Calculation of Thermodynamic Properties of Mg-Zn-Al Alloy

Zhiling Bai 1,a*, Bingke Qin1
1 Liupanshui Normal University, Liupanshui, Guizhou, China
*Corresponding author: email: zhilingbai@126.com

Abstract. The thermodynamic properties of Mg, Zn, Al binary alloys and ternary alloys were calculated by Miedema model and Toop model, and magnesium was selected as the asymmetric component. The results show that the mixing enthalpy, excess entropy and excess Gibbs free energy of Al-Zn binary alloy are all greater than zero. The thermodynamic values of Mg-Al and Mg-Zn binary alloys are relatively similar, and both are less than zero. Within the range of composition variation, the excess Gibbs free energy of Mg-Zn-Al ternary alloy is basically negative. In the Mg-poor and Mg-rich regions, the thermodynamic value of the alloy changes greatly. Excess Gibbs free energy and mixing enthalpy of magnesium-zinc-aluminum alloy can be reduced by adding zinc and aluminum.

1. Introduction
The Mg-Zn-Al is a heat-resistant magnesium alloy with low development cost[1]. Miedema model is a macroscopic model. The heat of formation of the binary alloy can be estimated by the parameters of the components in the alloy, and the thermodynamic values calculated by Miedema model are close to the experimental values[2]. Toop model is a commonly used model for calculating the thermodynamic properties of ternary alloy systems.

Miedema model is used to calculate the mixing enthalpy, excess entropy and excess Gibbs free energy of magnesium-aluminum, aluminum-zinc, and magnesium-zinc binary alloys. Toop model is used to calculate the mixing enthalpy and excess Gibbs free energy of magnesium-zinc-aluminum alloy.

2. Calculation model of thermodynamic properties

2.1. Miedema model [2]

\[
\Delta H_{ab} = f_{ab} = \frac{x_a M \cdot x_b N}{x_a V_a^{2/3} M + x_b V_b^{2/3} N} 
\]
\[
f_{ab} = 2 p V_a^{2/3} V_b^{2/3} \left[ \frac{q}{p} \cdot (\Delta n_{ws}^{1/3})^2 - (\Delta \phi)^2 - c \cdot \left(\frac{r}{p}\right) \right] 
\]

Where \( M = [1 + \mu_a x_a (\phi_a - \phi_b)] \); \( N = [1 + \mu_b x_b (\phi_b - \phi_a)] \); \( x_a \) and \( x_b \) are the mole fractions; \( V_a \) and \( V_b \) are molar volumes; \( \phi_a \) and \( \phi_b \) are electronegativities; \( n_{ws} \) are electron densities; \( \mu_a \), \( \mu_b \), \( p \), \( q \), \( r \) are constants, and \( q/p = 9.4 \); \( c \) is equal to 0.73 in liquid alloy, and \( c \) is equal to 1 in solid alloy.
2.2. Calculation method of activity of each component of binary alloy

For binary alloys, the relationship between $G_{ab}^E$, $S_{ab}^E$ and $\Delta H_{ab}$ is

$$G_{ab}^E = \Delta H_{ab} - T S_{ab}^E$$  \hspace{1cm} (3)

The relationship between excess entropy $S_{ab}^E$ and enthalpy change $\Delta H_{ab}$ is

$$S_{ab}^E = 0.1 \times \Delta H_{ab} \times [(1/T_{ma}) + (1/T_{mb})]$$  \hspace{1cm} (4)

$T_{ma}$ and $T_{mb}$ are the melting temperatures of $a$ and $b$ respectively.

When

$$C_{ab} = 1 - 0.1 \times T \times [(1/T_{ma}) + (1/T_{mb})]$$  \hspace{1cm} (5)

$$G_{ab}^E = C_{ab} \times \Delta H_{ab}$$  \hspace{1cm} (6)

The partial molar excess Gibbs free energy of $a$ is calculated as follows.

$$G_a^E = G_{ab}^E + (1 - x_a) \frac{\partial G_{ab}^E}{\partial x_a}$$  \hspace{1cm} (7)

The activity coefficients $\gamma_a$ and $\gamma_b$ can be calculated by formulas (8) and (9) to obtain specific values.

$$RT \ln \gamma_a = G_a^E + (1 - x_a) \frac{\partial G_{ab}^E}{\partial x_a}$$  \hspace{1cm} (8)

$$RT \ln \gamma_b = \frac{1}{x_a} (G_{ab}^E - RT x_a \ln x_a)$$  \hspace{1cm} (9)

The activity of each component can be obtained according to equation (10).

$$a_i = \gamma_i x_i$$  \hspace{1cm} (10)

3. Results and discussion

3.1. Calculation of thermodynamic functions of magnesium-zinc, magnesium-aluminum and aluminum-zinc binary alloys and the activity of each component

| Table 1 Parameter values of Mg, Zn and Al elements[2] |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Element         | $n_{ws}^{1/3} (u_{ws})^{1/3}$ | $\phi / V$     | $V^{2/3} / cm^2$ | $\mu$          | $T_m / K$      |
| Mg              | 1.17            | 3.45            | 5.8             | 0.10           | 923            |
| Zn              | 1.32            | 4.10            | 4.4             | 0.10           | 692            |
| Al              | 1.39            | 4.20            | 4.6             | 0.07           | 933            |

By substituting the parameters in Table 1 into equations (1) to (10), the enthalpy change, excess entropy, excess Gibbs free energy and activity value of each component of magnesium-zinc, magnesium-aluminum and aluminum-zinc binary alloys are obtained. Fig.1 shows the curves of $\Delta H$, $S^E$, $G^E$ and $\alpha$ of magnesium-zinc, magnesium-aluminum and aluminum-zinc at 1000 K. The other parameter values of the elements can be found in literature [2].

It can be seen from Fig.1 that the excess entropy, excess Gibbs free energy and mixing enthalpy of aluminum-zinc alloy are all greater than zero. The thermodynamic values of magnesium-aluminum and magnesium-zinc alloys are relatively similar and both are less than zero.

The absolute values of excess entropy, mixing enthalpy and excess Gibbs free energy of aluminum-zinc alloy are much smaller than those of magnesium-aluminum and magnesium-zinc alloys. The thermodynamic properties of Al-Zn alloy are different from those of magnesium-aluminum and magnesium-zinc alloys.
As shown in the activity curves in Fig. 1, the activity values of the elements of three alloys change basically the same as the composition content changes. The three alloys can be approximated as ideal melts.

Fig. 1 The curves of $\Delta H$, $S^E$, $G^E$ and $a$ of Mg-Zn, Mg-Al and Al-Zn binary alloys at 1000 K

3.2. Thermodynamic calculation of Mg-Zn-Al ternary alloy

Toop model can be used to estimate the thermodynamic properties of magnesium-zinc-aluminum alloy. According to the selection method of the asymmetric component in Toop model, magnesium is used as the asymmetric component. The thermodynamic properties of magnesium-zinc-aluminum alloy obtained from Toop model[3] are expressed as

$$
\Delta H_{MgZnAl} = \frac{x_{Mg}}{x_{Zn} + x_{Al}} \Delta H_{MgZn}(x_{Mg} - x_{Mg}) + \frac{x_{Al}}{x_{Zn} + x_{Al}} \Delta H_{MgAl}(x_{Mg} - x_{Mg}) + (x_{Zn} + x_{Al})^2 \Delta H_{ZnAl}(x_{Zn}, x_{Al})
$$

$$
G^E_{MgZnAl} = \frac{x_{Mg}}{x_{Zn} + x_{Al}} G^E_{MgZn}(x_{Mg} - x_{Mg}) + \frac{x_{Al}}{x_{Zn} + x_{Al}} G^E_{MgAl}(x_{Mg} - x_{Mg}) + (x_{Zn} + x_{Al})^2 G^E_{ZnAl}(x_{Zn}, x_{Al})
$$

(11)

(12)
In formulas (11) and (12) $\Delta H^E_{MgZnAl}$, $G^E_{MgZnAl}$, $\Delta H^E_{MgZn}$, $G^E_{MgZn}$ are the thermodynamic properties; $x_{Al}$, $x_{Mg}$ and $x_{Zn}$ are the mole fractions of aluminum, magnesium, and zinc in the magnesium-zinc-aluminum alloy, respectively.

In the ternary system, the composition of the two elements is kept at a fixed ratio, and the effect of the change of the composition of the other element on the thermodynamic properties of the alloy is studied[4-5]. The mole fraction ratio of the two elements in magnesium-zinc-aluminum alloy is shown in Table 2.

Table 2  The mole fraction ratio of the two elements in magnesium-zinc-aluminum alloy

| Cross Section | A   | B   | C   | D   | E   |
|---------------|-----|-----|-----|-----|-----|
| $x_{Mg}$,$x_{Al}$ | 1:9 | 3:7 | 5:5 | 7:3 | 9:1 |
| $x_{Zn}$,$x_{Al}$ | 1:9 | 3:7 | 5:5 | 7:3 | 9:1 |
| $x_{Mg}$,$x_{Zn}$ | 1:9 | 3:7 | 5:5 | 7:3 | 9:1 |

The relationships between excess Gibbs free energy, mixing enthalpy of magnesium-zinc-aluminum alloy and the element mole fraction is shown in Fig.2. When the mole fraction ratio of magnesium to aluminum is C, D and E, excess Gibbs free energy and mixing enthalpy of magnesium-zinc-aluminum alloy first decrease and then increase with the increase of the zinc mole fraction. When the mole fraction of magnesium to aluminum is A and B, excess Gibbs free energy and mixing enthalpy of magnesium-zinc-aluminum alloy increase slowly with the increase of zinc mole fraction. As the mole fraction of magnesium increases, excess Gibbs free energy and mixing enthalpy of magnesium-zinc-aluminum alloy decrease first and then increase.

When the mole fraction ratio of magnesium to zinc is A and B, excess Gibbs free energy and mixing enthalpy of magnesium-zinc-aluminum alloy first increase and then decrease with the increase of the mole fraction of aluminum; when the mole fraction ratio of magnesium to zinc is C and D, excess Gibbs free energy and mixing enthalpy of magnesium-zinc-aluminum alloy increase with the increase of aluminum mole fraction; when the mole fraction ratio of magnesium to zinc is E, excess Gibbs free energy and mixing enthalpy of magnesium-zinc-aluminum alloy first decrease and then increase with the increase of the aluminum mole fraction.

Within the range of composition variation, excess Gibbs free energy of magnesium-zinc-aluminum alloy is basically negative. In the Mg-poor and Mg-rich regions, the thermodynamic values of the alloy change greatly. Excess Gibbs free energy and mixing enthalpy of magnesium-zinc-aluminum alloy can be reduced by adding zinc and aluminum.
4. Conclusions

Miedema model is used to calculate mixing enthalpy, excess Gibbs free energy and excess entropy of magnesium, zinc and aluminum binary alloys, and magnesium is obtained as an asymmetric component. Toop model can be used to estimate the thermodynamic properties of magnesium-zinc-aluminum alloy. Within the range of composition variation, excess Gibbs free energy of magnesium-
zinc-aluminum alloy is basically negative. In the Mg-poor and Mg-rich regions, the thermodynamic values of the alloy change greatly. Excess Gibbs free energy and mixing enthalpy of magnesium-zinc-aluminum alloy can be reduced by adding zinc and aluminum.

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