

# Grain boundary diffusion of Ge in Mg and Mg-Al solid solution

J. Čermák<sup>1</sup>, I. Stloukal<sup>1\*</sup>, D. Eversheim<sup>2</sup>

<sup>1</sup>*Institute of Physics of Materials AS CR, Žižkova 22, CZ-61662 Brno, Czech Republic*

<sup>2</sup>*Helmholtz-Institut für Strahlen- und Kernphysik Universität Bonn, Nussallee 14–16, D-53115 Bonn, Germany*

Received 30 November 2005, accepted 20 January 2006

## Abstract

Diffusion characteristics of Ge in Mg and Mg-1.8wt.%Al alloy were studied. The measurement was carried out by serial sectioning and by residual activity methods in temperature interval 448–848 K. Due to extremely low bulk solubility, Ge diffusion occurs almost exclusively in grain boundaries (GB's). Hence, Ge diffusion coefficient  $D_b$  in GB's was directly evaluated at higher temperatures, whereas triple product  $P = D_b s \delta$  ( $s$ ,  $\delta$  – segregation factor and GB thickness, respectively) was measured in low-temperature region. Obtained values of  $D_b$  and  $P$  enabled to make a rough estimation of segregation factor  $s$  of Ge to GB's.

**Key words:** magnesium alloys, diffusion, grain boundaries, interface segregation

## 1. Introduction

Magnesium is a base of a wide variety of light commercial alloys that attract a constant attention of both applied [1] and basic research [2–6]. They are often precipitation strengthened by alloying the base with certain elements that form very stable intermetallic particles. For example, Tl, Ag, Ce and Sn form AB-type compounds with cubic lattice, Cu, Zn and Ni form fcc or hcp Laves phases and Si and Sn form fcc AB<sub>2</sub>-type compounds. Some of these elements show very low solubility (e.g., rare earth elements, Si, Tl), which may impart certain peculiar features to their diffusion in a polycrystalline alloy.

In the present paper, the diffusion of Ge in Mg and in Mg-1.8wt.%Al alloy is studied, which simulates the behaviour of extremely low-soluble elements (in Mg and in Mg-Al-based family of alloys [1, 7]).

## 2. Experimental

Experimental samples were machined from pure Mg (3N8) and from an alloy Mg-1.8wt.%Al (purity of Al – 5N), which was prepared by induction melting in Ar protective atmosphere. The mean grain

size of Mg and Mg-1.8wt.%Al alloy was about 1 mm and 0.2 mm, respectively. Samples were ground with metallographic papers and polished with OP-S suspension.

The nuclide <sup>68</sup>Ge was dripped on the polished sample surfaces in a form of 0.5M HCl solution of <sup>68</sup>Ge carrier (GeCl<sub>4</sub>; specific activity 18 GBq·mg<sup>-1</sup> of Ge) and dried by an infra-lamp.

The samples were wrapped in Ta foil and sealed together with Zr splinters in silica tubes under the protective gas atmosphere (Ar or a mixture Ar + 3 vol.% Cl<sub>2</sub>) at pressure slightly below the atmospheric pressure. For temperatures and diffusion times see Tables 1–4. The gas mixture Ar + Cl<sub>2</sub> suppresses the growth of oxides; hence, the measurement with the two annealing gas atmospheres gives the possibility to assess the effect of residual oxygen upon the diffusion characteristics.

The diffusion anneals were done at temperatures between 448 K and 848 K in horizontal furnaces; diffusion temperatures were stabilized within ± 1 K.

Diffusion measurement was carried out by residual activity (R) and serial sectioning (S) methods. The layers were taken-off by precise grinding and the relative concentration of diffusant was measured by low-level  $\alpha/\beta/\gamma$  counter CANBERRA 2400.

---

\*Corresponding author: tel.: +420 539 220 424; fax: +420 541 218 657; e-mail address: stloukal@ipm.cz

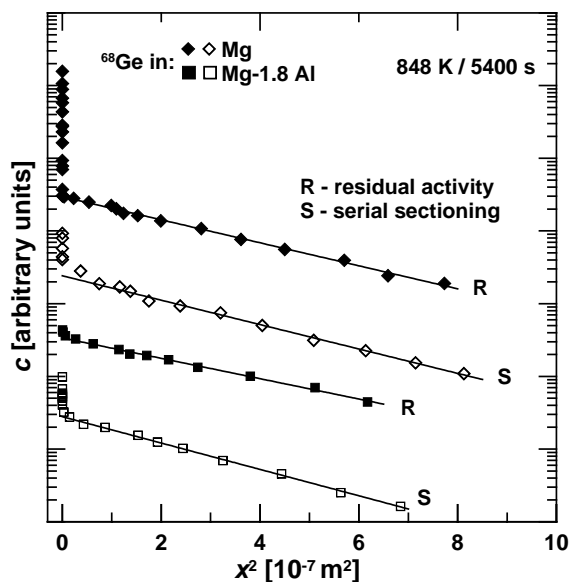


Fig. 1. Examples of penetration profiles of  $^{68}\text{Ge}$  in Mg (diamonds) and in Mg-1.8wt.%Al alloy (squares) obtained at higher temperatures.

### 3. Results and discussions

The penetration profiles  $c(x, t)$  ( $c$  – average relative concentration of Ge,  $x$  – penetration depth and  $t$  – diffusion time) are the primary experimental data. It was observed that the profiles consisted of surface hold-up, which was followed by a segment linear in co-ordinates  $\log c$  vs.  $x^2$  – see Fig. 1. At lower temperatures, the concentration tail linear in co-ordinates  $\log c$  vs.  $x^{6/5}$  was also observed – see Fig. 2.

#### 3.1. Near-surface parts of penetration profiles

Values of diffusion coefficient,  $D$ , obtained by fitting equation [8]

$$c(x, t) = \frac{M}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \quad (1)$$

to respective segments of measured profiles  $c(x, t)$  are listed in Tables 1 and 2. In Eq. (1),  $M$  stands for surface concentration of diffusant in time  $t = 0$ . As it can be seen in Fig. 3, the calculated  $D$ 's at highest temperatures (fitted by the full line) are close to values of  $D$  for  $^{71}\text{Ge}$  reported in our previous work [9], where the nuclide  $^{71}\text{Ge}$  was deposited by ion implantation technique.  $D$ 's for diffusion in Mg-1.8wt.%Al alloy follow the Arrhenius equation

$$D = (3.6_{-2.7}^{+11}) \times 10^{-5} \times \exp\left[-\frac{(104.9 \pm 8.8) \text{ kJ} \cdot \text{mol}^{-1}}{RT}\right] \text{ m}^2 \cdot \text{s}^{-1}. \quad (2)$$

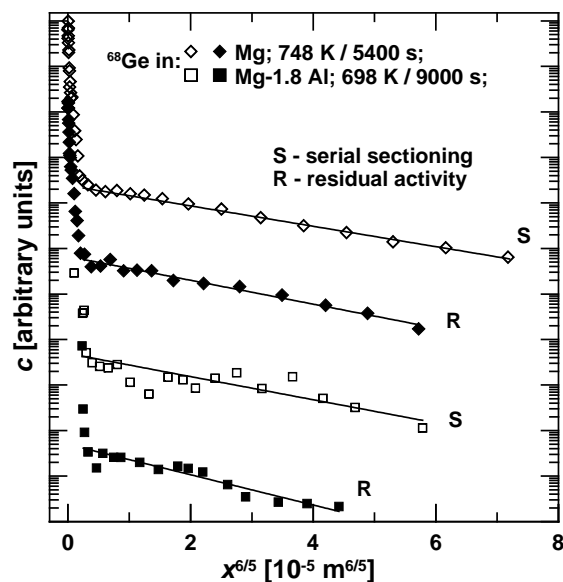


Fig. 2. Examples of penetration profiles of  $^{68}\text{Ge}$  in Mg (diamonds) and in alloy Mg-1.8wt.%Al (squares) obtained at lower temperatures.

Table 1. Diffusion coefficients  $D$  of  $^{68}\text{Ge}$  in Mg-1.8wt.%Al

$T$ [K]	$t$ [ $10^3$ s]	$D$ [ $\text{m}^2 \cdot \text{s}^{-1}$ ]	Method	Protective atmosphere	Mode
848	5.4	$1.4 \times 10^{-11}$	R	Ar + Cl <sub>2</sub>	$D_b$
		$1.1 \times 10^{-11}$	S		
798	585.7	$5.4 \times 10^{-12}$	R	Ar	$D_b$
		$5.1 \times 10^{-12}$	S		
748	5.4	$1.4 \times 10^{-12}$	R	Ar + Cl <sub>2</sub>	$D_b$
		$1.4 \times 10^{-12}$	R		
		$1.7 \times 10^{-12}$	S		
		$1.6 \times 10^{-12}$	S		
698	9.0	$3.3 \times 10^{-13}$	R	Ar + Cl <sub>2</sub>	$D_b$
		$9.2 \times 10^{-13}$	S		
648	14.4	$5.9 \times 10^{-15}$	R	Ar + Cl <sub>2</sub>	$D_{ef}$
		$2.5 \times 10^{-15}$	S		
548	50.4	$2.5 \times 10^{-18}$	R	Ar + Cl <sub>2</sub>	$D_{ef}$

It can be also seen in Fig. 3 that the values of  $D$  obtained both for  $^{68}\text{Ge}$  and  $^{71}\text{Ge}$  at higher temperatures are significantly greater than values that could be expected if the known bulk diffusivities of various non-transition elements (reported in [10]) are extrapolated to low temperatures. These are limited by dotted lines  $D_{\min}$  and  $D_{\max}$  in Fig. 3. This suggests that the values of  $D$  obtained in the present paper from Eq.

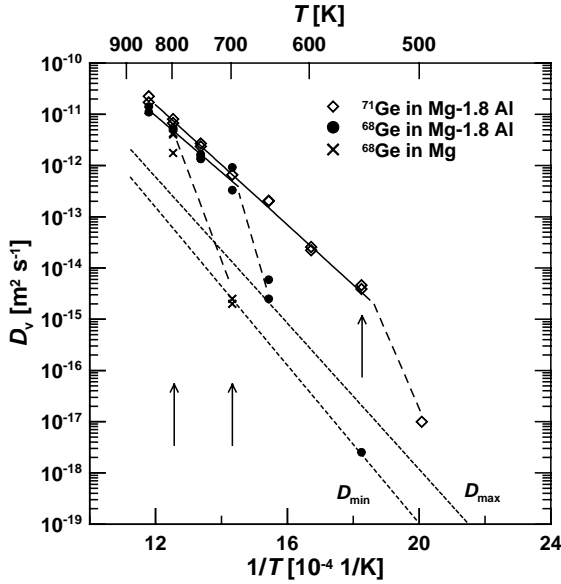


Fig. 3. Arrhenius diagram of measured diffusion coefficients  $D$ . Data for  $^{71}\text{Ge}$  taken from [9].

Table 2. Diffusion coefficients  $D$  of  $^{68}\text{Ge}$  in Mg

$T$ [K]	$t$ [ $10^3$ s]	$D$ [ $\text{m}^2 \cdot \text{s}^{-1}$ ]	Method	Protective atmosphere	Mode
848	5.4	$1.2 \times 10^{-11}$	R	Ar + Cl <sub>2</sub>	$D_b$
		$1.2 \times 10^{-11}$	S		
798	585.7	$1.8 \times 10^{-12}$	S	Ar + Cl <sub>2</sub>	$D_b$
798	5.4	$4.3 \times 10^{-12}$	R	Ar	$D_b$
		$4.0 \times 10^{-12}$	S		
698	9.0	$2.0 \times 10^{-15}$	R	Ar + Cl <sub>2</sub>	$D_{ef}$
		$2.5 \times 10^{-15}$	S		

(1) are effective diffusion coefficients,  $D_{ef}$ , that can be expressed as a combination of diffusion coefficients in GB's,  $D_b$  and in the bulk,  $D_v$  (Hart's mixing rule [11]):

$$D \cong D_{ef} = \tau D_b + (1 - \tau) D_v. \quad (3)$$

In Eq. (3),  $\tau$  denotes the relative mean time spent by the diffusing atom during the random walking *in* GB's (often replaced by the volume fraction of GB's,  $f$ ). For the strong segregating diffusant,  $\tau$  can be approximated by the following relation [12]

$$\tau = \frac{sf}{1 - f + sf}. \quad (4)$$

Hence, if the segregation factor  $s = c_b/c_{g0}$  ( $c_b$ ,  $c_{g0}$  – concentration in GB and in the grain close to

GB, respectively) is high enough, it can be easily seen that  $\tau$  goes to unity, and, at the same time,  $D_{ef}$  approaches the value of diffusion coefficient in GB (mode  $D_b$  in Tables 1, 2). At lower temperatures in turn, the mean diffusion path  $\sqrt{D_v t}$  is sufficiently small compared to the mean grain size  $L$  and the approximation  $\tau \cong 1$  does not hold more.  $D_{ef}$  decreases towards bulk diffusion coefficient  $D_v$ , which is schematically indicated by dashed lines in Fig. 3 and marked as a mode  $D_{ef}$  in Tables 1, 2. The break point between the  $D_b$  and  $D_{ef}$  modes (arrows in Fig. 3) varies before all with  $L$  (which caused observed difference between diffusion behaviour of Ge in Mg compared to that in Mg-1.8wt.%Al), and with the stopping effect of oxide *plugs* in entries of GB's at the free surface (GB's are easy accessible for  $^{71}\text{Ge}$  that was implanted *below* the surface than for the  $^{68}\text{Ge}$  that was dripped-and-dried).

### 3.2. GB diffusivity

Triple product  $P = s\delta D_b$  was evaluated from the slope of the flat tails of  $c(x, t)$  measured at lower temperatures using LeClaire's analysis of GB diffusion in type-B kinetics [13]. Since the penetration profiles measured in the present work provide no information on Ge *volume* diffusion, the  $D_v$ 's for In diffusion were used for the evaluation of the present data. Volume diffusion coefficients of In are very close to those of Sn [10] and, hence, it may be believed that it simulates quite well the diffusion behaviour of Ge, which is in the same group. Similar idea – simulation of Al volume diffusion by that of In – was proposed, e.g., in [14]. Using  $D_v$ 's reported in [15] ( $D_0 = 1.75 \times 10^{-4} \text{ m}^2/\text{s}$ ;  $Q_v = 143 \text{ kJ} \cdot \text{mol}^{-1}$ ), the triple product  $P$  was calculated from equation

$$P = p D_v^q t^{-r} \left( -\frac{\partial \ln c}{\partial x^{6/5}} \right)^{-u}. \quad (5)$$

Constants  $p$ ,  $q$ ,  $r$  and  $u$  are positive numbers known from the theory [13], the derivative is taken in the concentration tail (at great depths  $x$ ), where  $c$  is well linear in co-ordinates  $\ln c$  vs.  $x^{6/5}$ . The results are listed in Tables 3, 4. It can be seen that leakage parameter

$$\beta = \frac{P}{2D_v \sqrt{D_v t}} \quad (6)$$

is well above the unity in all the cases, which is the principal condition of type-B kinetics [13]. The temperature dependence of  $P$  can be described by Arrhenius equation (see in Fig. 4)

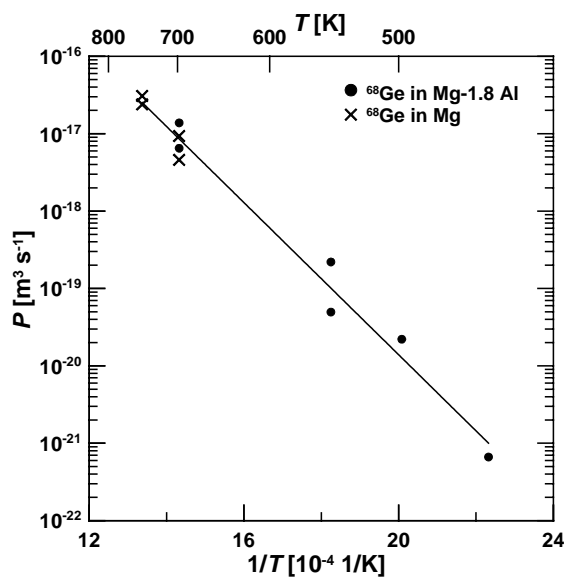
$$P = (1.4_{-0.9}^{+2.4}) \times 10^{-10} \times \exp \left[ -\frac{(95.8 \pm 4.6) \text{ kJ} \cdot \text{mol}^{-1}}{RT} \right] \text{ m}^3 \cdot \text{s}^{-1}. \quad (7)$$

Table 3. Characteristics of GB diffusion of  $^{68}\text{Ge}$  in Mg-1.8wt.%Al and segregation coefficient  $s$  to GB's

$T$ [K]	$t$ [ $10^3$ s]	$P$ [ $\text{m}^3\cdot\text{s}$ ]	$\beta$	$s$	Method	Protective atmosphere
698	9.0	$6.5 \times 10^{-18}$ $1.4 \times 10^{-17}$	166 354	$2.6 \times 10^4$ $5.4 \times 10^4$	R S	Ar + Cl <sub>2</sub>
548	50.4	$5.0 \times 10^{-20}$ $2.2 \times 10^{-19}$	13400 60100	$2.8 \times 10^4$ $1.2 \times 10^5$	R S	Ar + Cl <sub>2</sub>
498	198.6	$2.2 \times 10^{-20}$	338000	$1.2 \times 10^5$	R	Ar
448	1196	$6.5 \times 10^{-22}$	1320000	$6.2 \times 10^4$	S	Ar + Cl <sub>2</sub>

Table 4. Characteristics of GB diffusion of  $^{68}\text{Ge}$  in Mg and segregation coefficient  $s$  to GB's

$T$ [K]	$t$ [ $10^3$ s]	$P$ [ $\text{m}^3\cdot\text{s}$ ]	$\beta$	$s$	Method	Protective atmosphere
748	5.4	$2.4 \times 10^{-17}$ $3.1 \times 10^{-17}$	67 86	$2.8 \times 10^4$ $3.6 \times 10^4$	R S	Ar + Cl <sub>2</sub>
698	9.0	$4.6 \times 10^{-18}$ $9.3 \times 10^{-18}$	118 239	$1.8 \times 10^4$ $3.7 \times 10^4$	R S	Ar + Cl <sub>2</sub>

Fig. 4. Arrhenius diagram of GB diffusion of  $^{68}\text{Ge}$  in Mg (crosses) and in Mg-1.8wt.%Al (full points).

### 3.3. Estimation of segregation factor

The segregation factor  $s$  can be calculated from the relation  $s = P/\delta D_b$  using Eqs. (2), (7) and commonly accepted value of GB width  $\delta = 5 \times 10^{-10}$  m [13]. The results are listed in Tables 3, 4 and they are shown in

Fig. 5. Despite of a considerable amount of scatters, the temperature dependence of  $s$  can be described by the relation

$$s = (5.4_{-3.3}^{+8.2}) \times 10^3 \exp \left[ \frac{(10.6 \pm 4.6) \text{ kJ} \cdot \text{mol}^{-1}}{RT} \right], \quad (8)$$

(see the full straight line in Fig. 5). The obtained segregation enthalpy  $Q_s \cong -10.6 \text{ kJ} \cdot \text{mol}^{-1}$  agrees reasonably with typical values of equilibrium enhancement factors expected in the literature for other materials [16, 17] (between  $-20$  and  $-8 \text{ kJ/mol}$ ).

It can be noted that the ratio  $Q_P/Q_V = 0.66$  ( $Q_P$ ,  $Q_V$  – activation enthalpies of grain boundary and volume diffusion, respectively) seems to be quite reasonable (for activation enthalpy of volume diffusion, the value for In in Mg,  $Q = 143 \text{ kJ} \cdot \text{mol}^{-1}$ , can be taken).

## 4. Summary

Extremely low solubility of Ge in Mg and in Mg-1.8wt.%Al alloy gave a possibility to measure the diffusion coefficient,  $D_b$ , in grain boundaries. Together with triple products,  $P$ , measured at lower temperatures, the values of  $D_b$  enabled to make a rough estimation of segregation factor  $s$ . It was found that the Ge enrichment of GB's was of the order  $10^4$ – $10^5$ .

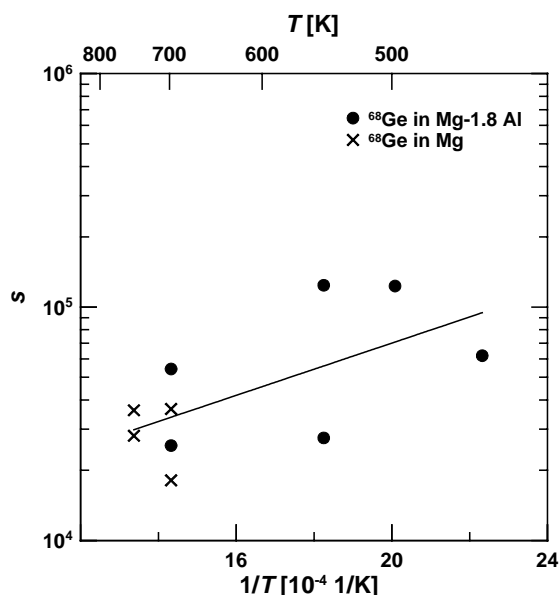


Fig. 5. Temperature dependence of segregation factor of Ge in Mg (crosses) and in Mg-1.8wt.%Al (full points).

#### Acknowledgements

The work was supported by the Czech Academy of Sciences – number of the projects S2041105 and AV0Z20410507 and GACR 106/03/1355.

#### References

[1] AVEDESIAN, M.—BAKER, H.: Magnesium and Magnesium Alloys. ASM Materials Park, OH 1999.

- [2] TROJANOVÁ, Z.: Kovove Mater., 43, 2005, p. 182.  
 [3] TROJANOVÁ, Z.—LUKÁČ, P.: Kovove Mater., 43, 2005, p. 73.  
 [4] MILIČKA, K.—DOBEŠ, F.: Kovove Mater., 43, 2005, p. 45.  
 [5] PAHUTOVÁ, M.—SKLENIČKA, V.—KUCHAŘOVÁ, K.—SVOBODA, M.—LANGDON, T. G.: Kovove Mater., 43, 2005, p. 34.  
 [6] JAGER, A.—LUKÁČ, P.—GARTNEROVÁ, V.: Kovove Mater., 42, 2004, p. 165.  
 [7] MASSALSKI, T. B.: Binary Alloy Phase Diagrams. ASM International, ASM/NIST 1996, CD-ROM.  
 [8] CRANK, J.: Mathematics of Diffusion. Oxford, Clarendon Press 1957.  
 [9] ČERMÁK, J.—EVERSHEIM, P. D.—ROTHOVÁ, V.—STLOUKAL, I.: In: Proceedings 14<sup>th</sup> International Metallurgical and Materials Conference METAL 2005. TANGER Ltd. 2005, CD-ROM.  
 [10] NONAKA, K.—SAKAZAWA, T.—NAKAJIMA, H.: Mater. Trans. JIM, 36, 1995, p. 1463.  
 [11] HART, E. W.: Acta Met., 5, 1957, p. 597.  
 [12] DIVINSKI, S. V.—HISKER, F.—KANG, Y.-S.—LEE, J.-S.—HERZIG, Chr.: Acta Mater., 52, 2004, p. 631.  
 [13] KAUR, I.—GUST, W.: Fundamentals of Grain and Interphase Boundary Diffusion. Stuttgart, Ziegler Press 1988.  
 [14] MEHRER, H.—EGGERSMANN, M.—GUDE, A.—SALAMON, M.—SEPIOL, B.: Mater. Sci. Eng. A, 239–240, 1997, p. 889.  
 [15] COMBRONDE, J.—BREBEC, G.: Acta Met., 20, 1972, p. 37.  
 [16] LEJČEK, P.—HOFMANN, S.: Critical Rev. in Solid State and Mater. Sci., 20, 1995, p. 1.  
 [17] HOWE, J. M.: Interfaces in Materials. New York, Chichester, Weinheim, Brisbane, Singapore, Toronto, John Wiley & Sons Inc. 1997.