J. Chem. Thermodynamics 65 (2013) 78–82

Contents lists available at SciVerse ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Thermodynamic measurement of Dy + Fe binary system by double Knudsen cell mass spectrometry

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ARTICLE INFO

Article history:
Received 23 January 2013
Received in revised form 14 May 2013
Accepted 19 May 2013
Available online 29 May 2013

Keywords:
Thermodynamics
Activity
Gibbs energy
Mass spectrometry

ABSTRACT

The activities of Dy in Dy–Fe alloys with Dy concentrations ranging from (7.0 to 89) at% were determined at (1273 to 1573) K by measuring the ion current of the vapor of Dy in equilibrium with Dy–Fe melts, $Dy_2Fe_{17} + \gamma Fe$, *etc.* The standard Gibbs energy of formation of Dy_2Fe_{17}, Dy_6Fe_{23}, $DyFe_3$, and $DyFe_2$ were calculated from the activities of Dy obtained from these measurements.

1. Introduction

Rare Earth (RE) metals are used in various functional materials, including permanent magnets [1,2], hydrogen storage alloys [3,4], and luminescent materials [5,6]. Due to the escalating demand for Nd–Fe–B–Dy magnets, the consumption of Nd and Dy has continued to increase dramatically. To achieve coercivity at high temperature, Dy is added to Nd–Fe–B magnets. The magnets used in the motors of hybrid automobiles contain *ca.* (3 to 10) wt% Dy. Since the resources and suppliers of Dy are extremely limited, development of a method for recycling Dy from discarded magnets is mandatory. However, a process for recycling RE metals from scrap magnets has not been developed, although the number of disposed magnets has recently increased [7,8].

The thermodynamic properties of RE metal systems at high temperatures cannot be readily evaluated *via* traditional methods due to the chemical affinity of RE metals with oxygen or other elements [9,10]. Therefore, information regarding the thermodynamic properties of Dy + Fe binary systems at high temperatures is not available and thermodynamic information on intermetallic compounds in these systems is extremely limited. Thermodynamic information on the Dy + Fe system is required for the design of recycling processes for Dy recovery from scrap Dy–Fe.

The vapor pressure of RE metals in equilibrium with the alloys can be measured while excluding the effect of oxygen by using double Knudsen cell mass spectrometry, given that this measurement technique utilizes high vacuum conditions. The thermodynamic properties of RE metals in alloys can be estimated from the vapor pressure, and those of Fe–La, Fe–Y, and Nd–Fe binary alloys have been investigated with this method [10–13]. This study reports the thermodynamic properties of Dy + Fe binary systems, measured by double Knudsen mass spectrometry.

2. Experimental

2.1. Preparation of alloys

Figure 1 shows the phase diagram of the Dy + Fe system. The Dy–Fe alloy specimens used in this study were prepared by melting reagent-grade Dy grains (Kojundo Chemical Laboratory Co., Ltd., 3N) and electrolytic iron under high vacuum (*ca.* $1.0 \cdot 10^{-3}$ Pa) using an electron beam melting technique. The apparatus for electron beam melting is described elsewhere [14]. The alloys were melted four or five times, and thorough, homogenous mixing was ensured by inverting or crushing the sample for each run. The chemical compositions of the master alloys were determined by chemical analysis using inductively coupled plasma atomic spectroscopy (ICP-AES, SPS4000, Seiko Instruments Inc.). The mole fractions of Dy in the prepared alloys were (0.07, 0.17, 0.23, 0.28, 0.57, 0.74, and 0.89) at%.

2.2. Double Knudsen cell mass spectrometry

The details of double Knudsen mass spectrometry are provided in previous studies [10,15]. In brief, in Knudsen cell mass spec-

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http://dx.doi.org/10.1016/j.jct.2013.05.034

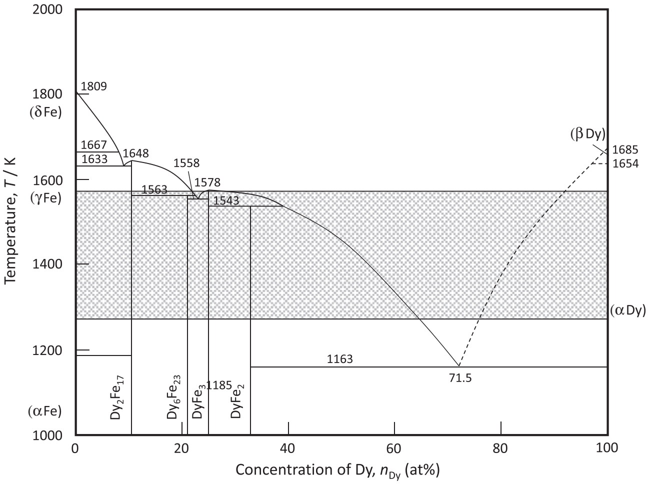

FIGURE 1. Phase diagram of Dy–Fe binary system.

trometry, the vapor pressure is detected as an ion current that is proportional to the pressure. The pressure, P_i, and ion current of species i, I_i, measured by the mass spectrometer, are related through the following fundamental equation [15]:

$$P_i = k_i T I_i, \tag{1}$$

where T and k_i are the absolute temperature and a constant that includes the device constant and ionization cross section of molecule i.

Double Knudsen cells allow the measurement of ion currents of evaporated species from two or more substances under identical conditions in an experimental run. Using the pure substance as a reference, the constant k_i can be regarded as equivalent for the substances, and thus, the activity of specimen i, a_i, can be deduced directly:

$$a_i = \frac{P_{i,specimen}}{P_{i,reference}} = \frac{I_{i,specimen}}{I_{i,reference}}, \tag{2}$$

where P_i and I_i are the vapor pressure and the ion current of species i in equilibrium with the substances, respectively.

The details of the experimental setup for the Double Knudsen Cell Mass Spectrometry are also described elsewhere [10–13]. A quadrupole mass spectrometer (QMS, Leybold Inficon 300M) was used to monitor and measure the ion currents of the evaporated species. The QMS was placed on top of the vacuum chamber in which the Knudsen cell unit was installed. The inside of the chamber was evacuated using a rotary pump and a turbo molecular pump (TMP, 0.5 m^3/s), and the residual gas pressure was kept below $1.0 \cdot 10^{-4}$ Pa during the experiments. The cell holder in the vacuum chamber could hold four Knudsen cells. Ion currents from each cell or the background could be detected individually by rotating the cell holder.

Reagent-grade pure Dy grain (Kojundo Chemical Laboratory Co., Ltd., 3N) was used as a reference for the Dy–Fe alloy measurements. Because Dy is easily oxidized in air, the Dy grain was preserved in spindle oil. The Dy–Fe alloys and Dy grains were placed into the high vacuum chamber and measurements were taken as soon as possible after removing the sample from the oil, grinding it with sandpaper, and rinsing in acetone and ethanol for a few minutes. About 0.2 g of the experimental specimen (*i.e.*, Dy–Fe alloy) and reference specimen (pure Dy) were charged into each Mo Knudsen cell with an Y_2O_3 inner crucible. The diameter of the cells was 10 mm, with a height of 20 mm and a thickness of 1 mm. The lid of the cell had an orifice; a lid with a diameter of 0.4 mm was used for the measurements.

The cell holder could hold four Knudsen cells as already mentioned. For each measurement, the experimental alloy was charged into two of these cells, one reference (pure Dy) was placed into a cell and the last cell was left empty to measure the ion current of the background. The experimental parameters, *i.e.*, temperature range, concentration of Dy in the Dy–Fe alloy, and evaluated phase are summarized in table 1.

3. Results and discussion

The Double Knudsen Cell Mass Spectrometry experiment was carried out for the Dy–Fe alloys using pure Dy as a reference substance. Figure 2 shows the result of ion current measurements acquired at 1473 K. Significant ion currents were detected from pure Dy and the Dy–Fe alloys at m/z = 158, and 160 to 164. These currents are assigned to ^{158}Dy, ^{160}Dy, ^{161}Dy, ^{162}Dy, ^{163}Dy, and ^{164}Dy. The ion current ratios were also in good agreement with the natural abundance of Dy (table 2). The sum of the ion currents at m/z = 158, 160 to 164 was used as the ion current of Dy for calculation of the activity.

No ion currents due to ^{54}Fe, ^{56}Fe, ^{57}Fe, and ^{58}Fe could be detected at m/z = 54, 56, 57, and 58 in most of the experiments, since the vapor pressure of these species in equilibrium with the alloys too low to be measured accurately.

The activity of Dy in the Dy–Fe alloys was determined from the ion currents using equation (2), and the results are listed in table 3 and are also shown as chemical potential versus temperature in figure 3.

3.1. 7.0 at%Dy–Fe alloy

Based on the phase diagram of the Dy + Fe binary system, the alloy exists as two phases comprising Dy_2Fe_{17} and γFe at (1273 to 1573) K. From the X-ray diffraction pattern of the alloy, the specimen was identified as a mixture of Dy_2Fe_{17} and αFe; therefore, it is believed that at the experimental temperature, the specimen comprised a mixture of Dy_2Fe_{17} and γFe. The activity of Dy in the 7.0 at%Dy–Fe alloy was evaluated at (1373 to 1573) K; the ion currents of the alloy were too small to detect at (1273 and 1323) K. The standard Gibbs energy of formation of Dy_2Fe_{17}, $\Delta G^0_{f,Dy_2Fe_{17}}$, was derived from the measured activities of Dy in the alloy. The equilibrium reaction in this alloy can be expressed as equation (3), and there is a relationship between the chemical potentials of component i, μ_i, since the chemical potentials on both sides should be equal when these phases are in equilibrium.

$$2\mathrm{Dy}(\alpha) + 17\mathrm{Fe}(\gamma) = \mathrm{Dy_2Fe_{17}}(\mathrm{s}), \tag{3}$$

$$\mu_{\mathrm{Dy_2Fe_{17}}} = 2\mu_{\mathrm{Dy}} + 17\mu_{\mathrm{Fe}}. \tag{4}$$

Equation (4) can be rewritten as equation (5) using the μ_i^0 values and the activities of i, $a_i^{\mathrm{eq}(3)}$. The activities, $a_i^{\mathrm{eq}(3)}$, refer to those when the chemical equilibrium expressed by reaction (3) is achieved; in short, when the species in reaction (3) are in equilibrium with each other.

$$\mu^0_{\mathrm{Dy_2Fe_{17}}} + RT\ln a^{\mathrm{eq}(3)}_{\mathrm{Dy_2Fe_{17}}} = 2\left(\mu^0_{\mathrm{Dy}} + RT\ln a^{\mathrm{eq}(3)}_{\mathrm{Dy}}\right) + 17\left(\mu^0_{\mathrm{Fe}} + RT\ln a^{\mathrm{eq}(3)}_{\mathrm{Fe}}\right). \tag{5}$$

The activities of Dy_2Fe_{17} are thus equal to unity since the compound is stoichiometric. The activities of Fe are equal to unity because Dy is saturated with Fe, and Fe is insoluble in Dy.

$$\mu^0_{\mathrm{Dy_2Fe_{17}}} - 2\mu^0_{\mathrm{Dy}} - 17\mu^0_{\mathrm{Fe}} = 2RT\ln a^{\mathrm{eq}(3)}_{\mathrm{Dy}}. \tag{6}$$

The following equations were, therefore, eventually derived.