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A thermodynamic study of the $D0_3$-ordered intermetallic compound Fe_3Al

Yongzhang Huang[a,1], Wenxia Yuan[b], Zhiyu Qiao[a],
Olga Semenova[c], Gabriel Bester[d], Herbert Ipser[c,*]

[a] School of Metallurgical and Ecological Engineering, University of Science & Technology Beijing, Beijing 100083, China
[b] School of Applied Science, Department of Chemistry, University of Science & Technology Beijing, Beijing 100083, China
[c] Department of Inorganic Chemistry/Materials Chemistry, University of Vienna, Währingerstr. 42, A-1090 Wien, Austria
[d] National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401, USA

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Abstract

Thermodynamic activities of aluminum in the iron–aluminum system were determined between about 720 and 850 K for the composition range between 23 and 33 at.% Al which includes the $D0_3$-ordered nonstoichiometric intermetallic compound Fe_3Al. For this purpose an electromotive force method with a single-crystal CaF_2 electrolyte was used, and the following cell arrangement was employed:

$(-)\mathrm{Pt}|\mathrm{Ir}|\mathrm{Al}_{0.85}\mathrm{Sn}_{0.15},\ \mathrm{Na}_3\mathrm{AlF}_6|\mathrm{CaF}_2|\mathrm{Al}_{1\pm x}\mathrm{Fe}_{3\pm x},\ \mathrm{Na}_3\mathrm{AlF}_6|\mathrm{Ir}|\mathrm{Pt}\,(+)$.

Activities of iron were obtained by means of a Gibbs-Duhem integration for the same composition range. The results of the activity measurements were interpreted in terms of a statistical–thermodynamic model for nonstoichiometric phases with the $D0_3$-superstructure based on defect formation energies from the literature. It was found that non-stoichiometry in Fe_3Al is caused by anti-structure atoms on two of the three possible sublattices.

Keywords: Metals and alloys; Intermetallics; Electromotive force; EMF; Thermodynamic properties; Thermodynamic modeling

1. Introduction

Iron aluminides form an interesting class of intermetallic materials which are candidates for substitution of stainless steels in structural applications at moderate to high temperatures [1]. Yet an extensive application of these alloys in engineering has been hindered by room-temperature brittleness which prevents the use of well-established processing routes of ferrous alloys [2]. Thus, two different major strategies have been proposed to improve room-temperature toughness of the materials [3–7]: thermo-mechanical processing and alloying with other elements, among them Cr, Zr, Mo, and B. However, one important step to understand the effect of alloying elements on the toughening of iron aluminides is a proper understanding of the thermodynamics of the Fe–Al system, especially in the temperature and composition range of interest.

Thermodynamic activities of aluminum in aluminium–iron alloys have been determined in the past by various authors. Radcliffe et al. [8] used an electromotive force (emf) method based on a galvanic cell with a liquid NaCl–KCl + $AlCl_3$ electrolyte to determine aluminum activities between 5 and 75 at.% Al in the temperature range 1048–1273 K. An isopiestic method was used by Eldridge and Komarek in which Al–Fe specimens were heated in a temperature gradient and equilibrated with Al vapor in a closed Al_2O_3 system [9]. Ichise et al. [10] used a Knudsen cell-mass spectrometric method to determine activities of aluminum and iron over a wide composition range between 1673 and 1873 K. The same experimental method was employed by Jacobson and Mehrotra in the temperature range between 1500 and 1670 K [11]. An emf method based on a solid galvanic cell with a single-crystal CaF_2 electrolyte was employed between 900 and 1070 K by Kleykamp and Glasbrenner for alloys with

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[*] Corresponding author. Tel.: +43 1 4277 52906; fax: +43 1 4277 9529.
E-mail address: herbert.ipser@univie.ac.at (H. Ipser).

[1] Present address: General Research Institute for Nonferrous Metals, Beijing 100088, China.

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compositions of up to about 60 at.% Al [12]. Very recently, Raj et al. used again a Knudsen cell-mass spectrometric method to determine thermodynamic activities between 1140 and 1600 K, however, only in the composition range of the cubic B2 phase [13]. Unfortunately, no experimental activities are available in the homogeneity range of the D0$_3$-compound Fe_3Al which is reported to be stable between about 25.5 and 32 at.% Al at 750 K and which disorders into the B2 structure at higher temperatures with a maximum of 820 K [14]. The main reason for this lack of data is certainly the difficulty to attain thermodynamic equilibrium at temperatures below 820 K using standard emf or vapor pressure methods.

Recently, Ipser et al. [15] developed a statistical–thermodynamic model for binary D0$_3$-phases to calculate the compositional variation of the aluminum activity in Fe_3Al at 500 K based on the energies of formation of the different types of point defects which had been obtained by *ab initio* calculations by Fähnle et al. [16]. However, since no corresponding experimental values were available at that time any test of the model equations was impossible. Thus, it was the aim of the present study to improve the experimental setup which would allow to obtain the thermodynamic activity of Al in the composition range of Fe_3Al by means of a solid state galvanic cell using single crystal CaF_2 as an electrolyte in the temperature range between about 720 and 850 K.

2. Experimental procedure

2.1. Experimental principle

The following solid-state galvanic cell, based on the principles outlined by Kiukkola and Wagner [17] and adapted to CaF_2 as an electrolyte (among others) by Levitskii [28,29], was used for the determination of the partial thermodynamic properties of the D0$_3$-phase Fe_3Al as a function of temperature and composition:

$$(-)\mathrm{Pt}|\mathrm{Ir}|\mathrm{Al}_{0.85}\mathrm{Sn}_{0.15},\ \mathrm{Na_3AlF_6}|\mathrm{CaF_2}|\mathrm{Al}_{1\pm x}\mathrm{Fe}_{3\pm x},\ \mathrm{Na_3AlF_6}|\mathrm{Ir}|\mathrm{Pt}(+)$$

The virtual reactions in the left-hand side and right-hand side electrode are, respectively:

$$\text{left}:\quad \mathrm{Al}_{(\mathrm{Al-Sn})} + 3\,\mathrm{Na}^+ + 6\mathrm{F}^- \rightarrow \mathrm{Na_3AlF_6} + 3\mathrm{e}^- \tag{1}$$

$$\text{right}:\quad \mathrm{Na_3AlF_6} + 3\mathrm{e}^- \rightarrow \mathrm{Al}_{(\mathrm{Al-Fe})} + 3\,\mathrm{Na}^+ + 6\mathrm{F}^- \tag{2}$$

This results in a total cell reaction for a virtual current of three moles of electrons from the left-hand to the right-hand side electrode:

$$\mathrm{Al}_{(\mathrm{Al-Sn})} \rightarrow \mathrm{Al}_{(\mathrm{Al-Fe})} \tag{3}$$

Hence, the measured emf-values of the cell are given by

$$E = -\left(\frac{RT}{3F}\right)\ln\frac{a_{\mathrm{Al(Al-Fe)}}}{a_{\mathrm{Al(Al-Sn)}}} \tag{4}$$

where E is the emf of the cell in V, F the Faraday constant, R is the gas constant, $a_{\mathrm{Al(Al-Fe)}}$ and $a_{\mathrm{Al(Al-Sn)}}$ the thermodynamic activities of Al in Fe_3Al and in the reference Al–Sn alloy, and T is the temperature in K. In order to achieve thermodynamic equilibrium within reasonable periods of time, an aluminum-rich Al–Sn alloy (15 at.% Sn) was selected as a reference electrode. This composition is characterized by a two-phase field between practically pure solid aluminum and a tin-rich liquid in the temperature range from 774 K (eutectic temperature) to about 873 K [18]. Thus, by definition, the activity of Al is unity in the reference electrode, and Eq. (4) reduces to

$$E = -\left(\frac{RT}{3F}\right)\ln a_{\mathrm{Al(Al-Fe)}} \tag{5}$$

With the following equations all partial thermodynamic properties of aluminum in Fe_3Al can be derived:

$$\Delta\bar{G} = RT\ln a_{\mathrm{Al}} = -3EF \tag{6}$$

$$\Delta\bar{S} = 3F\left(\frac{\partial E}{\partial T}\right) \tag{7}$$

$$\Delta\bar{H} = 3F\left[T\left(\frac{\partial E}{\partial T}\right) - E\right]. \tag{8}$$

2.2. Experimental procedure

The experimental setup that had been described earlier by Yuan et al. [19] was adapted to be used for emf measurements with solid CaF_2 as electrolyte. Altogether eleven samples were prepared in the composition range between 23 and 33 at.% Al; their nominal compositions are given in Table 1. Starting materials for all samples were iron (block, 99.99%, Institute of Physics, Chinese Academy of Sciences) and Al (foil, 99.999%, General Research Institute for Nonferrous Metals, P.R. China). Appropriate amounts of the pure elements were weighed and mixed and thereafter melted under Ar atmosphere in an arc furnace on a water cooled copper hearth. They were re-melted several times to guarantee homogeneity. The total mass of each sample was about 4 g. In order to check for any mass losses all samples were reweighed, and samples with losses of more than 0.5% were discarded resulting in composition values with uncertainties of better than ±0.5 at.%. The resulting ingots were filed with a diamond file, and the obtained powders were sealed under vacuum (approx. 10^{-3} mbar) in quartz tubes, annealed at 750 K for 10 days and quenched. The Al–Sn alloy with 15 at.% Sn for the reference alloy was prepared in a similar way.

The working electrodes for the emf-measurements were prepared by mixing Fe_3Al alloy powders with Na_3AlF_6 powder (99.9%, Beijing Chemical Reagent Company) in a mass ratio $m(\mathrm{Fe_3Al}):m(\mathrm{Na_3AlF_6}) = 1:1$. These mixtures were pressed into pellets under a pressure of about 5 GPa. The reference electrode ($Al_{0.85}Sn_{0.15}$, Na_3AlF_6) was prepared by mixing one part of $Al_{0.85}Sn_{0.15}$ alloy powder with one part of Na_3AlF_6 powder; it was pressed in the same way. Small crucibles made from single crystal CaF_2 (Ohyo Koken Kogyo Co., Ltd., Japan; 10 mm o.d., 8 mm i.d., 20 mm height) served as fluoride conducting electrolyte.

Platinum was used for the lead wires that served as outer connections. In order to avoid reactions between Pt and Fe_3Al or $Al_{0.85}Sn_{0.15}$, respectively, with the possible formation of very stable Al–Pt intermetallics, the electrodes of the galvanic cell were separated from the Pt leads by thin iridium foils as shown in Fig. 1. Earlier experiments with the intermetallic compound Pt_3In had shown that iridium was a material well suited for this purpose [20].

All measurements were performed under an atmosphere of purified Ar in the temperature range between 720 K and an upper temperature limit ranging

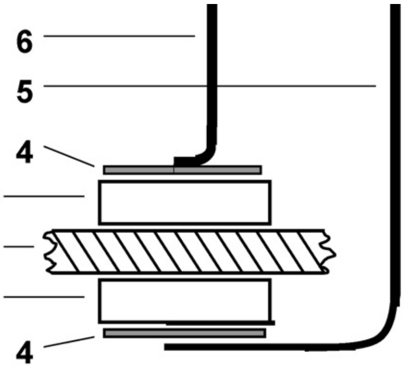

Fig. 1. Part of the cell assembly indicating the arrangement of the Ir foil between sample electrode and Pt lead wire: 1, single crystal CaF_2 crucible; 2, sample electrode; 3, reference electrode; 4, Ir foil; 5, lead wire (Pt) to sample electrode; 6, lead wire (Pt) to reference electrode.