DIFUZÉ $^{65}$Zn VE DVOUFÁZOVÉ EUTEKTICKÉ SLITINĚ

Mg – 33 wt.% Al

$^{65}$Zn DIFFUSION IN A TWO-PHASE EUTECTIC Mg – 33 wt.% Al

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Abstract

Diffusion of zinc in a two-phase eutectic alloy Mg – 33 wt.% Al and in its components, Mg – Al solid solution and in the intermetallic compound Mg\textsubscript{$^{17}$}Al\textsubscript{12}, was studied. The measurement of Zn diffusion coefficient was carried out by radiotracer technique in temperature interval 498 – 848 K. Zinc is believed to simulate the migration behavior of magnesium. It was observed that the interphase boundaries do not act as short-circuit paths. The study of the stability of the eutectic structure enabled to estimate the mean specific energy of the (Mg)/Mg\textsubscript{$^{17}$}A\textsubscript{12} phase interface.

1. INTRODUCTION

Mg – Al two-phase alloys are frequently applied before all in the automotive industry [1]. The best known of them is AZ91 alloy. Since its mechanical strength originates prevailing in precipitation hardening caused by ordered cubic compound Mg\textsubscript{17}Al\textsubscript{12} (β-phase) as a strengthening phase, much effort has been devoted to find out mechanisms of precipitation and structure-property correlations [2].

In the present work, diffusion coefficient of zinc is measured in structurally stabilized eutectic Mg – 33 wt.% Al and in β-phase. Zinc is an alloying element added to AZ91 alloy for solution strengthening. Moreover, it can be considered as a plausible element that simulates well the diffusion behavior of both the elements Mg and Al that form the base of the alloy. An attempt is also made, to estimate the specific energy of (Mg)/β interface.

2. EXPERIMENTAL

2.1 Alloy preparation

Experimental alloys were prepared by induction melting in protective Ar atmosphere from pure Mg (3N8) and Al (5N). The eutectic Mg – 33 wt.% Al (henceforth referred to as alloy $E$) was cast in copper mould, however, in case of Mg\textsubscript{17}Al\textsubscript{12} intermetallic compound
(composition Mg – 45 wt.% Al; referred to as alloy I), special procedure had to be found. Due to extreme brittleness of I, casting and following careful controlled annealing was applied. The procedure enabled to prepare the ingots of I in sufficient size for machining the diffusion samples. After the special treatment, I was free of dangerous internal stresses, without micro pores and internal cracks that could act as paths of rapid diffusion and could spoil the results of diffusion experiments.

2.2 Structure of alloys

The alloys structure after casting is shown in Figs. 1 and 2. It can be seen that E consisted of prolonged cells of mean width about 20 µm filled with fine lamellae. The interlamellar distance was about 0.5 µm. Structure of alloy I consisted of radial grains (with longer axis of grains perpendicular to the axis of cylindrical ingot). The mean lateral size of radial grains was about 0.1 mm.

The ingots were stabilization annealed (693 K / 15 h) in silica ampoules filled with Ar. Whereas the structure of alloy I, does not changed after the treatment, in case of alloy E, it was observed that the original fine lamellar structure of alloy E grew coarse by the termination migration mechanism [3]. The direction of growing lamellae preserved during the growth; later the (Mg) phase coagulated and became discontinuous in continuous matrix of β-phase. The final mean thickness of (Mg) particles was 4 µm and their lateral mean distance
(perpendicular to the direction of original lamellae) was about 10 \( \mu \text{m} \) – see Fig. 3.

It is known that there is orientation relationship between the both lattices in the two-phase Mg-Al alloys (see, e.g., in [4-8]). In the eutectic alloy \( E \), the selected area diffraction (SAD) revealed following orientation relationship between \( \beta \)-phase matrix and coherent (Mg) precipitates – see in Figs. 4 and 5:

\[
[211]_\beta \parallel [1 \bar{1} 0 0]_\text{Mg}
\]

and
\[
(0 \bar{1} 1)_\beta \parallel (0001)_\text{Mg}.
\]

It means that prevailing fraction of the total area of interface between the two phases in the alloy \( E \) has a relatively high degree of coherence.

Further trial anneals with two samples of alloys \( E \) and \( I \) that simulated the diffusion measurements have proved that the structure was well stable for the planned diffusion experiments.

2.3 Diffusion measurement

The diffusion samples of the coin-like form with diameter 10 mm and height 4 mm were machined of annealed ingots. In the case of alloy \( I \), very careful grinding had to be applied to prevent the brittle damage of the sample. One of the front bases was metallographically polished (mechanical grinding on metallographic papers and polishing with OP-S suspension).

Zinc diffusion measurement was carried out using serial sectioning and residual activity method. For detail see in [9].

3. RESULTS AND DISCUSSION

3.1 Serial sectioning method

The relative concentration \( c(x,t) \) can be directly obtained by this method [10]. Examples of measured profiles in co-ordinate \( \log c \) vs. \( x^2 \) are shown in Fig. 6. Diffusion coefficient \( D \) was obtained as a fitting parameter using the known thin film solution [11]

\[
c(x,t) = \frac{M k}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right),
\]

where \( M \) stands for surface density of diffusant at time \( t = 0 \) and \( k \) is proportionality constant between the concentration and the radioactivity. The values of \( D \) are summarized in Table 1.

3.2 Residual activity method

Residual radioactivity \( I_r \) of the sample after the removing of \( n \) layers of total thickness \( x_n \) is measured

\[
I_r(x_n,t) = \int_{x_n}^{\infty} c(\xi,t) \exp\left[-\mu (\xi - x_n)\right] d\xi,
\]

where \( \mu \) is attenuation coefficient. Fitting of Eq. (3) to experimental profiles \( I_r(x_n,t) \) with \( c \) according to Eq. (2) was done with the help of TableCurve optimization package. Examples of measured profiles are shown in Fig. 7 and fitted diffusion coefficients \( D \) are summarized in Table 1. Arrhenius diagram of zinc diffusion coefficients in alloys \( E \) and \( I \) is shown in Fig. 8.
Table 1. $^{65}$Zn diffusion coefficients. Average experimental error of $D$'s is about 5.4%.

<table>
<thead>
<tr>
<th>$T$(K) / $t$ (ks)</th>
<th>Method$^1$</th>
<th>Alloy I</th>
<th>Alloy E</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D$</td>
<td>$D_{ef}$</td>
<td>$D_{b}$</td>
</tr>
<tr>
<td></td>
<td>($10^{-15}$ m$^2$ s$^{-1}$)</td>
<td>($10^{-15}$ m$^2$ s$^{-1}$)</td>
<td>($10^{-13}$ m$^2$ s$^{-1}$)</td>
</tr>
<tr>
<td>698 / 176</td>
<td>S</td>
<td>47.6</td>
<td>62.5</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>48.4</td>
<td>72.3</td>
</tr>
<tr>
<td>673 / 259</td>
<td>S</td>
<td>15.6</td>
<td>24.0</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>15.0</td>
<td>25.2</td>
</tr>
<tr>
<td>648 / 504</td>
<td>S</td>
<td>4.39</td>
<td>8.46</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>4.20</td>
<td>8.64</td>
</tr>
<tr>
<td>623 / 864</td>
<td>S</td>
<td>1.97</td>
<td>4.29</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>1.69</td>
<td>4.40</td>
</tr>
<tr>
<td>598 / 865</td>
<td>S</td>
<td></td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>0.555</td>
<td>1.20</td>
</tr>
</tbody>
</table>

$^1$S – serial sectioning method, R – residual activity method
$^2$calculated according to [16]
$^3$kinetics EF – effective diffusion in two-phase alloy [15], AB – transition regime between type-A and type-B kinetics [16]

3.3 Diffusion in two-phase media

It should be noted at the beginning that there is no mathematical evidence that there is something like effective characteristic of heterogeneous media. As a matter of fact, however, there is huge number of experimental evidences that the heterogeneous media behaves as being homogeneous with some effective characteristic. Relations for calculating effective diffusivity in heterogeneous isotropic media are summarized in [12]. It is known that effective diffusion coefficient $D_{ef}$ in a two-phase alloy consisting of volume fractions $f_I$ and $f_{Mg}$ of phases with diffusivities $D_I$ and $D_{Mg}$, respectively, should lie in the interval given by inequality

$$\frac{D_I D_{Mg}}{D_I f_{Mg} + D_{Mg} f_I} \leq D_{ef} \leq D_I f_I + D_{Mg} f_{Mg}.$$  \hspace{1cm} (4)

More narrow bounds of possible values of $D_{ef}$ were derived in [13]

$$D_{Mg} + \frac{1}{D_I - D_{Mg}} + \frac{f_I}{3 D_{Mg}} \leq D_{ef} \leq D_I + \frac{1}{D_{Mg} - D_I} + \frac{f_I}{3 D_I}.$$  \hspace{1cm} (5)

The indeterminacy of $D_{ef}$ is an inherent property of random heterogeneous media resulting from the fact that generally nothing is known about the media but the fractions $f_I$ and $f_{Mg}$. It cannot be reduced without additional topologic information. The authors have shown that inequality (5) expresses maximum information about the $D_{ef}$ one can achieve only in terms of $f_I$ and $f_{Mg}$.

In Fig. 9, effective diffusion coefficients of $^{65}$Zn in E are plotted together with bounds calculated from Eqs. (4) and (5). For Zn diffusion coefficient in alloy Mg$_{17}$Al$_{12}$, values obtained in this work for alloy $I$ were taken

$$D_I = (1.7 \pm 1.1) \times 10^{-2} \exp \left[ - \frac{(155.0 \pm 5.6) \text{ kJ mol}^{-1}}{RT} \right] \text{ m}^2 \text{s}^{-1},$$ \hspace{1cm} (6)

and for Zn diffusion coefficients in (Mg) phase values calculated from equation [14]
were used. Aluminum solubility limit $c_{\text{Al}}$ (in wt.% Al) and volume fractions $f_i$ and $f_{\text{Mg}}$ at respective diffusion temperatures were estimated from equilibrium phase diagram Mg-Al [14]. It can be seen in Fig. 9 that calculated values of $D_{\text{ef}}$ fall well between the theoretical bounds defined by Eqs. (4) and (5) at three higher diffusion temperatures (marked as EF in Table 1). In this temperature interval, effective diffusion coefficient is well defined [15] and its temperature dependence can be written as

$$D_{\text{ef}} = \left(2.7 \pm ^{3.0}_{1.4}\right) \times 10^{-2} \exp \left[-\frac{(155.1 \pm 4.2) \text{ kJ mol}^{-1}}{RT}\right] \text{ m}^2 \text{ s}^{-1}. \tag{8}$$

At temperatures $T < 648$ K, values of $D_{\text{ef}}$ are higher than expected ones; they are even out of
the rough limits given by Eq. (4). This is, most likely caused by diffusion along interphase boundaries.

### 3.4 Diffusion along interphase boundaries

The fact that values of \( D_{\text{ef}} \) obtained at two lowest diffusion temperatures \( T = 598 \) K and \( T = 623 \) K fall above the upper theoretical bound (see Fig. 9) indicates that short-circuit diffusion along the (Mg)/\( \beta \) interphase boundaries should be considered. At these temperatures, the mean diffusion path in \( \beta \)-phase is very close to mean distance between the laths in alloy \( E \), and hence, it is obvious that the evaluation of diffusion profiles can be done neither within type-A nor type-B kinetics [15].

The transition type-AB kinetics was studied numerically in paper [16]. It was found by Monte Carlo method that the penetration profile is approximately linear in co-ordinates \( \ln c \) vs. \( x^{1.5} \) in such a case and the slope can be used for estimation of interface diffusion coefficient \( D_b \) from relation

\[
D_b \approx 16.48 \frac{D^{0.1}}{\delta^{0.2}} t^{0.9} \left( \frac{\partial \ln c}{\partial x^{1.5}} \right)^{4/3}.
\] (9)

In paper [16], Eq. (9) was derived for the grain boundary diffusion in one-phase polycrystal without grain boundary segregation. However, one can expect that it can be well applied also in the present case: The dependence of \( D_b \) on volume diffusion coefficient \( D \) and on boundary width \( \delta \) is very weak and, hence, a single value calculated as a mean of both diffusion coefficients \( D = (D_I + D_{Mg})/2 \) can well serve as an acceptable approximation of effective bulk diffusion coefficient \( D \) that characterizes the leakage from the interphase boundary. Analogous reasoning applies for the thickness of the interphase boundary that can be approximated by the value \( \delta \approx 5 \times 10^{-10} \) m recommended in [15] for grain boundaries. Further, negligible segregation of Zn to interphase boundaries can be expected if we consider relatively good solubility of Zn in the Mg-Al alloy [27].

In Fig. 10, it can be seen that the penetration profiles obtained by serial sectioning method are reasonably well linear in co-ordinates \( \ln c \) vs. \( x^{1.5} \) in accordance with the conclusions drawn in [16] for the type-AB kinetics. The fit of Eq. (3) with \( c \sim \exp(-Ax^{1.5}) \) to profiles measured by residual activity method is shown in Fig. 11. The slopes of straight lines in Fig. 11 and fit parameters \( A \) in case of residual activity method were used to evaluation of \( D_b \) from Eq. (9). Results are listed in Table 1.

![Fig.10](image1.png)

Fig.10. Penetration profiles of \(^{65}\text{Zn}\) in alloy \( E \) measured at two lower temperatures, plotted in coordinates \( \ln c \) vs. \( x^{1.5} \); serial sectioning method.

![Fig.11](image2.png)

Fig.11. Penetration profiles of \(^{65}\text{Zn}\) in alloy \( E \) measured at two lower temperatures, plotted in coordinates \( \ln c \) vs. \( x^{1.5} \); residual activity method.
It can be seen in Fig. 8 that the activation enthalpies of effective bulk diffusion $Q_{\text{ef}}$ (155 ± 4.2 kJ mol$^{-1}$) and interphase diffusion $Q_b$ (158 ± 10 kJ mol$^{-1}$) are the same in frame of experimental error. Using the semi-quantitative relation between $Q_{\text{ef}}$ and $Q_b$ [18]

$$Q_b = Q_{\text{ef}} - N_A \alpha' \gamma a^2,$$

(10)

where $N_A$, $\alpha'$, $\gamma$ and $a$ are Avogadro’s constant, structure parameter (close to 2 for vacancy diffusion mechanism), specific interphase boundary energy and jump distance, respectively, it can be expected that the value of $\gamma$ is very low for the (Mg)/$\beta$ interface.

3.5 Estimation of specific interphase boundary energy $\gamma$

Specific (Mg)/$\beta$ interphase boundary energy $\gamma$ is a very important parameter that enters the nucleation and growth rate [3] of strengthening $\beta$-phase. The time dependence of mean interlamellar distance $d$ was measured during the isothermal anneal performed at one chosen temperature $T = 613$ K – see Fig. 12. Let us presume that the time development of $d$ can be described by expression [18]

$$d^n = d_0^n + \alpha G t,$$

(11)

where $d_0$ is the value of $d$ at time $t = 0$, $G$ is the parameter of appropriate mass transport process, $\alpha$ is a dimensionless parameter which depends on the phase geometry and the scaling exponent $n$ takes values between 1 and 4. Fitting Eq. (11) leads to $n \approx 3$, which is a value indicating that the coarsening is a process controlled by volume diffusion [18]. In such a case, for plate-like precipitates the value of $\alpha \approx 2400$ (mean value estimated from optical micrographs according to theory in [19]) and $G$ can be written as [19]

$$G = \frac{f \gamma V_m}{2 p RT} D.$$

(12)

In Eq. (12), $f$ is a function of chemical composition of the both phases $f = c_{\text{Mg}}(1 - c_{\beta})/(c_{\text{Mg}} - c_{\beta})^2$, $V_m$ is molar volume, and $p$, $R$, and $T$ are parameter tending to $\pi$, gas constant and absolute temperature respectively. $D$ is diffusion coefficient characterizing the atom migration process that controls the particle growth. Fitting Eq. (11) to $d$’s measured at $T = 613$ K and taking $f = f(T)$ from equilibrium phase diagram, $V_m = 1.3 \times 10^{-5}$ m$^3$, $p \approx \pi$, and $D = \min (D_h, D_{\text{Mg}}) = D_h$, value $\gamma \approx 140$ mJ m$^{-2}$ can be obtained. This is much smaller than literature values of specific grain boundary energy $\gamma_b$ (270 – 400 mJ m$^{-2}$ [20]). However, it explains reasonably the observed grain boundary wetting in alloy $E$ (Fig. 13) where the relation $\gamma_b \geq 2 \gamma$ should be fulfilled [21]. It can be also noted that the value of $\gamma \approx 140$ mJ m$^{-2}$ obtained in the present
paper agrees reasonably with the value $\gamma = 114 \text{ mJ m}^{-2}$ reported in [31] for the nucleation stage of $\beta$ precipitation in (Mg) matrix. Further, the value of $\gamma \approx 140 \text{ mJ m}^{-2}$ gives relatively small difference between the activation enthalpies of volume and boundary diffusion ($Q_{ef} - Q_b \approx 7 \text{ kJ mol}^{-1}$), from Eq. (10) which is less than experimental error of the difference in activation enthalpies $Q_{ef}$ and $Q_b$ obtained in the present diffusion experiment.

4. SUMMARY

Coefficient of $^{65}$Zn heterodiffusion in Mg$_{17}$Al$_{12}$ intermetallic and effective diffusion coefficient of $^{65}$Zn in stabilized (693 K/15 h) eutectic Mg – 33 wt.\% Al was measured in the temperature region 598 – 698 K using serial sectioning and residual activity methods. Zn diffusion coefficients in the interphase boundaries of the eutectic alloy, $D_b$, were estimated at two lower temperatures. An attempt was made to assess the value of specific interphase boundary, $\gamma$. Obtained value of $\gamma$ is about one half of known values of specific grain boundary energy, which explains the solid state wetting observed in the present work in alloy E.

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