were unbroken. The effect of these applied forces in the diffusion process was checked by EPMA. The provided concentration profiles showed the development of no diffusion zone, i.e., the applied force during the production of the samples has no effect in the diffusion process.

Diffusion annealing was carried out in thermal oven model: Nabertherm Model L5 (30-3000^{o}C). The temperatures used were: 320^{o}C, 350^{o}C and 380^{o}C. For each temperature there were used six different annealing times: 1h, 4h, 9h, 16h, 25h and 36h.

The annealed couples were mechanically cut and then they were mounted in epoxy.

RESULTS AND DISCUSSIONS

In the micrograph shown in Figure 2 we can easily see the presence of β- and γ-phase, along with the mixed crystal zone on either side of the sample. The microscope used was Neophot 30, ZeisJena.

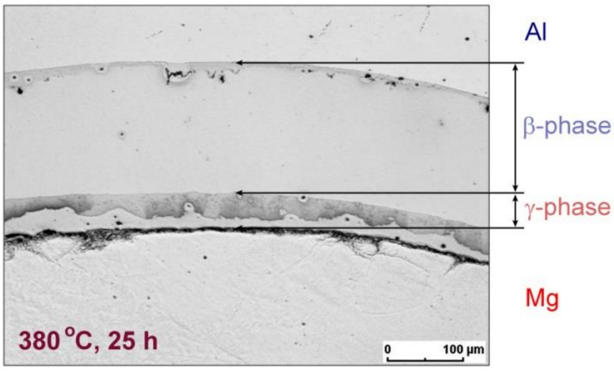

Figure 2. Micrograph of an annealed sample at 380^{o}C, for 25h.

The concentration profiles were obtained by the use of WDX EPMA analysis. The electron probe micro-analyzer used was JXA-8900. The measurement line was perpendicular with the diffusion zone and there were used 600 – 1200 measurement points, 0.5 – 1 µm apart.

Figure 3 shows the concentration profiles for two of our samples. It can be seen that a diffusion profile is established in the mixed crystal zone.

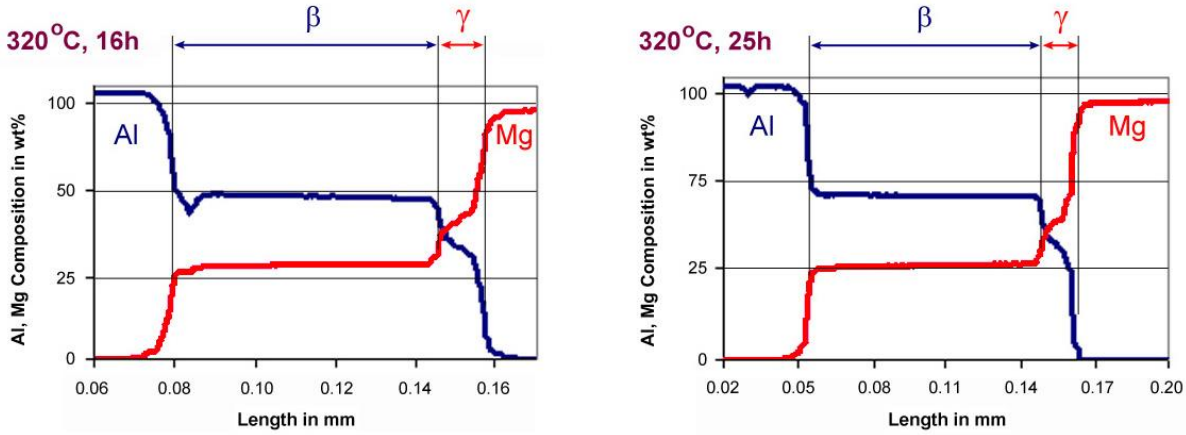

Figure 3. Concentration profiles of two annealed samples at 320^{o}C. The time was (left) 16h and (right) 25h.

The diffusion coefficients of Mg and Al in α- and δ-solid solutions respectively, were calculated using the second Fick's law, for independent concentration case [5].

In the case of a diffusion coefficient which is independent from the concentration, the Fick's second law can be written in the form, [5,8],

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

This equation has the form of a linear second-order partial differential equation for the concentration field $C(x,y,z,t)$. If boundary and initial conditions are properly selected, the solutions of this equation, can be written as [5,8],

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

The diffusion coefficient of Mg in α-solid solution was calculated using the slope of the straight line, which represent the dependence of $erf^{-1}(1\text{-}2c/c_0)$ versus x (Figure 4). The diffusion coefficients of Al in δ-solid solution was calculated in the same way.

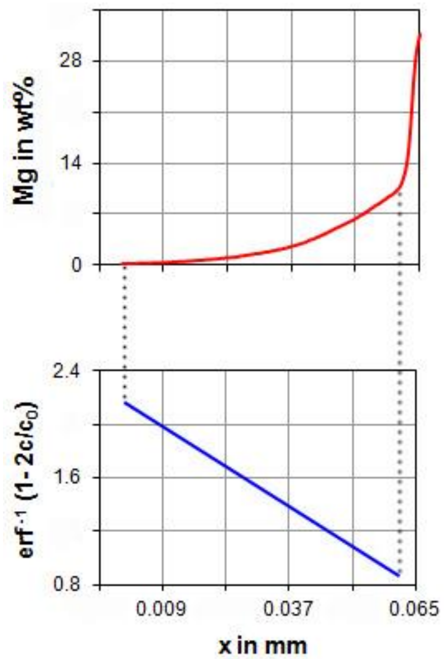

Figure 4. The concentration profile developed in the α -solid solution (up) and the straight line representing the plot of $erf^{-1}(1\text{-}2c/c_0)$ versus x (down).

The diffusion coefficients depends only on the temperature and not on the annealing time and therefore the diffusion coefficients were averaged for each temperature [10]. The results are listed in Table 1.

Table 1. **The average diffusion coefficients**

Temperature (^{o}C)	D_α^{Mg} (m^2/s)	D_δ^{Al} (m^2/s)
320	9.54×10^{-16}	2.36×10^{-16}
350	2.02×10^{-15}	6.16×10^{-16}
380	5.15×10^{-15}	8.26×10^{-16}

The diffusion coefficient follows an Arrhenius relationship [5,6,7,8,],

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

By getting the logarithms of both sides of the above equation, we end up in a liner equation.

The graphical representation of such an equation is shown in Figure 4.

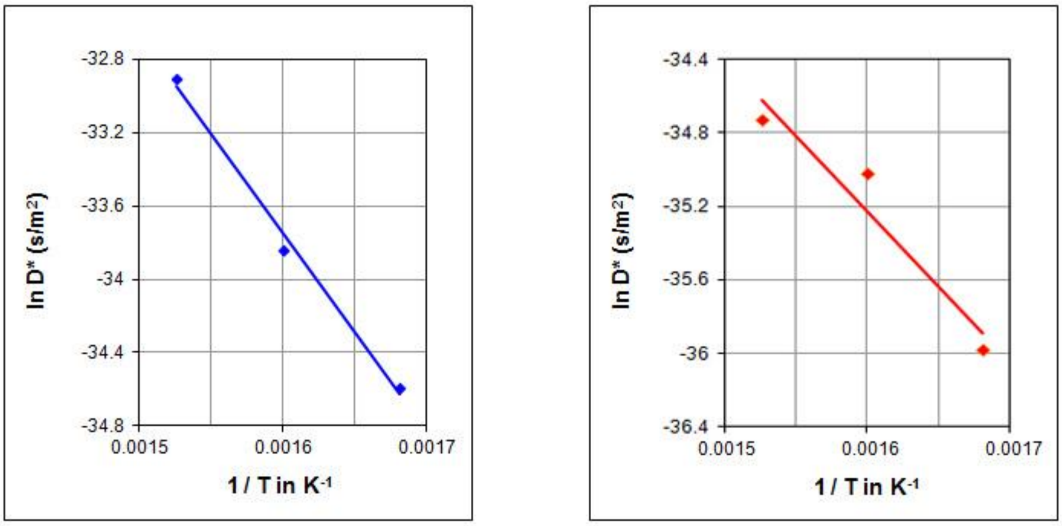

Figure 4. The plot of $\ln D_{\alpha}^{Mg}$ versus 1/*T* (left) and that of $\ln D_{\delta}^{Al}$ versus 1/*T* (right).

Table 2 shows the corresponding activation energies and the frequency factors, which were calculated based on the above mentioned Arrhenius relationship.

Table 2. **The activation energies and the frequency factor**

$Q(\alpha)$ [J/mol]	$D_0(\alpha)$ (m²/s)	$Q(\delta)$ [J/mol]	$D_0(\delta)$ (m²/s)
9.02×10^4	9.06×10^{-8}	6.77×10^4	2.41×10^{-10}

SUMMARY AND CONCLUSIONS

The diffusion couple prepared by pressing a Magnesium cylinder into a cylindrical hole of Aluminum offers very good possibilities in performing interdiffusion experiments.

By the use of light microscopy and EPMA analysis it was possible to detect the presence of β- and γ-phase according to the Mg-Al phase diagram along with the mixed crystal zone on either side of the diffusion zone.

EPMA analyses confirmed that a diffusion profile was also established in the mixed crystal regions.

The diffusion coefficients of Mg and Al in α- and δ-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 were 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 annealing temperature, enables the calculation of the corresponding activation energies and the frequency factor.

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