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# Thermodynamic calculation on metallic thermoreduction during preparation of aluminum-rare master alloys<sup>①</sup>

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**[Abstract]** A thermodynamic calculation method on metallic thermoreduction during preparation of aluminum-rare metal alloys was presented. Taking preparation of aluminum-scandium master alloys using aluminum and magnesium thermoreduction of scandium chloride as an example, this method was applied and the results were testified by experiment.

**[Key words]** scandium; master alloys; metallic thermoreduction; thermodynamic calculation

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## 1 INTRODUCTION

Recently aluminum-rare metal alloys attract much interest. Metallic thermoreduction, in which oxides and chlorides of rare metal are reduced and in situ alloyed by aluminum, has the best prospect in all production methods of aluminum-rare metal alloys. However this method is more complex, and many aspects should be considered during process designing.

1) Due to high price of rare metal, the yield rate of rare metal should be increased as much as possibly, for example, by using excessive reducing agents. 2) For different rare metal compounds, due to their different stability, suitable metal reducing agents should be selected so as not to deteriorate the properties of alloys. 3) Some impurities are very harmful to the properties, therefore, their contents in aluminum-rare metal alloys should be controlled strictly, and the reaction container should be made of inert materials.

In order to decrease the amount of experimental research with the maximal limitation, the method of calculation and prediction should be extensively used in process designing. The primary work is to select initial components to determine the external conditions of reduction with the thermodynamic calculation results. In this article, taking the preparation of aluminum-scandium master alloys using aluminum and magnesium thermoreduction of scandium chloride as an example, some thermodynamic calculations and experimental verifications were performed.

## 2 EQUILIBRIUM THERMODYNAMIC CALCULATION IN METALLIC THERMOREDUCING REACTION

### 2.1 Calculation of standard equilibrium constant

Rare metal oxides and halides can be reduced by different metals. The standard equilibrium constants of various reducing reactions can be calculated according to the thermodynamic data of reactants and products, and suitable rare metal compounds and the corresponding metal reducing agents can be determined preliminarily. It's better to calculate equilibrium constants at different temperatures, then the suitable thermoreduction temperature can be determined.

### 2.2 Calculation of empirical equilibrium constant

Standard equilibrium constant is expressed by the activities of components at the standard chemical equilibrium. However, the reducing reactions in preparing aluminum-rare metal alloys occur in actual systems and the most concern about process designing is the equilibrium concentration of each component rather than their activities, therefore, empirical equilibrium constant should be calculated and standard equilibrium constant need to be modified according to the following aspects.

#### 2.2.1 Activity coefficient of rare metal compounds in fused salt system

To facilitate reducing reaction, reaction should occur in the liquid/liquid interface between fused salt of rare metal compounds and reducing agent metal, so it is very necessary to study the activity coefficients of rare metal compounds in fused salt system. For example, when using rare metal chlorides, fused salt system based on NaCl-KCl is usually selected; when using Li or Mg as reducing agent, LiCl or MgCl<sub>2</sub> is contained in fused salt system.

Activity coefficient is a function of temperature and concentration. Considering that rare elements should be utilized sufficiently, their conversion rates

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are generally high and the equilibrium concentrations of rare metal chlorides in fused salt system are very low, the limit activity coefficients of rare metal chlorides can be adopted in calculations.

The thermodynamic properties on halides of yttrium, lanthanum, cerium, neodymium and praseodymium have been reported<sup>[1~7]</sup>. Based on those studies, thermodynamic properties of other rare metal chlorides can be predicted<sup>[8]</sup>.

To optimize the fused salt system, the equilibrium constant related to initial concentrations of different rare metal compounds, salt mixture ratio and consumption of the reducing agent need to be calculated.

### 2.2.2 Activity coefficients of rare metal and reducing agent in alloy solution

During reducing reaction, rare metal produced by reduction and excessive metal reducing agent were in-situ alloyed by aluminum. When reducing agent and rare metal have a big solubility in aluminum, alloy solution forms; when there is a small solubility, aluminum solid solution forms and the activity coefficients of metals need to be considered; when there is only a very small solubility or even insolubility, single phase will form and the activity coefficient is equal to 1. If intermetallic compound forms by aluminum and reduced rare metal, Gibbs free energy of formation should be considered at the same time.

### 2.2.3 Effect of side reaction

For complex reaction system, the effect of side reaction on chemical equilibrium should be considered, too. When solid oxide of rare metal is used as raw material, it should be considered whether reducing agent oxide and raw material can form more stable complex oxide. If that is true, it will lower the conversion rate. Sometimes reducing agent oxide and aluminum form more stable complex oxide. At this condition the reducing agent will be substituted, then it will affect the activity coefficient of reducing agent.

## 2.3 Estimation of equilibrium conversion rate and determination of process conditions

After synthetically considering all factors in 2.2, calculating empirical equilibrium constant and combining initial concentrations of reducing agent and rare metal compound, equilibrium concentration and conversion rate of rare metal and its compound can be calculated according to the expression of empirical equilibrium constant, and process designing of metallic thermoreduction can be optimized according to the moving principle of chemical equilibrium.

Only considering all above factors, the calculation result of equilibrium constant is useful in practice. Therefore, starting out from processing, economy and other criterions, experimental route can be determined effectively after analyzing the above calculation result. Because thermodynamic databases that can be used to calculate actual system are inadequate,

some special methods, for example, analogical analysis referring to thermodynamic data of some borides and trialuminides, has to be adopted in thermodynamic calculation.

## 3 THERMODYNAMIC CALCULATION AND OPTIMIZATION OF PROCESSING CONDITIONS

In this section, the preparation of scandium master alloys using aluminum and magnesium thermoreduction of scandium chloride is taken as an example.

### 3.1 Calculation of Gibbs formation energy of Al<sub>3</sub>Sc intermetallic compound

Scandium and aluminum can form Al<sub>3</sub>Sc intermetallic compounds which are insoluble in aluminum<sup>[9]</sup>, Gibbs formation energy of Al<sub>3</sub>Sc must be estimated before thermodynamic calculation. The formation enthalpy of Al<sub>3</sub>Sc reported by several references has much difference. The limit activity coefficient of scandium in aluminum at eutectic temperature, calculated by Petrashkevich<sup>[10]</sup> is  $4.5 \times 10^{-7}$ , and the estimated Gibbs formation energy of Al<sub>3</sub>Sc is  $-128 \text{ kJ/mol}$ . However, according to the relations of enthalpy, entropy, activity and temperature measured at high temperature when scandium dissolves in aluminum reported by Ref. [11], the estimated Gibbs formation energy of Al<sub>3</sub>Sc is  $-147 \text{ kJ/mol}$ .

The procedures of estimating standard formation enthalpy of Al<sub>3</sub>Sc is as following: 1) estimate standard formation enthalpy of Al<sub>3</sub>Sc ( $-168 \text{ kJ/mol}$ ) by variation regularities of standard formation enthalpies of transition-metal trialuminides of subgroup IV~VI reported by Ref. [12]; 2) process standard formation enthalpies of some transition-element diborides and trialuminides of subgroup III~V (Table 1) with the method of least squares, obtaining the following linear relationship,

$$\Delta H_f^\ominus(\text{MeAl}_3) = 0.505406 \Delta H_f^\ominus(\text{MeB}_2) + 3.957268 \text{ (KJ/mol)};$$

3) according to the above linear relationship and the standard formation enthalpy of Sc<sub>3</sub>B<sub>2</sub> ( $-307 \pm 15 \text{ kJ/mol}$ )<sup>[13]</sup>, the standard formation enthalpy of Al<sub>3</sub>Sc can be calculated ( $-159 \text{ kJ/mol}$ ); 4) the estimated formation entropy of Al<sub>3</sub>Sc by the average values of formation entropies of other transition-metal trialuminides is  $22.0 \text{ J/mol}$ , which is in accordance with the measured result in Ref. [11]; 5) without considering that heat capacity of Al<sub>3</sub>Sc varies with temperature, only considering the fusion enthalpy and entropy of aluminum, the estimated Gibbs formation energy of Al<sub>3</sub>Sc at eutectic temperature is  $-138 \text{ kJ/mol}$ , which is very near to the average values in Refs. [10~12].

After considering Gibbs formation energy of Al<sub>3</sub>Sc, the correction coefficient of equilibrium con-

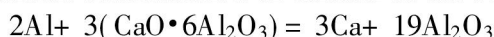
**Table 1** Standard formation enthalpies of some transition metal diborides and trialuminides

Element	$\Delta H_f^\ominus$ (Diboride)	$\Delta H_f^\ominus$ (Ttrialuminide) / (kJ·mol <sup>-1</sup> )	
	/(kJ·mol <sup>-1</sup> )	Reference value	Calculated value
Ti	-280 <sup>[14]</sup>	-147 <sup>[13]</sup>	-155
Zr	-323 <sup>[14]</sup>	-182 <sup>[13]</sup>	-178
Hf	-336 <sup>[14]</sup>	-185 <sup>[13]</sup>	-185
V	-204 <sup>[13]</sup>	-108 <sup>[13]</sup>	-114
Nb	-175 <sup>[12]</sup>	-119 <sup>[13]</sup>	-99
Ta	-209 <sup>[13]</sup>	-112 <sup>[13]</sup>	-117
Gd	-82 <sup>[14, 15]</sup>	-44 <sup>[14, 15]</sup>	-45
Sc	-307 <sup>[13]</sup>	-168 <sup>[13]</sup>	-159

stant in metallic thermoreducing reaction at 1100 K is  $6 \times 10^6$ . This result shows that the equilibrium constant increases greatly due to the formation of  $\text{Al}_3\text{Sc}$  compound. During the reaction, the equilibrium concentration of  $\text{Al}_3\text{Sc}$  is very low, so the yield rate of scandium is near to 100%.

### 3.2 Effect of other factors

The activity coefficient of magnesium in dilute solution of aluminum is  $0.6^{[16]}$ , according to the equilibrium concentration of calcium in the reaction of



and the thermodynamic data of compounds ( $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ )<sup>[17, 18]</sup>, the limit activity coefficient of calcium is estimated to be  $10^{-3}$ . Sodium is basically insoluble in aluminum and exists in a single phase whose activity is equal to 1. Therefore, when using magnesium and calcium as reducing agent and considering the effect of activity coefficient of reducing metal, the correction coefficients of equilibrium constant are 0.5 and  $3 \times 10^{-5}$ .

According to the thermodynamic data of halides on yttrium, lanthanum, cerium, neodymium and praseodymium<sup>[1~7]</sup>, the activity coefficients of scandium chloride in fused salt system of NaCl, KCl or NaCl+KCl are estimated to be  $5 \times 10^{-5}$ ,  $4 \times 10^{-8}$  and  $10^{-6}$ , respectively.

### 3.3 Calculation of equilibrium constant in reducing reaction

Considering the formation enthalpy of  $\text{Al}_3\text{Sc}$  and the activity coefficient of each component, referring to the data of inorganic matters thermodynamic database of National Bureau of Standards, the equilibrium constants of different materials containing Sc which are reduced by different reducing agents at 1100 K are calculated and listed in Table 2.

### 3.4 Estimation of equilibrium conversion rate

Supposing that the initial mole concentration of scandium chloride is 25%, the ultimate concentration of magnesium chlorides and calcium chlorides is

**Table 2** Equilibrium constants at 1100 K

Material	Reducing agent	Equilibrium constant
$\text{Sc}_2\text{O}_3$ solid	Al	$9.2 \times 10^{-7}$
	Na	$1.6 \times 10^{11}$
	Mg	$5.7 \times 10^{-4}$
	Ca	$7.6 \times 10^3$
$\text{ScCl}_3$ fused salt	Al	$* 4.7 \times 10^{-6}$
	Na	$9.5 \times 10^{13}$
	Mg	$1.6 \times 10^3$
	Ca	$8.6 \times 10^{14}$
$\text{ScF}_3$ solid	Al	$6.6 \times 10^{-9}$
	Na	$1.3 \times 10^{-2}$
	Mg	1.2
	Ca	$3.6 \times 10^7$
$\text{ScCl}_3$ in NaCl	Al	$* 1.4 \times 10^{-2}$
	Na	$2.9 \times 10^{16}$
	Mg	$5.8 \times 10^6$
	Ca	$4.9 \times 10^{13}$
$\text{ScCl}_3$ in KCl	Al	$* 1.1 \times 10^{-5}$
	Na	$4.6 \times 10^{15}$
	Mg	$3.1 \times 10^4$
	Ca	$9.2 \times 10^{10}$

\* Gaseous monatomic  $\text{AlCl}_3$

33.3%. If the ultimate concentration of  $\text{ScCl}_3$  in KCl and NaCl is 50%. The average activity coefficient of  $\text{MgCl}_2$  in NaCl and KCl is 0.25 and  $0.07^{[8]}$ , respectively. Referring to data in Ref. [19], the activity coefficient of  $\text{CaCl}_2$  in NaCl and KCl is 0.32 and 0.13, according to Gibbs-Duham formula. NaCl-KCl system is ideal fused salt<sup>[2]</sup>. Therefore, the residual concentration of scandium chloride can be calculated, according to the equilibrium constant listed in Table 2, when the permitted concentration of residual reducing agent reaches the highest (see Table 3).

**Table 3** Calculated value and estimated value of residual concentration of scandium chloride

[NaCl]:[KCl]	Reducing agent	$[\text{ScCl}_3] / (\text{mol} \cdot \text{L}^{-1})$
10:1 (estimation)	Na	$3.4 \times 10^{-17}$
	Mg	$1.7 \times 10^{-4}$
	Ca	$6.5 \times 10^{-7}$
0:1 (estimation)	Na	$2.2 \times 10^{-16}$
	Mg	$3.2 \times 10^{-2}$
	Ca	$3.4 \times 10^{-4}$
2:1 (experiment)	Na	can not be found
	Mg	
	Ca	

The calculation results in Table 2 and Table 3 show that scandium chloride is easy to be reduced and can be reduced to Sc by Na, Ca and Mg, but can't by Al. Na and Ca are very strong reducing agents. Considering that Na and Ca are not only harmful to the properties of aluminum alloy, but also very expensive, and industrial aluminum alloys containing Sc usually contain 2% ~ 5% Mg, Mg is the most suitable metal reducing agent. When using Mg as reducing agent in NaCl-KCl fused salt system at 1100 K,

the conversion rate of Sc can reach 100%. During the reducing reaction, aluminum and the reduced scandium are in-situ alloyed and the reducing reaction can be greatly accelerated.

#### 4 EXPERIMENTAL VERIFICATION

The experimental apparatus is a sealed reactor consisting of vertical electric furnace, graphite crucible and feeder. Beforehand, adding Al and Mg to reactor and adding a small amount of mixture of NaCl and KCl as fluxing agent. When the temperature reached 750~800 °C, Al and Mg in reactor were melted, then adding chloride fused salt block containing scandium chloride to reactor through the feeder<sup>[20]</sup>. Reducing process can be performed in stirring condition. The productivity of this kind of apparatus is 10 kg per furnace.

According to the chemical analysis result, the average content of Sc in the obtained master alloy ingot is 2% (mass fraction). When the experiment ends, scandium chloride can't be found in salt phase, which is in accordance with the calculation result.

#### 5 CONCLUSIONS

1) A thermodynamic calculation method of selecting processing route was presented, and the possible combined equilibrium constant table was determined, corresponding to the interactive actual equilibrium constants of initial and ultimate products, the ultimate concentrations of the initial materials can be estimated at different conditions.

2) An empirical formula of standard formation enthalpy of rare element trialuminide estimated according to formation enthalpy of the corresponding diboride was given.

3) Taking preparation of aluminum-scandium master alloys using aluminum and magnesium thermoreduction of scandium chloride as an example, this kind of calculation method was applied and the results were testified by experiment.

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