THERMODYNAMIC PROPERTIES OF Al–Ce–Mn (or Zn) LIQUID SOLUTIONS①

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ABSTRACT

Thermodynamic properties of Al–Ce–Mn and Al–Ce–Zn liquid systems were studied by direct equilibrium method at 700 and 800 ℃ respectively. The results obtained include: equilibrium products, their standard Gibbs energies of formation, equilibrium constants of reactions and activity interaction coefficients between Ce and Mn or Zn in liquid aluminum.

Key words: aluminum–base solutions cerium manganese zinc thermodynamic properties

1 INTRODUCTION

Because of their good effects of purification, modyfication and alloying on the structure and properties of alloys[1–2], rare earth elements have been widely used in the production and processing of aluminum alloys. The thermodynamic properties of aluminum-base dilute solutions have been studied by some authors[3–8], but scarcely have the rare earth elements been involved in. To investigate the thermodynamic properties of rare earth elements in aluminum-base solutions, the interactions between Ce and S, Cu, Si, Mg or Fe have been studied[9–10], and in this paper, those between Ce and Mn or Zn are studied further.

2 EXPERIMENTAL

The studies were carried out with aluminum crucibles in a vertical-placed Mo–wire resistance furnace under high-purity argon atmosphere. The purity of starting materials was $>99.9\%$. To reach equilibrium, the melt of Al–Ce–Mn system was kept at 800 ℃ for 90 min and the one of Al–Ce–Zn system was kept at 700 ℃ for 60 min. The samples were extracted from the melts with quartz tubes and then quenched in cold water rapidly. The contents of components were limited within 0～1.5 wt–% and determined by spectral analysis. The compositions of equilibrium products were identified by electron diffracton and energy spectrum analysis with a TEM.

According to calculated result, the volatility of Zn could be neglected in experiment.

3 RESULTS AND DISCUSSION

3.1 *Equilibrium Products*

The structure of the equilibrium phases could be determined with the monocrystalline electron diffraction patterns under TEM

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and their compositions with the energy spectrum results, therefore, the equilibrium products were identified as $AlCe_2Mn_3$ for Al–Ce–Mn system and as Al_2CeZn_2 and Ce_3Al_{11} for Al–Ce–Zn one.

3.2 *Equilibrium Constants*

For the two systems, equilibrium reactions could be written as

$$Al_iCe_jM_k(s) = i[Al](1)+j[Ce]+k[M] \quad (1)$$

Under the conditions of the experiments, the contents of Ce, Mn and Zn were very low and Al could be regarded as pure substance, so $a_{Al}=1$ and equilibrium constant $K_{Al_iCe_jM_k}=a_{Ce}^{j}\cdot a_{m}^{k}$ and apparent one $K'_{Al_iCe_jM_k}=[\%Ce]^j\cdot[\%M]^k$, hence,

$$K_{Al_iCe_jM_k}=(f_{Ce}[\%Ce])^j(f_M[\%M])^k \quad (2)$$

$$\lg K_{Al_iCe_jM_k}=\lg K'_{Al_iCe_jM_k}+j\lg f_{Ce}+k\lg f_M$$
$$=\lg k'_{Al_iCe_jM_k}+j(e_{Ce}^{Ce}[\%Ce]+e_{Ce}^{M}[\%M])$$
$$+k(e_M^M[\%M]+e_M^{Ce}[\%Ce]) \quad (3)$$

Because of low values of salt-interaction coefficients, $e_{Ce}^{Ce}[\%Ce]$ and $e_M^M[\%M]$ could be neglected. In addition, $e_M^{Ce}=(M_M/M_{Ce})\,e_{Ce}^{M}=Ae_{Ce}^{M}$, thus equation (3) was arranged as

$$-\lg K'_{Al_iCe_jM_k}=-\lg K_{Al_iCe_jM_k}+e_{Ce}^{M}(j[\%M]+kA[\%Ce]) \quad (4)$$

For Al–Ce–Mn system, $i=1$, $j=2$, $k=3$, $A=0.39$ and for Al–Ce–Zn, $i=2$, $j=1$, $k=2$, $A=0.47$, then equation (4) was rewritten for the two systems, respectively, as follows:

$$-\lg K'_{AlCe2Mn3}=-\lg K_{AlCe2Mn3}+e_{Ce}^{Mn}\times(2[\%Mn]+1.17[\%Ce]) \quad (5)$$

$$-\lg K'_{Al2CeZn2}=-\lg K_{Al2CeZn2}+e_{Ce}^{Zn}\times([\%Zn]+0.94[\%Ce]) \quad (6)$$

The experimental data of the two systems were calculated using equations (5) and (6) and shown in Fig. 1 and 2, respectively.

The data with low contents of components being treated with least square method, linear equations for the two systems were de

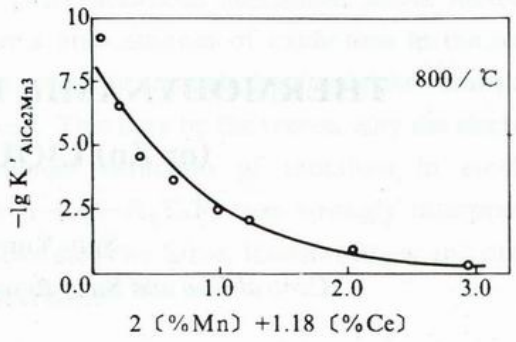

Fig. 1 Concentration dependence of $-\lg K'_{AlCe2Mn3}$ in liquid aluminum

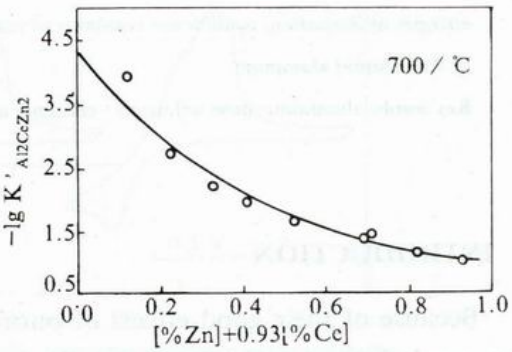

Fig. 2 Concentration dependence of $-\lg K'_{Al2CeZh2}$ in liquid aluminum

rived, respectively, as follows:

$$-\lg K'_{AlCe2Mn3}=7.76-5.19(2[\%Mn]+1.18[\%Ce])\ (r=0.93) \quad (7)$$

$$-\lg K'_{Al2CeZn2}=4.35-5.54([\%Zn]+0.93[\%Ce])\ (r=0.96) \quad (8)$$

Hence, at 800 ℃, $\lg K_{AlCe2Mn3}=-7.76$, $K_{AlCe2Mn3}=1.76\times10^{-8}$ and when at 700 ℃, $\lg K_{Al2CeZn2}=-4.35$, $K_{Al2CeZn2}=4.48\times10^{-5}$.

3.3 *Standard Gibbs Energies of Formation of Equilibrium Products*

The standard Gibbs energies of formation of the equilibrium products, $AlCe_2Mn_3$ and Al_2CeZn_2, were determined in liquid aluminum as, respectively

$$\triangle G^0_{AlCe2Mn3}=-RT\ln(1/K_{AlCe2Mn3})$$
$$=-159.3\ \text{kJ/mol}$$

$$\triangle G^{0}_{Al2CeZn2} = -RT\ln(1 / K_{Al2CeZn2}) = -81.0 \text{ kJ / mol}$$

3.4 *Activity Interaction Coefficients Between* Ce *and* Mn *or* Zn

The slope of equation (4) was the activity interaction coefficient, e^{M}_{Ce}. According to the comparisons between equation (5) and (7) or (6) and (8), the coefficients were determined: $e^{Mn}_{Ce} = -5.19$, $e^{Zn}_{Ce} = -5.54$. In addition, $e^{Ce}_{Mn} = 0.39$, $e^{Mn}_{Ce} = -2.03$, $e^{Ce}_{Zn} = 0.47$, $e^{Zn}_{Ce} = -2.59$, $\varepsilon^{Mn}_{Ce} = \varepsilon^{Ce}_{Mn} = (230M_{Mn} / M_{Al})$, $e^{Mn}_{Ce} = -2{,}430$, $\varepsilon^{Zn}_{Ce} = \varepsilon^{Ce}_{Zn} = (230M_{Zn} / M_{Al})$, $e^{Zn}_{Ce} = -3{,}088$.

4 CONCLUSIONS

(1) The equilibrium products are identified as $AlCe_2Mn_3$ for Al–Ce–Mn system and as Al_2CeZn_2 and Ce_3Al_{11} for Al–Ce–Zn one.

(2) The equilibrium constant is 1.76×10^{-8} at 800 ℃ for the reaction $AlCe_2Mn3_{(s)} = Al_{(l)} + 2[Ce] + 3[Mn]$ and 4.48×10^{-5} at 700 ℃ for $Al_2CeZn2_{(s)} = 2Al_{(l)} + [Ce] + 2[Zn]$.

(3) The standard Gibbs energy of formation of the equilibrium product is −159.3 kJ / mol for $AlCe_2Mn_3$ at 800 ℃ and −81.0 kJ / mol for Al_2CeZn_2 at 700 ℃, respectively, in liquid aluminum.

(4) The activity interaction coefficients between Ce and Mn at 800 ℃ are $e^{Mn}_{Ce} = -5.19$, $e^{Ce}_{Mn} = -2.03$, $\varepsilon^{Mn}_{Ce} = \varepsilon^{Ce}_{Mn} = -2{,}430$; and those between Ce and Zn at 700 ℃ are $e^{Zn}_{Ce} = -5.54$, $e^{Ce}_{Zn} = -2.59$, $\varepsilon^{Zn}_{Ce} = \varepsilon^{Ce}_{Zn} = -3{,}088$.

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