Thermodynamic properties of liquid Sc-Al alloys: model calculations and experimental data

A B Shubin¹, K Yu Shunyaev¹

¹Institute of Metallurgy, Urals Division of RAS, 101 Amundsena St., Ekaterinburg, 620016, Russia

E-mail: fortran@list.ru

Abstract. Thermodynamic information available for binary scandium-aluminium system has been obtained earlier by e.m.f. and calorimetry methods and also by semi-empirical approaches described in literature. In this work these data were reconsidered for all intermetallides in Sc-Al system. To calculate the excess thermodynamic functions of liquid Sc-Al alloys special computer program package have been used. The enthalpies of mixing of liquid scandium and aluminium were found in all the composition range of the phase diagram at the temperatures 1873, 1973 and 2073 K.

1. Introduction

The thermodynamic properties of scandium-aluminium system were investigated by different authors [1-5]. Thermochemistry of solid Sc-Al alloys has been studied mainly in the papers [2-4]. In the number of cases different researchers present the data with significant disagreements. Liquid alloys properties systematized in [5] also show the disperancy for different measurement methods.

The circumstances mentioned above caused the need of critical estimation of the thermochemical characteristics of solid scandium-aluminium alloys. Besides that, the modern software packages allow to calculate (on the basis of models accepted) the properties of liquid solutions in this binary system.

The aim of the present work is the estimation and mutual coordination of the experimental data for all the intermetallic compounds (IMC) in Sc-Al system and, also, investigation of the liquid solutions thermodynamics in all the composition range on the basis of ISIP model. Here ISIP is “an ideal solution of interaction products”.

The software package “Terra” including ISIP algorithm and using in this study is the result of further development of the known program complex “Astra” [6]. This program contains in the database (DB) thermodynamic properties of a few thousand substances.

In order to calculate the thermochemical properties of any system in wide temperature range the program uses a fixed set of initial data concerning the components the system consists of.

To determine the calculation parameters for the thermodynamic modelling (TM) program different methods can be used: both the expert estimation of experimental data and semi-empirical approaches like Miedema model which described in details, for example, in the monograph [6].

In this study, the thermodynamic properties of pure metallic scandium were taken from [7]. Thermodynamic functions of aluminium were used directly from “Terra” package DB.
Comparing the TM results for ISIP model [8] and the data calculated using simple ideal solution approximation one can find an excess thermodynamic functions of the liquid alloy (enthalpy, entropy and Gibbs energy).

2. Results and discussion
Four intermetallic compounds were found in Sc-Al system: ScAl$_3$, ScAl$_2$, ScAl, Sc$_2$Al [3]. Measured integral heats of formation of the IMC in Sc-Al system taken from different experimental works are shown in the table 1.

Table 1. Standard enthalpies of formation ($\Delta_f H^{\circ}_{298}$) of the intermetallic compounds in scandium-aluminium system.

| IMC   | $\Delta_f H^{\circ}_{298}$, kJ/mol-at | [2] | [3] | [4] | assessed |
|-------|--------------------------------------|-----|-----|-----|----------|
| ScAl$_3$ | 41.3                                 | 43.5 | 59.8 | 42.6 |
| ScAl$_2$ | 47.6                                 | 48.0 | 94.1 | 47.8 |
| ScAl   | 67.1                                 | 46.0 | 62.0 | 51.1 |
| Sc$_2$Al | 42.6                                 | 37.0 | 28.2 | 41.0 |

One can see that the data of the study [2] (e.m.f.) are in good agreement with the data of the work [3] (calorimetry) for IMC ScAl$_3$ and ScAl$_2$. At the same time, the data differences for the other intermetallics are significant. The data [4] (HCl solution calorimetry) are considerably different also for ScAl$_3$ and ScAl$_2$ compounds. Nevertheless, these data were taken into account.

Many attempts to calculate integral enthalpies and other IMC properties using semi-empirical approaches are known. One of most successful of them is the Miedema model. Using of this model for calculation of the concentration dependence of $\Delta_f H^{\circ}$ requires the knowledge of the number of adjusted parameters (electronegativity parameter etc.).

The Miedema approach to calculation of standard formation enthalpies was successfully applied to R-Me alloys in the study [9]. Here R is rare earth metal or actinide; Me is p-metal from the group: Al,Ga,In,Tl,Sn,Pb,Sb,Bi. Model parameters found on the basis of the known experimental data allowed to describe these data with the confidence interval for any point approximately ± 13 kJ/mol-at. According to [9] this prediction accuracy is considerably higher than the imprecision of the experimental $\Delta_f H^{\circ}$ determination. Nevertheless, taking into account great systematic differences between the results of different scientific groups, the model prediction may be very useful to estimate unknown values or to analyze strongly different experimental data.

The assessed values of enthalpies of formation of intermetallides have been calculated by the following procedure. Initially we found the squared deviations of the experimental points from the theoretical curve (calculated using adapted Miedema model [9]). Further we assumed the statistical weight for each experimental value. This weight was inversely proportional to the squared deviations mentioned. Of course, the weights for each intermetallide were normalized and their sum was reducted to 1. The assessed value of the enthalpy has been calculated by averaging of the experimental values with the corresponding weights.

It can be shown that assessed values of the heats of formation are close to those calculated by the Miedema model adapted for given alloys group [9].

The other thermodynamic characteristics required to obtain the properties of Sc-Al liquid alloys were calculated using semi-empirical equations described in the monograph [6].

Besides the enthalpies of formation, the following data for each Sc-Al intermetallide were estimated:
1. Standard entropy at 298.15 K ($S^0_{298}$).
2. Enthalpy change when the substance is heating from 0 to 298.15 K ($H^0_{298} - H^0_0$).
3. Temperature and enthalpy of congruent or incongruent melting.
4. Temperature dependence of heat capacity at 0.1 MPa ($C_p$) which can be defined in the temperature range specified as the polynomial: $C_p(T) = a + by + cy^2 + dy^3 + e \times 10^5 T^{-2}$, where $y = T \times 10^{-3}$.
5. Heat capacity at the temperatures higher than melting point.

To describe the real composition and thermodynamic properties of liquid Sc-Al melts we used the ISIP model mentioned above [6]. The modelling have been carried out in the inert atmosphere (Ar) at the pressure 0.1 MPa in all the composition range of the phase diagram, in the temperature interval 1873-2073 K.

The thermodynamic functions of the following substances were taken into account: gaseous Al, Al$_2$, Sc, Ar and condensed Sc, Al, ScAl$_3$, ScAl$_2$, ScAl, Sc$_2$Al. The composition of “reference” ideal solution included only Sc and Al. According to the ISIP model, the compositions of associates (which are present in the solution) are the same with the compositions of the real intermetallic compounds in the system. Therefore, the “real” solution besides Sc and Al included the associates ScAl$_3$, ScAl$_2$, ScAl and Sc$_2$Al.

The results of molar composition calculation for liquid Sc-Al alloys at 1873 K are presented in figure 1. It can be seen that maximum concentrations of Sc$_m$Al$_n$ associates approximately conform to the compositions of corresponding intermetallics.

![Figure 1. Molar fractions of associates in Sc-Al melt at 1873 K.](image1.png)

![Figure 2. Calculated (this work, solid curve) and experimental ([5,10], dashed curve, circles) enthalpies of mixing in Sc-Al system. T=1873 K.](image2.png)

The excess thermodynamic functions (see table 2) can be easily found as the difference of the enthalpy (entropy, Gibbs energy) calculated in ISIP model and the same function determined using ideal solution model.

Integral enthalpies of mixing ($\Delta H_{mix}$) for liquid Sc-Al alloys are shown in figure 2. One can see that there is significant difference between calculated and experimental values. The value of deviation is about 5-12 kJ/mol-at for compositions with 10-40 at.% Sc. According to [5] the data of the paper [10] show systematically lower (in absolute value) enthalpies in the sequence Sc-Y-La. This conclusion agrees with the calculation results obtained in this work.
**Table 2.** Temperature and composition dependencies of the excess integral thermodynamic functions in liquid Sc-Al alloys.

| $X_{\text{Sc}}$ | 1873 K | 1973 K | 2073 K |
|-----------------|--------|--------|--------|
|                 | $-\Delta H_{\text{ex}}$, J/mol-at | $-\Delta G_{\text{ex}}$, J/mol-at | $-\Delta H_{\text{ex}}$, J/mol-at | $-\Delta G_{\text{ex}}$, J/mol-at | $-\Delta H_{\text{ex}}$, J/mol-at | $-\Delta G_{\text{ex}}$, J/mol-at |
| 0.1             | 14468  | 14668  | 14346  | 14684  | 14226  | 14703  |
| 0.2             | 28340  | 27544  | 28069  | 27508  | 27806  | 27487  |
| 0.3             | 38507  | 36223  | 38159  | 36111  | 37817  | 36015  |
| 0.4             | 43650  | 39991  | 43267  | 39806  | 42885  | 39640  |
| 0.5             | 45553  | 40645  | 45151  | 40393  | 44751  | 40163  |
| 0.6             | 43520  | 38427  | 43246  | 38163  | 42957  | 37912  |
| 0.7             | 36012  | 32433  | 35879  | 32245  | 35378  | 32065  |
| 0.8             | 24737  | 23101  | 24692  | 23015  | 24643  | 22932  |
| 0.9             | 12495  | 12019  | 12484  | 11994  | 12470  | 11969  |

**Acknowledgments**

This research is supported by the Russian Foundation for Basic Research (RFBR) grants 04-03-33109, 06-08-01290, 07-02-01049 and the Integration Project of Urals and Siberian Divisions of RAS.

**References**

[1] Royset J and Ryum N 2005 International material reviews 50 19
[2] Shubin A B, Yamshchikov L F, Yatsenko S P and Zobnin S S 1999 Metally N6 121
[3] Cacciamani G, Riani P, Borzone G, Parodi N, Saccone A, Ferro R, Pisch A, Schmid-Fetzer R. 1999 Intermetallics 7 101
[4] Pyagay I N and Vakhobov A V 1990 Metally N5 55
[5] Lebedev V A, Kober V I and Yamshchikov L F 1989 Thermochemistry of alloys of rare earths and actinides. Handbook. (Chelyabinsk: Metallurgia)
[6] Moiseev G K, Vatolin N A, Marshuk L A and Il’ inikh N I 1997 Temperature dependences of the Gibbs energy for some inorganic compounds (alternative database ASTRA.OWN) (Ekaterinburg: Urals Division of RAS)
[7] Leonidov V Ya, Aristova N M, Bergman G A, Furkalyuk M Yu, Khandamirova N E and Yungman V S 1997 The system of key thermodynamic functions of scandium and its compounds Preprint IHT RAS/1-410
[8] Moiseev G K, Il’ inikh N I, Kulikova T V 2004 thermochemical properties of phases and thermodynamic characteristics of melts in Al-Ce system Structure and properties of the metallic and slag melts: Proc. 11th Russian Conf. vol.2 pp 260-264
[9] Shubin A B, Yamshchikov L F and Raspopin S P 1986 Izv. VUZ. Tzvetnaya metallurgia N4 73
[10] Litovskii V V, Valishev M G, Esin Yu O, Geld P V and Petrushevskii M.S. 1986 Russ. J. Phys. Chem. 60 2310