



COMPARISON OF THERMOPHYSICAL PROPERTIES OF Mg-Ga AND Mg-Pb ALLOYS AT 1000 K

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ABSTRACT

Concentration-dependent thermophysical properties of molten Mg-Pb and Mg-Ga alloys at 1000 K was compared using the Redlich Kister equation by optimizing exponential interaction energy parameters based on the R-K polynomials framework. The mixing behavior was investigated by giving more emphasis to the role of temperature-dependent interaction energy parameters. Our study shows that the magnesium gallium alloy is slightly interacting than the magnesium lead alloy. The surface tension and viscosity of both alloys was compared using the Butler equation as improved by Kaptay and KRP (Kozlov-Ronanov-Petrov) approach respectively. The surface tension of Mg-Pb liquid alloy increases but decreases in Mg-Ga alloy with an increase in the concentration of Mg. The viscosity has a nonlinear variation for both alloys with the increase in the concentration of magnesium.

Keywords: Artificial miscibility gap, Energy parameters, Polynomials, Surface tension, Viscosity.

INTRODUCTION

Due to the dramatic change in the behavior of various useful properties of alloys than constituent elements, the alloys have wide application in industries. But it is tedious and time-consuming to study all properties experimentally. Different theoretical models have been developed to explore the thermodynamic behaviors of the binary molten alloys (Bhatia & March, 1975; Bhatia & Singh, 1984; Singh & Mishra, 1988). The limitation of such models is that they can predict the behavior of alloys nearly at melting temperature.

The alloys in the molten state are studied in metallurgy and industry for high-temperature application as well. Hence the mixing behavior of elements of the alloys at high temperatures was considered a prime concern to all metal physicists, metallurgists, and chemists (Shrestha *et al.*, 2017). The Redlich-Kister (R-K) equation (Redlich & Kister, 1948) is considered an important tool to understand the thermodynamic property like excess Gibbs free energy of binary molten alloy at high temperatures. The equation was formulated using linear temperature-dependent energy interaction parameters called R-K polynomials.

But there arises an artificial miscibility gap or artifact in some binary alloys using such linear interaction parameters for the high-temperature study of the alloys (Mehta *et al.*, 2020; Gohivar *et al.*, 2020). To avoid the problem raised by artifact, theoretician Kaptay (2017) suggested modifying the temperature-dependent linear interaction parameter to exponential parameter in the R-K

polynomials framework where the parameters are exponentially dependent on temperature.

The present work aims to compare the concentration dependence of different properties of molten alloys Mg-Pb and Mg-Ga at temperature 1000 K by optimizing exponential temperature-dependent interaction parameters of both the alloys in the R-K polynomials framework as suggested by Kaptay (2004). Magnesium and its alloys when used in the automobile industry contribute remarkably to the fuel economy as well as the conservation of the environment. The latest technology in the coating as well as alloying of magnesium has reduced the creep and corrosion resistance behavior of the alloys at elevated temperature and corrosive environments (Kulekci, 2008). The properties of the alloys under the investigation include excess Gibb's free energy, enthalpy, entropy, chemical activity, concentration fluctuation in long-wavelength limit, surface tension, and viscosity. These studies provide knowledge of the interaction, bond strength, and stability of phases (Panthi *et al.*, 2021).

On the other hand, the knowledge of the structural adjustment of constituent atoms in the molten alloys is pictured out by the qualitative study of microscopic function; the concentration fluctuation in the long-wavelength limit ($S_{cc}(o)$). Similarly, the information of surface, as well as transport nature of alloys are provided by surface tension and viscosity (Koirala, 2018; Koirala *et al.*, 2014; Singh & Koirala, 2015). Here, it tried to study the surface tension and viscosity of the alloys using the Butler equation as improved by Kaptay (2019) and Kozlov *et al.* (1983) approaches.

THEORETICAL MODEL AND DATA

The excess Gibbs free energy (ΔG^{XS}), enthalpy (ΔH), and the excess entropy (ΔS^{XS}) of a binary alloy are related by the standard relation as;

$$\Delta G^{XS} = T \left(\frac{\Delta H}{T} - \Delta S^{XS} \right) \quad (1)$$

Similarly, the excess Gibbs free energy of an alloy is given by the R-K equation (Redlich & Kister, 1948) as;

$$\Delta G^{XS} = c_1 c_2 \sum_{i=0}^n L_i (c_1 - c_2)^i \quad (2)$$

Where c_1 and c_2 are the concentration of the constituent elements of the alloy and L_i is the linear temperature-dependent interaction parameter between the components of an alloy known as R-K polynomial. It is related to temperature (T), enthalpy like semi-empirical coefficient (a_i) and entropy like semi-empirical coefficient (b_i) of R-K Polynomials as;

$$L_i = T \left(\frac{a_i}{T} - b_i \right) \quad (3)$$

The total Gibbs free energy of an alloy is related to the excess Gibbs free energy and ideal Gibbs energy of the alloy as;

$$\begin{aligned} \Delta G &= \Delta G^{XS} + \Delta G^{id} \\ &= \Delta G^{XS} + RT(c_1 \ln c_1 + c_2 \ln c_2) \end{aligned} \quad (4)$$

From equations (2) and (3)

$$\Delta G^{XS} = c_1 c_2 \sum_{i=0}^n T \left(\frac{a_i}{T} - b_i \right) (c_1 - c_2)^i \quad (5)$$

From equations (1) and (5), we get

$$\Delta H = c_1 c_2 \sum_{i=0}^n a_i (c_1 - c_2)^i \quad (6)$$

$$\Delta S^{XS} = c_1 c_2 \sum_{i=0}^n b_i (c_1 - c_2)^i \quad (7)$$

According to Kaptay (2004), the exponential temperature-dependent interaction parameters of a binary alloy can be written as;

$$K_i = h_i \exp \left(-\frac{T}{t_i} \right) \quad (8)$$

Where, h_i (J/mol) and t_i (K) are semi-empirical parameters.

From equations (1), (5), (6), and (7), the derivations for enthalpy and excess entropy of a binary liquid alloy are obtained as shown below.

$$\Delta H = c_1 c_2 \sum_{i=0}^n \left(1 + \frac{T}{t_i} \right) h_i \exp \left(-\frac{T}{t_i} \right) (c_1 - c_2)^i \quad (9)$$

$$\Delta S^{XS} = c_1 c_2 \sum_{i=0}^n \frac{h_i}{t_i} \exp \left(-\frac{T}{t_i} \right) (c_1 - c_2)^i \quad (10)$$

The entropy of mixing is given by the standard formula as

$$\Delta S = \left(\frac{\Delta H}{T} - \frac{\Delta G}{T} \right) \quad (11)$$

The structural arrangement of the atoms of an alloy in terms of concentration fluctuation in the long-wavelength limit ($S_{cc}(0)$) is calculated from the standard relation as;

$$S_{cc}(0) = RT \left[\frac{\partial^2 \Delta G}{\partial c^2} \right]_{T,P,N}^{-1} \quad (12)$$

From equations (1), (4), (9), (10) and (12)), we get.

$$\begin{aligned} S_{cc}(0) &= RT \left[\frac{RT}{c_1 c_2} - 2K_0 + (-12c_1 + 6)K_1 \right. \\ &\quad \left. + (-48c_1^2 + 48c_1 - 10)K_2 \right. \\ &\quad \left. + (-160c_1^3 + 240c_1^2 - 108c_1 \right. \\ &\quad \left. + 14)K_3 \right]^{-1} \end{aligned} \quad (13)$$

In liquid, the viscous flow depends on the cohesive interaction, and this interaction results from the grouping of geometric and electronic shell effects (Starace *et al.*, 2008). The KRP equation for liquid alloy was developed to consider the cohesion interaction in terms of the enthalpic effect to incorporate the viscous flow in the liquid alloy. The equation at temperature T is expressed as;

$$\ln \eta = c_1 \ln \eta_1 + c_2 \ln \eta_2 - \frac{\Delta H_M}{3RT} \quad (14)$$

Where, η and η_i (i=1,2), are the viscosity of the alloy and viscosity of individual components respectively. The change in viscosity with temperature for the metals is given as (Brandes & Brook, 2013);

$$\eta_i = \eta_0 \exp \left(\frac{E}{RT} \right) \quad (15)$$

Where, η_0 and E for metal are constants and their units are similar to the unit of viscosity and energy per mole, respectively.

The surface tension of an alloy by the Butler equation as improved by Kaptay at temperature (T) is

$$\sigma = \frac{S_i^0}{S_i} \sigma_i^0 + \frac{RT}{S_i} \ln \frac{C_i^S}{C_i^b} + \frac{G_i^{S,XS} - G_i^{b,XS}}{S_i} \quad (16)$$

Where, σ_i^0 and S_i^0 are surface tension and molar surface area of pure liquid metal, S_i is the partial molar surface area of component i respectively. $G_i^{s,xs}$, and $G_i^{b,xs}$ are the partial excess free energy of mixing in the surface and bulk of constituent components of the alloy, respectively.

The partial excess Gibbs energy of i^{th} a component of an alloy is related to the excess Gibbs energy by the relation given below (Egry *et al.*, 2010).

$$G_i^{xs} = \Delta G^{xs} + \sum_{j=1}^2 (\delta_{ij} - c_j) \frac{\partial(\Delta G^{xs})}{\partial c_j} \quad (17)$$

Where, δ_{ij} is the Kronecker delta function.

The molar surface area of each metal is expressed as (Kaptay, 2008);

$$S_i^0 = \chi \left(\frac{M_i^0}{\rho_i^0} \right)^{2/3} N^{1/3} \quad (18)$$

Where, M_i^0 , ρ_i^0 , χ , and N is molar mass, the density of each pure metal at its melting temperature, geometrical constant, and Avogadro's number, respectively. The expression of the geometrical constant is given as;

$$\chi = \left(\frac{3f_V}{4} \right)^{\frac{2}{3}} \frac{\pi^{\frac{1}{3}}}{f_S} \quad (19)$$

Where, f_V and f_S are volume and surface packing fractions, respectively. The values of these packing fractions depend on the type of crystal structure of every pure component of alloys. The surface tension (σ_i^0) and density (ρ_i^0) of metal at temperature T are expressed as (Brandes & Brook, 2013);

$$\sigma_i^0 = \sigma_i + \frac{\partial \sigma}{\partial T} (T - T_0) \quad (20)$$

$$\rho_i^0 = \rho_i + \frac{\partial \rho}{\partial T} (T - T_0) \quad (21)$$

Where, σ_i and ρ_i are surface tension and density of the metal at its melting temperature (T_0), respectively. The terms $\frac{\partial \sigma}{\partial T}$ and $\frac{\partial \rho}{\partial T}$ are temperature derivatives of surface tension and density, respectively.

RESULTS AND DISCUSSION

The exponential temperature-dependent interaction parameters for the alloys Mg-Pb and Mg-Ga were optimized using equation (8). The parameters for both alloys are given in Table 1.

Table1. The exponential temperature-dependent interaction parameters of molten Mg-Pb and Mg-Ga alloys

Mg-Pb	Mg-Ga
$K_0 = -37785.91 \exp(-7.16783 \times 10^{-5} T)$	$K_0 = -40495.1 \exp(-5.9256 \times 10^{-5} T)$
$K_1 = 22239.43 \exp(-1.8401 \times 10^{-4} T)$	$K_1 = -12829.43 \exp(-2.4428 \times 10^{-4} T)$
$K_2 = 505013.86 \exp(-8.7964 \times 10^{-3} T)$	$K_2 = 31004.45 \exp(-8.9101 \times 10^{-3} T)$
$K_3 = -60866.13 \exp(-3.5504 \times 10^{-3} T)$	

K_0 , K_1 , K_2 , and K_3 are zeroth, first, second and third-order of exponential temperature-dependent interaction parameters, respectively

The parameters thus optimized were used to compare different properties of binary alloys Mg-Pb, and Mg-Ga at temperature 1000 K. During the calculation of parameters, it did not apply statistical method like mean square deviation or others for the best fit, and hence the parameters used here are considered as appropriate for the study.

Thermodynamic properties

For the theoretical analysis of the thermodynamic property, we considered equations (5), (9), and (11) as mentioned above. The excess Gibbs free energy of the molten alloys was computed by the R-K polynomials framework. The computed excess free energy of mixing for both alloys is shown in Fig. 1.

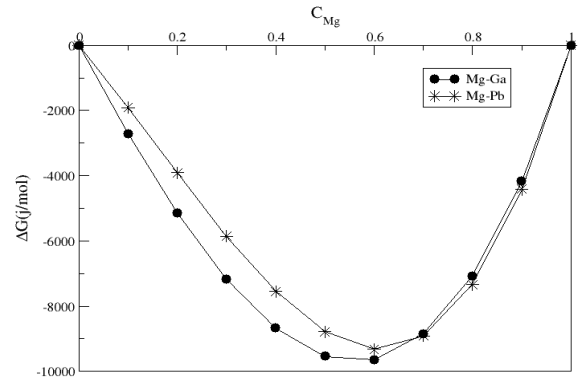


Fig. 1. Excess Gibbs free energy of mixing vs. concentration of Mg

It was observed that below 0.7 concentration of Mg, the alloy Ga-Mg seemed to be more interacting but above the 0.7 concentration of Mg, it was slightly less interacting than the alloy Mg-Pb. Similarly, the computed values of enthalpy of mixing for both the alloys are shown in Fig. 2 which tells that the enthalpy of mixing of Mg-Ga is more negative up to 0.7 concentration of Mg than the alloy Mg-Pb. Thus from both Figs. 1 and 2, it can be said that the binary liquid alloy Mg-Ga seems to be more interacting at a lower concentration of Mg, whereas it is nearly equally interacting with Mg-Pb at a higher concentration of Mg for both the alloys.

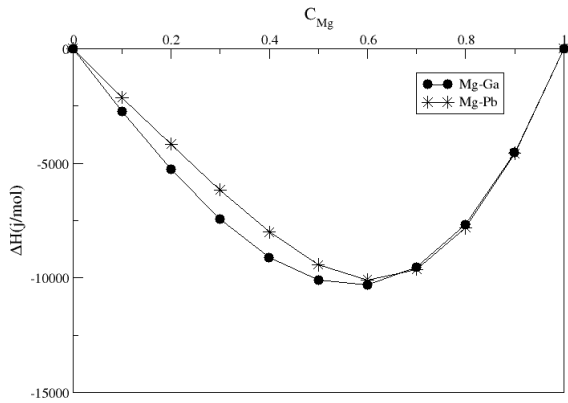


Fig. 2. Enthalpy of mixing vs. concentration of Mg

The computed values of entropy of mixing which mainly provide knowledge of constitutive molecular properties or specific molecular effects in the mixture, for both the alloys are shown in Fig. 3. It is clear from the figure that the entropy change of mixing for both the alloys remains nearly the same.

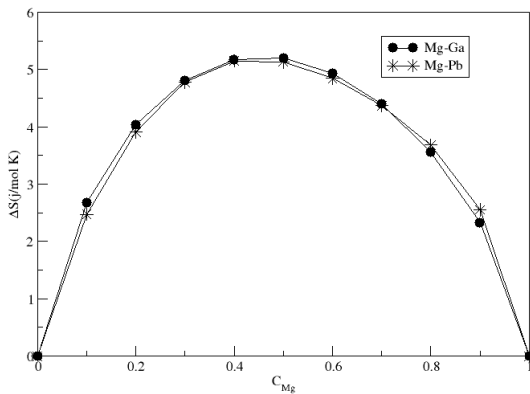


Fig. 3. The entropy of mixing vs. concentration of Mg

Structural properties

There is no direct way to distinguish the grouping of constituent atoms of the mixture. Thus, the identification of the arrangement of atoms in an alloy is very difficult.

However, experimentally the local arrangement of atoms of a constituent of the mixture can be studied by diffraction method, but it is a difficult task too. To overcome this problem and to study the arrangement of constituent atoms theoretically, the determination of Concentration fluctuations in long-wavelength limit $S_{cc}(0)$ was considered an important tool (Bhatia & Thornton, 1970). At a given concentration, the alloy is said to have the complex tendency if $S_{cc}(0) < S_{cc}^{id}(0)$, whereas it has the segregating tendency if $S_{cc}(0) > S_{cc}^{id}(0)$.

The computed values of $(S_{cc}(0))$ at various concentrations of magnesium for both alloys are given in Fig. 4. Figure cleared that at about 0.15 concentration of Mg, the alloy Pb-Mg has segregating tendency but above this concentration of Mg, it showed an ordering nature. The alloy Mg-Ga has an ordering nature within the entire concentration of Mg.

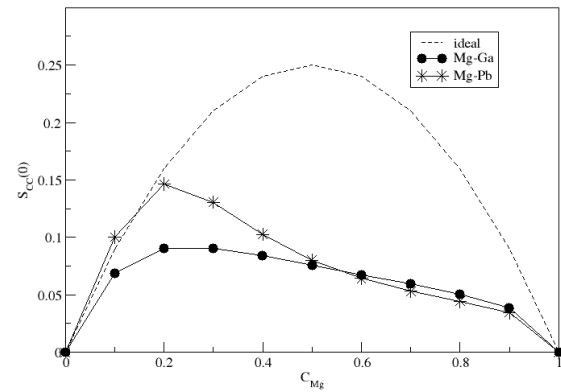


Fig. 4. Concentration fluctuation in long-wavelength limit vs. concentration of Mg

Viscosity

Viscosity is considered an important atomic transport property of liquid alloys. We used the KRP equation for the comparison of the atomic transport behavior of Mg-Pb and Mg-Ga alloys at 1000 K as a function of concentration. The viscosity of the alloys thus computed is compared in Fig. 5. The viscosity of Mg-Pb alloy was found to be more than Mg-Ga alloy with the increase in the concentration of Mg. But for both the alloys the viscosity increased up to 0.6 concentration of Mg and then it decreased beyond that concentration of Mg.

Surface tension

To calculate the surface tension by the improved derivation of the Butler equation, the densities, partial excess Gibbs free energies, and surface tensions, and the component metals at the temperature of the investigation are required. Surface tensions and densities of constituent metals at 1000 K were calculated from their values at

respective melting temperatures by using equations (20) and (21), respectively. For the unknown or negligible excess molar volume of the alloy, the partial molar volume was replaced by the molar volume of the pure component and hence the partial surface area (S_i) of each component was replaced by surface area (S_i^0) of the same pure component (Kaptay, 2020, 2019).

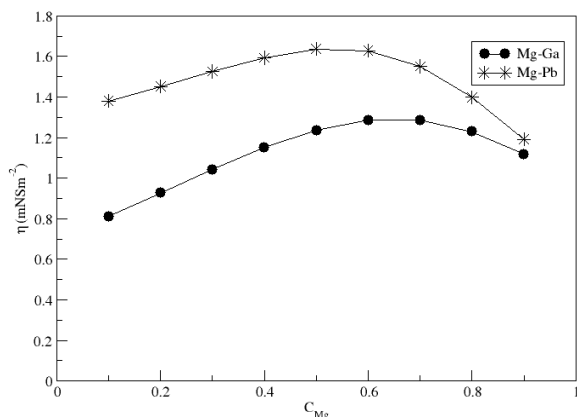


Fig. 5. Viscosity vs. concentration of Mg

Figure 6 is the graph of computed values of surface tension of binary liquid Mg-Pb and Mg-Ga alloys. In the case of alloy Mg-Ga, the surface tension decreased whereas it increased for the alloy Mg-Pb alloy with the increase in the concentration of Mg indicating that the Mg atoms tend to remain on the surface in the case of Mg-Ga alloy whereas the lead atoms show the tendency to remain on the surface of Mg-Pb alloy.

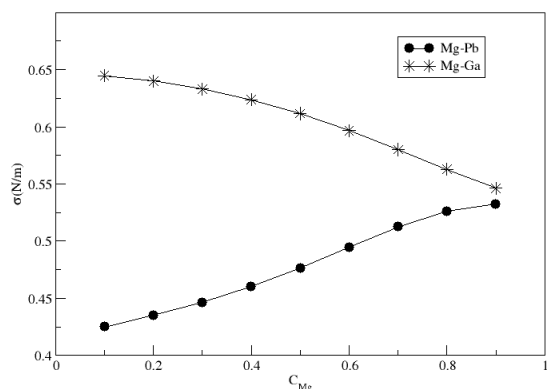


Fig. 6. Surface tension vs. concentration of Mg

CONCLUSION

The comparison of the thermodynamic, structural, and microscopic behavior of binary liquid magnesium lead and magnesium gallium alloys at 1000 K alloy under the assumption of exponential temperature-dependent interaction parameters explains that the magnesium

gallium is somewhat interacting than magnesium lead alloy. The theoretical study shows that the magnesium gallium alloy has more ordering nature within the whole range of concentration. The surface tension of the Mg-Ga alloy decreases but it increases in the case of Mg-Pb alloy but viscosity at first increases and then decreases with an increase in the concentration of magnesium.

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