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THE EMF MEASUREMENTS IN THE Al-Mg SYSTEM

BADANIA SIŁ ELEKTROMOTORYCZNYCH W UKŁADZIE Al-Mg

Having several industrial applications the Al-Mg alloys were investigated in solid state. The EMF technique with a liquid electrolyte was applied to obtain thermodynamic properties in one-phase and two-phase regions in central part of the system. Measurements were performed in two manners: 1° for constant magnesium concentration $X(\mathrm{Mg}) = 0.410$ and 0.475 and different temperatures, changing from $T = 663$ to 920 K, and 2° for constant temperature $T = 673$; 698 and 703 K, when the concentration of the alloy in the cell was changed $X(\mathrm{Mg}) = 0.41 \div 0.52$ with the aid of the coulometric titration. The EMF $= f[T]$ or EMF $= f[X(\mathrm{Mg})]$ relations was obtained in this way, as well as the points on the phase equilibrium lines of the system.

The determined results show that in the central part of the investigated system, except β and γ solid phases, additionally only ε phase exists for the concentration near $X(\mathrm{Mg}) = 0.44$. There was not found existence of ζ phase. The ε phase appears as a result of the reaction $\beta + \gamma = \varepsilon$, at the temperature 698 or 700 K. That temperatures are about 16 K higher than that proposed in earlier papers.

Przedmiotem badań były, mające wiele przemysłowych zastosowań, stopy Al-Mg w stanie stałym. Zastosowano technikę pomiaru sił elektromotorycznych SEM w ogniwach z ciekłym elektrolitem w celu określenia własności termodynamicznych w obszarach jedno i dwufazowych, w centralnej części układu. Pomiary przeprowadzono na dwa sposoby: 1° dla stałych stężeń magnezu $X(\mathrm{Mg}) = 0.410$ i 0.475 oraz zmienianych temperatur w zakresie $T = 663$ to 920 K oraz 2° dla stałych temperatur $T = 673$; 698 i 703 K oraz zmienianych na drodze kulometrycznego osadzania stężeń magnezu $X(\mathrm{Mg}) = 0.41 \div 0.52$. Tym sposobem określono zależności SEM $= f[T]$ oraz SEM $= f[X(\mathrm{Mg})]$, jak również punkty na liniach równowagowych badanego układu.

Uzyskane wyniki wskazują, że w centralnej części ukałdu, poza fazami β oraz γ, wystpuje ponadto jedynie faza ε dla stężeń bliskich $X(\mathrm{Mg}) = 0.44$. Nie stwierdzono

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istnienia fazy ζ. Faza ε pojawia się jako rezultat reakcji $\beta + \gamma = \varepsilon$, w temperaturze 698 lub 700 K. Temperatury te są o około 16 K wyższe od sugerowanych we wcześniejszych pracach.

1. Introduction

Because of its good physical and mechanical properties, the Al-Mg system plays an important role in the group of the light alloys. That binary alloys, as well as (Al-Mg)-base multicomponent alloys have a lot of commercial applications. That is a reason why, for many years, the Al-Mg alloys have been intensively examined in many laboratories. However, the biggest number of papers which can be found in the literature concern the alloys in liquid state. Because of important experimental difficulties, the number of experimental thermodynamic data for the Al-Mg alloys in solid state is very low. According to magnesium activity a(Mg) in solid solutions, there is only one paper, published by Brown and Pratt [1].

As it was mentioned in the author's previous work [2], also experimental results for equilibrium relations in the Al-Mg phase diagram are very limited. The most recent experimental data and results of modeling have been published by Su et al. [3] and Liang et al. [4]. The new EMF studies on the Al-Mg gamma phase were performed by the author in [5].

In this work, new experimental thermodynamic data for the Al-Mg solutions are presented. The galvanic cell method was used, which made it possible to determine magnesium activity a(Mg) in γ phase, as well as, in $\beta+\gamma$, $\beta+\varepsilon$, $\varepsilon+\gamma$, $L+\beta$ and $L+\gamma$ two phase regions. The experimental procedure which was used made it possible to measure also the points on the equilibrium phase boundaries in the central part of the Al-Mg system.

2. Experimental

2.1. Preparation of alloys

A special care was taken for the preparation of alloys. All the details of the preparation were described in the previous work [5]. The weighted amounts of metals were melted and then cast in the form of rods. All the operations were done in M. Brown Company glove box with high purity argon atmosphere. Each sample was annealed at the temperatures between 300 and 430°C for 150 to 450 hours and then quenched in ice water. For comparison some of the samples were used without anealing.

2.2. Galvanic cell measurements

By means of galvanic cell method employing a liquid electrolyte, electromotive force (E) measurements were performed with the aid of concentration cell of the type:

$$Mg(s) \mid MgCl_2 + (KCl\text{-}LiCl)_{eut} \mid Al\text{-}Mg(s).$$

To obtain magnesium activities $a(\mathrm{Mg})$, or partial Gibbs free energy $\Delta G(\mathrm{Mg})$, the relations (1) was used:

$$\ln a(\mathrm{Mg}) = -\frac{2 \cdot F}{R \cdot T} E, \qquad \Delta G(\mathrm{Mg}) = R \cdot T \ln a_{\mathrm{Mg}} \tag{1}$$

where: F — Faraday's constant, R — gas constant, T — temperature in [K].

The cell shown in Fig. 1 was assembled in a glove box and then placed in a resistance furnace. The experimental runs were controlled by a computer pro-

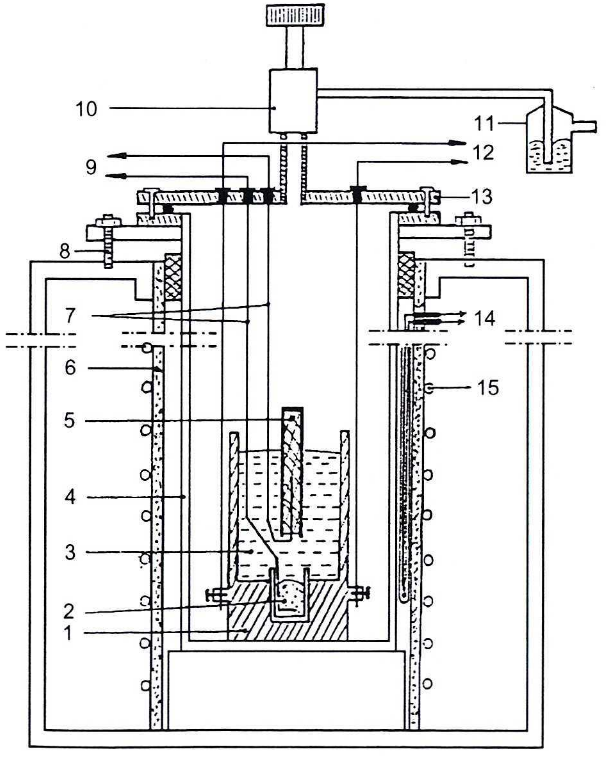

Fig. 1. Experimental arrangement used in emf studies.

1. Cell crucible (Fe)
2. Alloy electrode: solid (Al-Mg) alloy in Al_2O_3 crucible
3. Electrolyte
4. Quartz tube
5. Reference electrode : solid Mg in Mo crucible
6. Furnace tube
7. Electrode leads (Ta)
8. Distance rod
9. To potentiometer
10. Gas valve
11. Bubbler
12. Thermocouple (Mo/Ni)
13. Brass cover
14. Thermocouple of "Omega" temperature controller
15. Power supply

gram. Both, the temperature and EMF values were simultanously visualised on the monitor and saved on the computer disk.

3. Results

The measurements were performed in two manners: 1° for constant magnesium concentration $X(\mathrm{Mg}) = 0.410$ and 0.475 and different temperatures, changing from $T = 663$ to 920 K, and 2° for constant temperature $T = 673$; 698 and 703 K, whereas the concentration of the alloy in the cell was changed $X(\mathrm{Mg}) = 0.41 \div 0.52$ with the aid of the coulometric titration. Both procedures made it possible to obtain EMF $= f[T]$ or EMF $= f[X(\mathrm{Mg})]$ relations. During the experimental runs the characteristics of those relations changed when the phase boundary was crossed. The points on the phase equilibrium lines were determined in this way. In the case of the manner when EMF $= f[T]$ relations were measured, experiments have been performed in both, increasing and decreasing temperature. However, more consistent results were obtained in increasing way.

TABLE 1

Temperature and concentration dependences of EMF measured in the cell (I)

$X(\mathrm{Mg})$	Phase region	$E = a + b\cdot T$		Temperature [K]	Phase region	$E = a + b\cdot X(\mathrm{Mg}) + c\cdot X^2(\mathrm{Mg})$		
		a	b			a	b	c
0.410	L	−19.6	0.06851	673	$\beta+\varepsilon$	26.7		
	$L+\beta$	−278.3	0.42483		ε	175.2	−343.8	
	$\beta+\gamma$	−73.4	0.14063		$\varepsilon+\gamma$	23.9		
	$\varepsilon+\gamma$	8.4	0.02368		γ	−1007.4	4213.0	−4302.2
0.475	L	12.6	0.02457	698	$\beta+\varepsilon$	27.4		
	$L+\gamma$	−232.1	0.36000		ε	209.2	−415.0	
	$\beta+\gamma$	−23.1	0.07083		$\varepsilon+\gamma$	26.6		
	$\varepsilon+\gamma$	−7.6	0.04857		γ	−461.5	2091.7	−2238.1
0.520	L	−29.0	0.06400	703	$\beta+\gamma$	27.9		
	$\gamma+L$	1490.1	−2.00000		γ	−205.1	1103.6	−1285.7
	γ	22.9	−0.00379					
0.575	L	−30.8	0.06330					
	$\gamma+L$	−452.9	0.63750					
	γ	6.8	0.00526					

The parameters of both mentioned above EMF relations obtained by means of the least square method, are collected in Table 1, whereas the graphical presentation of the results is shown in Fig. 2–4. In that figures, T [K] or $X(\mathrm{Mg})$ values of the detected points on the equilibrium lines are also indicated. In Fig. 5, where $\Delta G(\mathrm{Mg}) = f[T]$ is shown, the comparison of own data with those from [1] is presented.

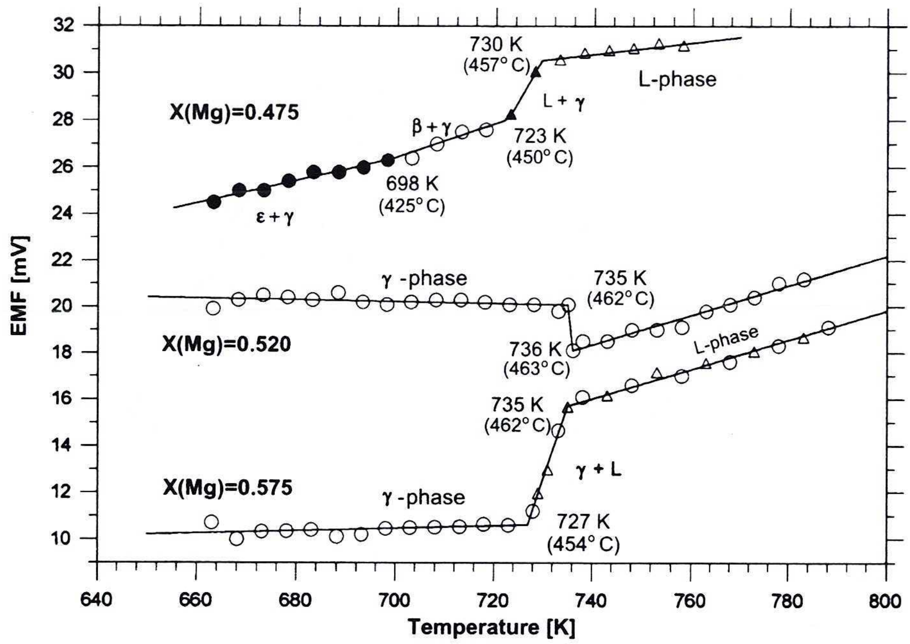

Fig. 2. Experimentally measured in [5] relation EMF = $f[T]$ for concentrations $X(\mathrm{Mg}) = 0.575$ and 0.520, and in this work for $X(\mathrm{Mg}) = 0.475$

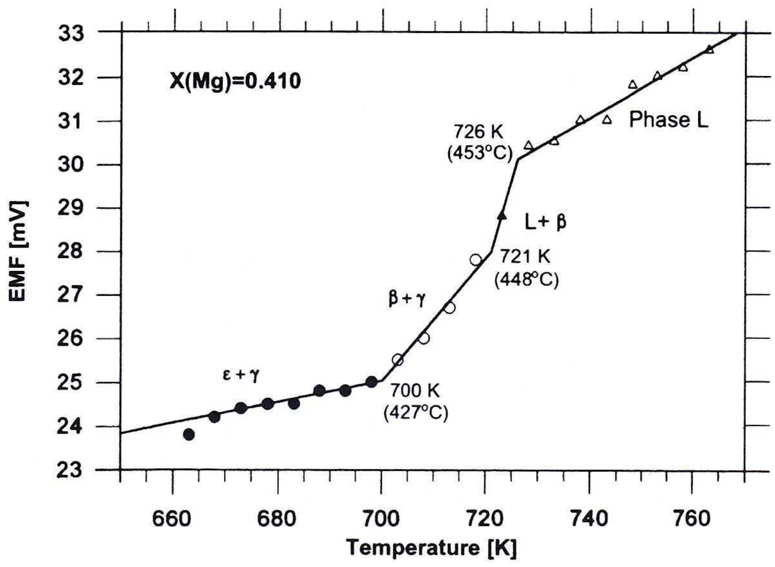

Fig. 3. Experimentally measured relation EMF = $f[T]$ for concentration $X(\mathrm{Mg}) = 0.410$

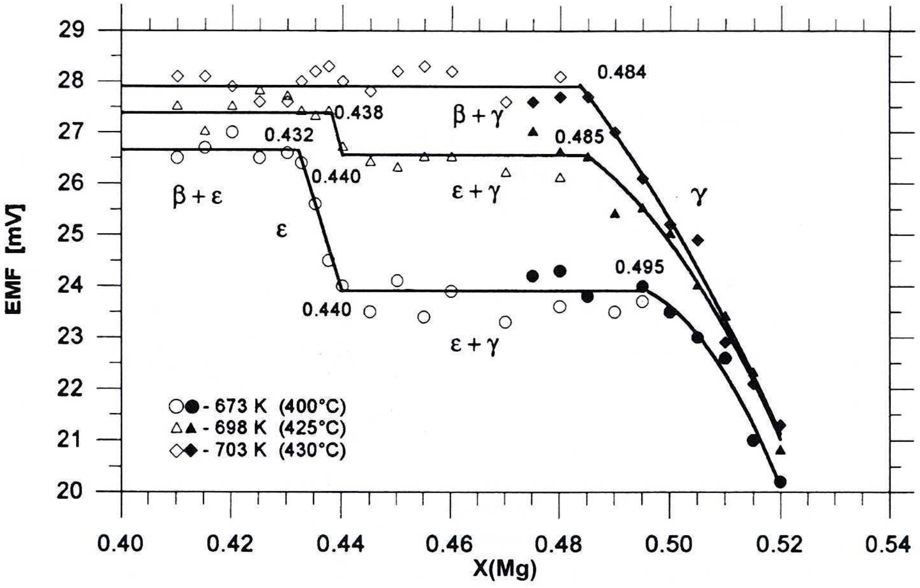

Fig. 4. Experimentally measured relation EMF = $f[X(\mathrm{Mg})]$ for temperatures T = 673, 698 and 703 K

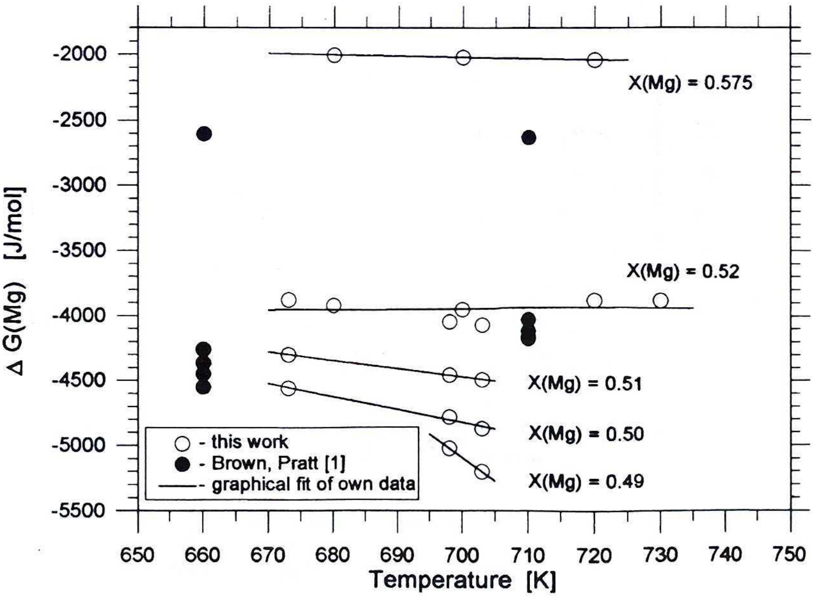

Fig. 5. The relation of partial magnesium Gibbs free energy vs. temperature. The comparison of values calculated from experimental results (with the aid of Eq. (1)) and from literature [1]

4. Conclusions

The determined results show that in the central part of the investigated system, except β and γ solid phases, additionally only ε phase exists for the concentration near $X(\mathrm{Mg}) = 0.44$. The existence of ζ phase, suggested by Schurmann and Voss [6], was not confirmed in this work.

It was found that the ε phase appears as a result of the reaction $\beta + \gamma = \varepsilon$, at the temperature 698 or 700 K. That temperatures are about 16°C higher than that proposed in earlier papers of Su et al. [3] and Liang et al. [4].

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REFERENCES

[1] J.A. Brown, J.N. Pratt, Metall. Trans. **1**, 2743–2750 (1970).
[2] W. Zakulski, Z. Moser, Arch. Metallurgy **43**, 201–214 (1998).
[3] H.L. Su, M. Harmelin, P. Donnadieu, C. Bätzner, H.J. Seifert, H.L. Lukas, G. Effenberg, F. Aldinger, J. Alloys Comp. **247**, 5765 (1997).
[4] P. Liang, T. Tarfa, J.A. Robinson, S. Wagner, P. Ochin, M.G. Harmelin, H.J. Seifert, H.L. Lukas, F. Aldinger, Thermochimica Acta **314**, 87–110 (1998).
[5] W. Zakulski, T. Czeppe, Proceedings of the International Conference "Progress in Computing of Physicochemical Properties", Warszawa, 18–20 November, 1999.
[6] E. Schürmann, H.J. Voss, Giessereiforschung **33**, 43–46 (1981).

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