THERMODYNAMIC PROPERTIES OF Al-Ce-Pb (or Sn) LIQUID SOLUTIONS①

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ABSTRACT

Thermodynamic properties of Al-Ce-Pb and Al-Ce-Sn liquid systems were studied by direct equilibrium method at 800 C. The results obtained include: equilibrium products, their standard Gibbs energies of formation, equilibrium constants of reactions and activity interaction coefficients between Ce and Pb or Sn in liquid aluminum.

Key words: aluminum-base solutions cerium lead tin thermodynamic properties

1 INTRODUCTION

Because of their good effects of purification, modification 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 the rare earth elements in aluminum-based solutions, the interactions between Ce and some important elements have been studied[9,10], and in this paper, those between Ce and Pb or Sn are studied.

2 EXPERIMENTAL

The studies were carried out with alumina crucibles in a vertical-placed Mo-wire resistance furnace under high-purity argon atmosphere, the accuracy of the temperature measurement with a DWT—702 instrument was ±2 C. The purity of starting materials was ≥ 99.9%. To reach equilibrium, the melts were kept for 60 min at 800 C for the two systems, Al-Ce-Pb and Al-Ce-Sn. 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 selected areas electron diffraction (SAED) studies and the energy dispersive spectrum analyses with a transmission electron microscope (TEM).

According to the calculated result, the volatility of Pb and Sn could be neglected under the conditions of the experiment.

3 RESULTS AND DISCUSSION

3.1 *Equilibrium Products*

The samples being analysed with the TEM, the structure of the equilibrium phases could be determined with the SAED patterns and their compositions with the energy dispersive spectrum results, therefore, Ce_3Al_{11} was identified for both of the two systems. A $[10\bar{1}]$ diffraction pattern of Ce_3Al_{11} was

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shown in Fig. 1.

Besides, there existed Ce_mPb_n or Ce_iSn_j for the two systems, respectively, but their exact compositions had not been identified reliably. This was because that Ce, Pb and Sn have larger atomic semi-diameters, so Ce_mPb_n and Ce_iSn_j phases are thicker. It is difficult to transmit electron beam through them, and enough diffraction patterns had not been obtained.

Fig. 1 $[10\bar{1}]$ SAED pattern of the Ce_3Al_{11} phase

3.2 *Equilibrium Constants*

For both of the two systems, equilibrium reactions could be written as

$$Ce_3Al_{11(s)} = 11Al_{(l)} + 3[Ce] \quad (1)$$

under the conditions of the experiments, the contents of components were very low and Al could be regarded as pure substance, so $a_{Al} = 1$ and equlibrium constant $K_{Ce_3Al_{11}} = a_{Ce}^3$ and apparent one

$$K'_{Ce_3Al_{11}} = [\%Ce]^3, \text{ hence,}$$

$$K_{Ce_3Al_{11}} = (f_{Ce}[\%Ce])^3 \quad (2)$$

$$\lg K_{Ce_3Al_{11}} = \lg K'_{Ce_3Al_{11}} + 3\lg f_{Ce} = \lg K'_{Ce_3Al_{11}} + 3(e^{Ce}_{Ce}[\%Ce] + e^{M}_{Ce}[\%M]) \quad (3)$$

Because of low values of self-interaction coefficients, the term, $e^{Ce}_{Ce}[\%Ce]$, could be neglected. Then equation(3) was arranged as

$$-\lg K'_{Ce_3Al_{11}} = -\lg K_{Ce_3Al_{11}} + 3e^{M}_{Ce}[\%M] \quad (4)$$

The experimental data of the two systems were calculated using equation (4) and shown in Fig. 2.

The data with low contents of components being treated with least square method, linear equations for the two systems were derived, respectively, as follows:

$$-\lg K'_{Ce_3Al_{11}} = 4.20 - 8.54[\%Pb] \quad (r = 0.94) \quad (5)$$

$$-\lg K'_{Ce_3Al_{11}} = 4.05 - 5.52[\%Sn] \quad (r = 0.98) \quad (6)$$

According to the results of the two systems, at 800 C, the values of $\lg K_{Ce_3Al_{11}}$ were -4.20 and -4.05, respectively, the average of them was -4.13. Hence, the equilibrium constant of reaction(1) was $K_{Ce_3Al_{11}} = 7.48 \times 10^{-5}$.

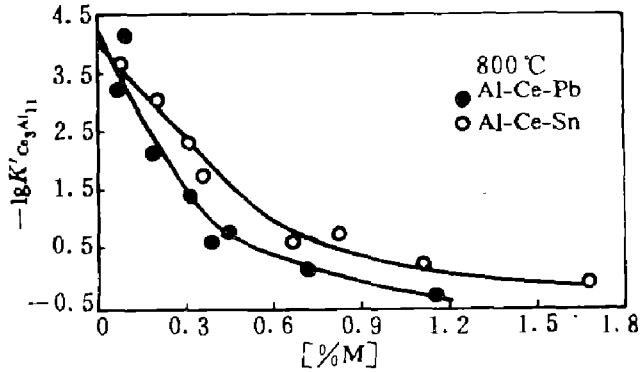

Fig. 2 Concentration dependences of $-\lg K'_{Ce_3Al_{11}}$ in liquid aluminum

3.3 *Standard Gibbs Energy of Formation of Equilibrium Product*

The standard Gibbs energy of formation of the equilibrium product, Ce_3Al_{11}, was determined as, in liquid aluminum:

$$\Delta G^{\circ}_{Ce_3Al_{11}} = -RT\ln(1/K_{Ce_3Al_{11}}) = -84.8 \text{ kJ/mol}$$

3.4 *Activity Interaction Coefficients Between* Ce *and* Pb *or* Sn

The slope of equation(4) was equal to $3e^{M}_{Ce}$. According to the comparisons between equations(4) and(5) or(6), the coefficients were determined: $e^{Pb}_{Ce} = -2.85$, $e^{Sn}_{Ce} = -1.84$. In addition, $e^{Ce}_{Pb} = (M_{Pb}/M_{Ce})$, $e^{Pb}_{Ce} = 1.48$, $e^{Pb}_{Ce} = -4.21$, $e^{Ce}_{Sn} = (M_{Sn}/M_{Ce})$, $e^{Sn}_{Ce} = 0.85$, $e^{Sn}_{Ce} = -1.56$ (to Page 51)

perimental determination by cooling down to low temperature at a certain rate. We conclude that the sluggish diffusion of rare earth solutes at low temperature and the relatively low purities of original materials are the key factors bringing about errors in final measurement results.

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$e_{Ce}^{Sn}=0.85$, $e_{Ce}^{Sn}=-1.56$, $\varepsilon_{Ce}^{Pb}=\varepsilon_{Pb}^{Ce}=(230M_P/M_{Al})$

$e_{Ce}^{Pb}=-5\ 027$, $\varepsilon_{Ce}^{Sn}=\varepsilon_{Sn}^{Ce}=(230M_{Sn}/M_{Al})$,

$e_{Ce}^{Sn}=-1\ 861$.

4 CONCLUSIONS

(1) The equilibrium products are identified as Ce_3Al_{11} for both of the two systems. Besides, there exists Ce_mPb_n or Ce_iSn_j for them, respectively;

(2) The equilibrium constant is 7.48×10^{-5} at 800 C for reaction $Ce_3Al_{11(s)}=11Al_{(l)}+3[Ce]$ in liquid aluminum;

(3) The standard Gibbs energy of formation of the equilibrium product, Ce_3Al_{11}, is −84.8 kJ/mol at 800 C in liquid aluminum;

(4) At 800 C, the activity interaction coefficients between Ce and Pb are: $e_{Ce}^{Pb}=-2.85$, $e_{Pb}^{Ce}=-4.21$, $\varepsilon_{Ce}^{Pb}=\varepsilon_{Pb}^{Ce}=-5\ 027$, and these between Ce and Sn are: $e_{Ce}^{Sn}=-1.84$, $e_{Sn}^{Ce}=-1.56$, $\varepsilon_{Ce}^{Sn}=\varepsilon_{Sn}^{Ce}=-1\ 861$.

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