Thermodynamic calculation of intermetallic compounds in AZ91 alloy containing calcium

WU Yu-feng(吴玉锋), DU Wen-bo(杜文博), NIE Zuo-ren(聂祚仁),
CAO Lin-feng(曹林锋), ZUO Tie-yong(左铁镛)

College of Materials Science and Engineering, Beijing University of Technology, Beijing 100022, China

Abstract: Based on the Miedema model and Chou model, the activities of different solute components in Mg-Al-Zn, Mg-Ca-Zn and Mg-Al-Ca ternary systems were calculated. The results show that the variety of zinc content has little influence on the activity of Al or Ca, and the interaction of Zn and Al or Ca can be neglected when the mass fraction of Zn is lower than 2% in the AZ91 alloy containing calcium (noted as Mg-Al-Zn-Ca system). Therefore, the possible intermetallic compounds in the Mg-Al-Zn-Ca system can be predicted by directly calculating the Gibbs free energies of the reactions in Mg-Al-Ca system. The calculated Gibbs free energies in the Mg-Al-Ca system indicate that Al_2Ca phase can take priority of depositing, which agrees with the experimental results in references. The consistency of calculation and experiment proves that the intermetallic compounds in the Mg-Al-Zn-Ca system can be predicted by the Miedema model and Chou model.

Key words: AZ91 alloy; Mg-Al-Zn alloy; Mg-Ca-Zn alloy; Mg-Al-Ca alloy; Al_2Ca; Miedema model; Chou model; Gibbs free energy

1 Introduction

Magnesium alloy is regarded as a promising structural material in the 21 century because of its excellent properties such as low density, high specific strength, good castability and machinability[1−5]. The common magnesium alloy AZ91 is, however, unsuitable for using at the temperatures above 120 ℃ because of its poor creep resistance and strength at elevated temperatures[2]. Adding other elements, like calcium, is an important method to improve the mechanical properties of AZ91 at elevated temperatures. The studies [2, 6, 7] showed that the added calcium can modify the as-cast microstructure and improve the mechanical properties of AZ91 alloy at both room and elevated temperatures because of the existence of Ca in β-$Mg_{17}Al_{12}$ phase. However, up to now the thermodynamic calculation of the intermetallic compounds in the AZ91 alloy containing calcium (noted as Mg-Al-Zn-Ca system) has not been reported.

Miedema model has been widely used to calculate some thermal properties of binary alloys[8, 9]. Chou model is more convenient to predict excess Gibbs free energy and activity coefficients of different components in ternary system than the other thermodynamic models[10−12]. The purpose of the present paper is to calculate the activities of different solute components in Mg-Al-Zn, Mg-Ca-Zn and Mg-Al-Ca alloy systems and to predict the deposited phases in the Mg-Al-Zn-Ca system based on the Miedema model and Chou model.

2 Calculation model

2.1 Miedema model

According to Miedema model[8], the heat of formation, ΔH_{ij}, in the binary liquid i—j alloy can be calculated as

$$\Delta H_{ij} = f_{ij} \frac{x_i[1+u_i x_j(\phi_i - \phi_j)]x_j[1+u_j x_i(\phi_j - \phi_i)]}{x_i V_i^{2/3}[1+u_i x_j(\phi_i - \phi_j)] + x_j V_j^{2/3}[1+u_j x_i(\phi_j - \phi_i)]}$$

(1a)

in which

$$f_{ij} = 2p_{ij}V_i^{2/3}V_j^{2/3}\{(q/p)[(n_{ws}^{1/3})_j - (n_{ws}^{1/3})_i]^2 - \\ -(\phi_i - \phi_j)^2 - a(r/p)\}\big/(n_{ws}^{1/3})_j^{-1} + (n_{ws}^{1/3})_i^{-1} \quad (1b)$$

where x_i and x_j represent the molar fractions of components i and j, respectively; V is the molar volume, ϕ is the electron negativity, n_{ws} is the electron density; u, p, q, a and r are all empirical constants, q/p=9.4. a equals 1.0 for solid alloys and 0.73 for liquid alloys containing a transition metal and a nontransition metal, respectively, and a equals 0 for the other alloys. All the parameters above are obtained from Refs.[8, 13].

In a binary system, the relation between G_{ij}^E and ΔH_{ij}, S_{ij}^E is given by

$$G_{ij}^E = \Delta H_{ij} - TS_{ij}^E \quad (2)$$

where T is the absolute temperature of system.

Considering the absolute value of S_{ij}^E is much smaller than the absolute value of ΔH_{ij}, let S_{ij}^E=0, then, $G_{ij}^E = \Delta H_{ij}$. Hence,

$$G_{ij}^E = \\ f_{ij}\frac{x_i[1+u_ix_j(\phi_i - \phi_j)]x_j[1+u_jx_i(\phi_j - \phi_i)]}{x_iV_i^{2/3}[1+u_ix_j(\phi_i - \phi_j)] + x_jV_j^{2/3}[1+u_jx_i(\phi_j - \phi_i)]}$$

$$(3)$$

where f_{ij} can be got from Eqn.(1b).

2.2 Calculation of activities of different solute components in ternary alloy systems

According to Chou model[10, 11], the excess Gibbs free energy in the ternary liquid i—j—k alloy can be calculated as

$$G^E = \frac{x_ix_jG_{ij}^E}{(x_i+\xi_{ij}x_k)(x_j+\xi_{ji}x_k)} + \frac{x_jx_kG_{jk}^E}{(x_j+\xi_{jk}x_i)(x_k+\xi_{kj}x_i)} + \\ \frac{x_kx_iG_{ki}^E}{(x_k+\xi_{ki}x_j)(x_i+\xi_{ik}x_j)} \quad (4)$$

where x_i, x_j and x_k are the molar fractions of components i, j and k, respectively; ζ is an analogical coefficient, which is a special parameter introduced by Chou model, and its physical meaning and calculative method have been given in Ref.[10]. G_{ij}^E, G_{jk}^E and G_{ki}^E are calculated according to Eqn.(3).

The activity coefficient of any component $m(m=i, j, k)$ can be calculated as follows[10, 11]:

$$RT\ln\gamma_m = G^E + \frac{\partial G^E}{\partial x_m} - (x_i\frac{\partial G^E}{\partial x_i} + x_j\frac{\partial G^E}{\partial x_j} + \\ x_k\frac{\partial G^E}{\partial x_k}) \quad (5)$$

$$\frac{\partial G^E}{\partial x_i} = \frac{A_1(A_2+A_3)}{A_4^2} + \frac{B_1(B_2+B_3)}{B_4^2} - \frac{C_1C_2}{C_3^2} \quad (6)$$

where

$$A_1 = f_{ij}x_j[1+u_i(\phi_i - \phi_j)(x_j + \xi_{ji}x_k)]$$

$$A_2 = [u_j(\phi_j - \phi_i)(x_i + \xi_{ij}x_k)^2 + \xi_{ij}x_k]\cdot \\ [1+u_i(\phi_i - \phi_j)(x_j + \xi_{ji}x_k)]V_i^{2/3}$$

$$A_3 = (x_j + \xi_{ji}x_k)[1+u_j(\phi_j - \phi_i)(x_i + \xi_{ij}x_k)]^2V_j^{2/3}$$

$$A_4 = (x_i+\xi_{ij}x_k)[1+u_i(\phi_i - \phi_j)(x_j + \xi_{ji}x_k)]V_i^{2/3} + \\ (x_j+\xi_{ji}x_k)[1+u_j(\phi_j - \phi_i)(x_i + \xi_{ij}x_k)]V_j^{2/3}$$

$$B_1 = f_{ki}x_i[1+u_i(\phi_i - \phi_k)(x_k + \xi_{ki}x_j)]$$

$$B_2 = [u_k(\phi_k - \phi_i)(x_k + \xi_{ki}x_j)^2 + \xi_{ik}x_j]\cdot \\ [1+u_i(\phi_i - \phi_k)(x_k + \xi_{ki}x_j)]V_i^{2/3}$$

$$B_3 = (x_k + \xi_{ki}x_j)[1+u_k(\phi_k - \phi_i)(x_i + \xi_{ik}x_j)]^2V_i^{2/3}$$

$$B_4 = (x_i+\xi_{ik}x_j)[1+u_i(\phi_i - \phi_k)(x_k + \xi_{ki}x_j)]V_i^{2/3} + \\ (x_k+\xi_{ki}x_j)[1+u_k(\phi_k - \phi_i)(x_i + \xi_{ik}x_j)]V_k^{2/3}$$

$$C_1 = f_{jk}x_jx_k$$

$$C_2 = \xi_{jk}[1+u_j(\phi_j - \phi_k)(x_k + \xi_{kj}x_i)]^2V_k^{2/3} + \\ \xi_{kj}[1+u_k(\phi_k - \phi_j)(x_j + \xi_{jk}x_i)]^2V_k^{2/3}$$

$$C_3 = (x_j+\xi_{ik}x_i)[1+u_j(\phi_j - \phi_k)(x_k + \xi_{kj}x_i)]V_j^{2/3} + \\ (x_k+\xi_{kj}x_i)[1+u_k(\phi_k - \phi_j)(x_j + \xi_{jk}x_i)]V_k^{2/3}$$

$\frac{\partial G^E}{\partial x_m}$ (m=j, k) can be calculated by Eqn.(6).

According to the $\gamma_m(m=i, j, k)$ calculated by Eqn.(5), the activities of component $m(m=i, j, k)$ can be obtained:

$$a_m = \gamma_m \cdot x_m \ (m=i, j, k) \quad (7)$$

3 Results and discussion

3.1 Mg-Al-Zn and Mg-Ca-Zn ternary system

Fig.1 shows the activities of Al and Zn as a function of mass fraction of Zn in AZ31, AZ44 and AZ412 at 1 000 K. Fig.2 shows the activities of Ca and Zn as a function of mass fraction of Zn in Mg-Ca-xZn(x=1, 2, 5)

at 1 000 K. These two figures indicate that the increase in mass fraction of Zn increases the activity of Al in Mg-Al-Zn ternary system; while the increase in mass fraction of Zn decreases the activity of Ca in Mg-Ca-Zn ternary system. The change of activities of Al and Ca component with mass fraction of Zn is, however, extremely small, when the mass fraction of Zn is lower than 2%. Moreover, it is suggested that a small content of Zn is difficult to form intermetallic compounds with other components like Al and Ca based on the consideration that the solubility of Zn in Mg matrix is comparatively high[14]. Therefore the possible inter-metallic compounds in Mg-Al-Zn-Ca system are predicted by calculating simply the Gibbs free energies of the reactions between Mg-Ca and Al-Ca in Mg-9Al-xCa systems, ignoring the purpose of Zn component.
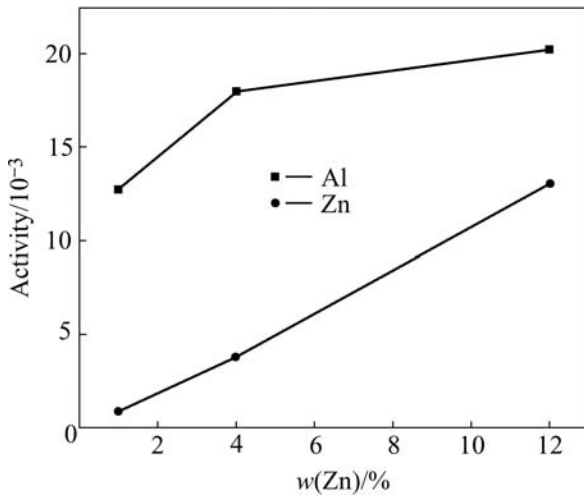

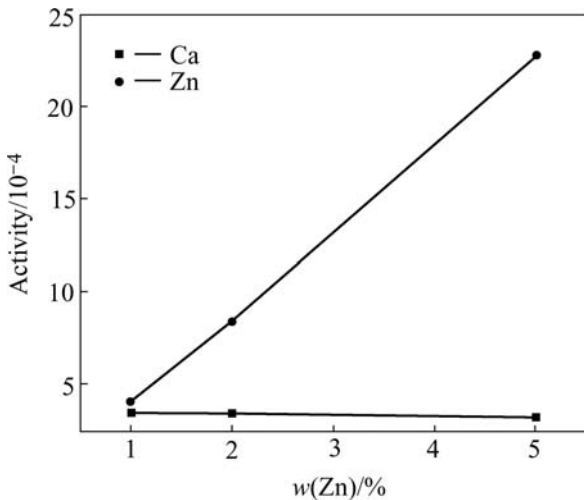**Fig.1** Activities of Al and Zn as function of mass fraction of Zn at 1 000 K

Fig.2 Activities of Ca and Zn as function of mass fraction of Zn at 1 000 K

3.2 Mg-Al-Ca ternary system

The calculated activities of Al and Ca components at 900 K in Mg-9Al-xCa(x=0.5, 1, 3) systems are listed in Table 1.

Table 1 Activities of Al and Ca component in Mg-9Al-xCa(x= 0.5, 1, 3) at 900 K

w(Ca) %	a (Al)	a (Ca)
0.5	3.9843×10^{-2}	1.7491×10^{-5}
1.0	3.9378×10^{-2}	3.6990×10^{-5}
3.0	3.7803×10^{-2}	1.3269×10^{-4}

According to Al-Ca and Mg-Ca binary phase diagrams, the intermetallic compounds of which the melting point is higher than 900 K include Al$_2$Ca, Al$_4$Ca and Mg$_2$Ca. Hence the possible reactions in Mg-9Al-xCa(x=0.5, 1, 3) systems at 900 K can be given as follows:

$$2[Al]+[Ca] = Al_2Ca(s) \tag{a}$$

$$\Delta G_a = \Delta G_a^\Theta + RT \ln \frac{a(Al_2Ca)}{a^2([Al])a([Ca])} \tag{8}$$

$$4[Al]+[Ca] = Al_4Ca(s) \tag{a'}$$

$$\Delta G_{a'} = \Delta G_{a'}^\Theta + RT \ln \frac{a(Al_2Ca)}{a^4([Al])a([Ca])} \tag{9}$$

$$2[Mg]+[Ca] = Mg_2Ca(s) \tag{a''}$$

$$\Delta G_{a''} = \Delta G_{a''}^\Theta + RT \ln \frac{a(Mg_2Ca)}{a^2([Mg])a([Ca])} \tag{10}$$

Reactions(a), (a') and (a'') can be obtained by simplifying these reactions as follows:

$$2Al(s)+Ca(s)=Al_2Ca(s) \tag{b}$$
$$4Al(s)+Ca(s)=Al_4Ca(s) \tag{b'}$$
$$2Mg(s)+Ca(s)=Mg_2Ca(s) \tag{b''}$$
$$Al(s)=[Al] \tag{c}$$
$$Ca(s)=[Ca] \tag{d}$$
$$Mg(s)=[Mg] \tag{e}$$

Since (a)＝(b)－2(c)－(d), (a')＝(b')－4(c)－(d), (a'')＝(b'')－2(e)－(d), ΔG_a^Θ, $\Delta G_{a'}^\Theta$ and $\Delta G_{a''}^\Theta$ can be denoted as

$$\Delta G_a^\Theta = \Delta G_b^\Theta - 2\Delta G_c^\Theta - \Delta G_d^\Theta$$

$$\Delta G_{a'}^\Theta = \Delta G_{b'}^\Theta - 4\Delta G_c^\Theta - \Delta G_d^\Theta$$

$$\Delta G_{a''}^\Theta = \Delta G_{b''}^\Theta - 2\Delta G_e^\Theta - \Delta G_d^\Theta$$

Let pure Al(s), Ca(s), Mg (s), Al$_2$Ca(s) and Al$_4$Ca(s) be standard state, respectively, then

$$\Delta G_c^\Theta = 0, \Delta G_d^\Theta = 0, \Delta G_e^\Theta = 0$$

thus,

$$\Delta G_{a}^{\Theta} = \Delta G_{b}^{\Theta},\ \Delta G_{a'}^{\Theta} = \Delta G_{b'}^{\Theta},\ \Delta G_{a''}^{\Theta} = \Delta G_{b''}^{\Theta}$$

According to the thermodynamic data in Ref.[15], the values of ΔG_{a}^{Θ}, $\Delta G_{a'}^{\Theta}$ and $\Delta G_{a''}^{\Theta}$ at 900 K are calculated as follows, respectively.

$$\Delta G_{a}^{\Theta} = -204\ 935\ \text{J/mol},\ \ \Delta G_{a'}^{\Theta} = -202\ 978\ \text{J/mol},$$

$$\Delta G_{a''}^{\Theta} = -35\ 238\text{J/mol}$$

Substituting ΔG_{a}^{Θ}, $\Delta G_{a'}^{\Theta}$, $\Delta G_{a''}^{\Theta}$, $a([\text{Mg}])=1$, $a(\text{Al}_2\text{Ca})=1$ and $a(\text{Al}_4\text{Ca})=1$ into Eqns.(8), (9) and (10), ΔG_{a}, $\Delta G_{a'}$ and $\Delta G_{a''}$ at different mass fraction of Ca are obtained, which are shown in Fig.3. It can be found that $\Delta G_{a} < \Delta G_{a'} < 0$, $\Delta G_{a''} > 0$ when the mass fraction of Ca changes from 0.5 to 3. It indicates that Al_2Ca phase, not Al_4Ca phase, can take priority of depositing, while Mg_2Ca phase does not deposit. Moreover, the higher the mass fraction of Ca is, the more negative the ΔG_{a} is, and the greater the trend to formation of Al_2Ca phase is.
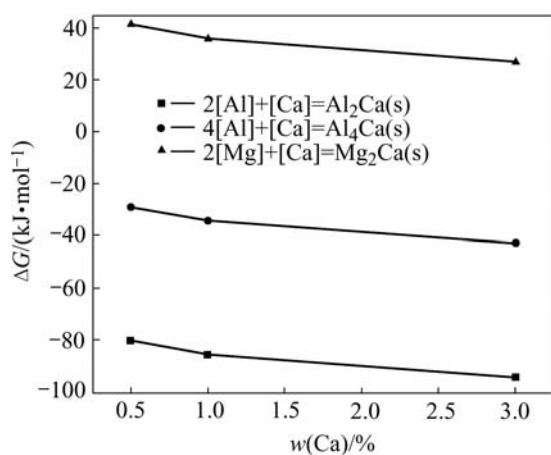

Fig.3 ΔG of different reactions as function of mass fraction of Ca at 900 K

The study in Ref.[16] indicated that only Al_2Ca and α-Mg were found in Mg-9Al-0.5Zn-0.1Be-xCa alloy, while Al_4Ca and Mg_2Ca did not precipitate during cooling. Al_2Ca precipitated prior to β-$\text{Mg}_{17}\text{Al}_{12}$ and prevented the increase of the grain size. With the mass fraction of Ca increasing from 0.5 to 3, the amount of Al_2Ca increased and the effect on the refinement of grains became prominent. These experimental phenomena agree well with the results in this paper. Al_2Ca precipitates at the temperature near to AZ91 alloy solidification and makes itself easy to go into β-$\text{Mg}_{17}\text{Al}_{12}$ phase and improves the thermal stability of β-$\text{Mg}_{17}\text{Al}_{12}$ phase. This just gives the reason for why Ca mostly exists in β-$\text{Mg}_{17}\text{Al}_{12}$ phase and improves the thermal stability of the AZ91 alloy introduced by Refs.[2, 17].

4 Conclusions

Based on the Miedema model and Chou model, the activities of different solute components in Mg-Al-Zn, Mg-Ca-Zn and Mg-Al-Ca systems are studied. The following conclusions are obtained.

1) In the Mg-Al-Zn and Mg-Ca-Zn alloy systems, the variety of its quantity has little influence on the activities of Al or Ca when the mass fraction of Zn is lower than 2%, therefore, the interaction of Zn and Al or Ca can be neglected. The intermetallic compounds appeared possibly in the Mg-Al-Zn-Ca system can be predicted by simply calculating the Gibbs free energies of different intermetallic compounds in Mg-9Al-xCa.

2) In Mg-9Al-xCa alloy systems, the calculated results indicate that Al_2Ca phase can take priority of depositing at 900 K, which is near to the solidification temperature of AZ91 alloy. This agrees with the experimental results in Refs.[6, 16, 17]. The consistency of calculation and experiment proves that it is feasible to predict the intermetallic compounds in AZ91 alloys containing calcium by the Miedema model and Chou model.

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