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Letter

Thermodynamic properties of the intermetallic compounds $Re_2Fe_{14}B$ ($Re \equiv La$, Ce, Y)

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Abstract

The intermetallic compounds $Re_2Fe_{14}B$ ($Re \equiv La$, Ce, Y) with tetragonal structure were prepared. The chemical thermodynamic properties of the compounds were studied by using a galvanic cell with a CaF_2 single crystal as a solid electrolyte having an Re/ReF_3 reference electrode in the temperature range 900–1020 K.

1. Introduction

Since the discovery that Invar-type anomalies are also present in compounds of the type $Re_2Fe_{14}B$ ($Re \equiv La$, Ce, Y) with tetragonal structure by Givord *et al.* in 1985 [1], its Invar-type magnetic anomalies by which the compounds may be utilized as promising "permanent magnet materials in modern electric drives" are of considerable interest from both theoretical and practical points of view [2–4].

Therefore, investigations on the physical properties of these compounds, such as magnetic and electrical properties, have been carried out [4, 5]. However, there are few studies devoted to the chemical aspects of the properties of the compounds, in particular the thermal stability of the compounds.

The purpose of the present work is to study the chemical thermodynamic properties of the compounds by using a galvanic cell technique with a CaF_2 single crystal as a solid electrolyte having an Re/ReF_3 reference electrode.

2. Experimental details

2.1. *Materials*

Pure iron was smelted in an electron beam furnace and then heated in pure H_2 at 1550 °C for more than 10 h to remove as far as possible traces of oxygen, and thus the purity of the iron product is higher than 99.95%. Rare earth metals were twice purified in a vacuum casting arc furnace with a copper crucible in ultrapure argon gas atmosphere; their purities were higher than 99.5%. Boron with a purity of 99.99% was heated in vacuum in a tungsten furnace at 1300 °C for 2 h to remove absorbed gas.

Rare earth fluorides ReF_3 was prepared by the reaction

$$Re_2O_3(s) + 6NH_4HF_2(s) \longrightarrow 2ReF_3(s) + 6NH_4F(g) + 3H_2O(g)$$

at 300 °C for 10 h. The purity of ReF_3 was higher than 99% with a residual small amount of Re_2O_3. However, for cerium, the CeF_3 was synthesized using CeO_2 as the starting material by the reaction

$$3CeO_2(s) + 8NH_4HF_2(s) \longrightarrow 3CeF_3(s) + \tfrac{1}{2}N_2(g) + 6H_2O(g) + 7NH_4F(g)$$

at 300 °C for more than 10 h.

All the fluorides were heated at 500 °C under a vacuum of better than 10^{-3} Pa for 5–6 h in order to remove the remaining NH_4F and H_2O.

The product was identified exclusively as a single-phase ReF_3 by X-ray diffraction (XRD) analysis.

Compounds $RE_2Fe_{14}B$ were prepared from the purified rare earth, iron and boron by vacuum casting in an arc furnace in an ultrapurified argon atmosphere and then were wrapped in molybdenum foil and sealed in an evacuated quartz ampoule for homogenization which was realized with annealing at 900 °C for 3 weeks. All samples subsequent to the homogenization were confirmed by XRD to be single phase with a tetragonal structure.

2.2. *Cell assembly*

Powder mixtures of ReF_3 and rare earth with weight ratio 9:1 were compressed to a pellet 10 mm in diameter and 4 mm thick as a reference electrode. The pellets were sealed in an evacuated quartz ampoule to anneal at 650 °C for 2 weeks.

The pellets of the mixture of $Re_2Fe_{14}B$ and ReF_3 were prepared by the same process with same weight ratio and size as mentioned above.

The experimental arrangement is shown in Fig. 1. Details of the cell assembly were described in a previous paper [6].

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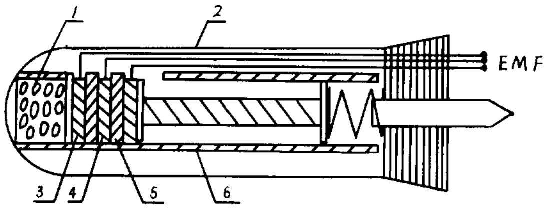

Fig. 1. Apparatus used for e.m.f. measurements: 1, La; 2, quartz tube; 3, electrodes; 4, reference electrode; 5, CaF_2 electrolyte; 6, alumina tube.

2.3. Experimental procedure

The cell assembly was placed in a vertical resistance furnace with double windings of Fe–Cr–Al wire. The temperature in the oven zone was controlled to ±1 K by a DWK 702 temperature controller.

The e.m.f. of the cell was measured in the temperature range 900–1020 K with a Keithley 610C solid state electrometer (10^{14} Ω) and a high impute impedance (10^{11} Ω) 192 digital voltmeter. The values of the e.m.f.s were taken when the variations in the e.m.f.s were within ±1 mV. In order to ensure that the cell was in equilibrium, the reversibility of the electrode processes was ascertained by momentarily polarizing for several seconds and it was verified that the cell e.m.f. values returned to their original values. The e.m.f. values were reproducible within ±0.2 mV. The reproducibility of the e.m.f. was better when measurements were from low to high temperature.

After completion of the experiment, the samples and the surface of the CaF_2 single crystal as well as the electrode were examined carefully. No evidence of cracking or corrosion was found. XRD analysis indicated that no changes in composition and structure were detected.

3. Results and discussion

The following galvanic cells have been investigated for the intermetallic compounds $La_2Fe_{14}B$, $Ce_2Fe_{14}B$ and $Y_2Fe_{14}B$ respectively;

$\mathrm{Mo|La,\ LaF_3|CaF_2|LaF_3,\ La_2Fe_{14}B|Mo}$ (920–1000 K)

$\mathrm{Mo|Ce,\ CeF_3|CaF_2|CeF_3,\ Ce_2Fe_{14}B|Mo}$ (900–980 K)

$\mathrm{Mo|Y,\ YF_3|CaF_2|YF_3,\ Y_2Fe_{14}B|Mo}$ (920–1020 K)

The electrode reaction may be written as the anodic reaction

$$\mathrm{Re + 3F^- \longrightarrow ReF_3 + 3e^-} \tag{1}$$

and the cathodic reaction

$$\mathrm{ReF_3 + 3e^- \longrightarrow [Re]_{Re_2Fe_{14}B} + 3F^-} \tag{2}$$

Thus the overall cell reaction may be written as

$$\mathrm{Re(s) \longrightarrow [Re]_{Re_2Fe_{14}B}} \tag{3}$$

The measured cell e.m.f. values were plotted as function of temperature and are shown in Fig. 2.

The variation in e.m.f. for $La_2Fe_{14}B$ and $Ce_2Fe_{14}B$ is linear with temperature. The equations obtained by regressive analysis are as follows:
for Lanthanum,

$$E(\mathrm{mV}) = 631.176 - 0.4356T \pm 2.31 \tag{4}$$

for Cerium,

$$E(\mathrm{mV}) = 661.08 - 0.5852T + 1.20 \tag{5}$$

However, the variation in e.m.f. with temperature for $Y_2Fe_{14}B$ can be expressed as the equation

$$E(\mathrm{mV}) = 14.18 + 3.143 \times 10^{-1}(T-970) + 3.616 \times 10^{-3}(T-970)^2 \pm 1.6 \tag{6}$$

The Gibbs free energy change associated with the virtual cell reaction (3) can be calculated using the following relationship:

$$\Delta G_{[\mathrm{Re}]} = -nFE \tag{7}$$

where n is the equivalent transference number of F^-, E is the e.m.f. and F is the Faraday constant. If pure solid phase rare earth is chosen as the standard state, the activity of rare earth is unity, and then

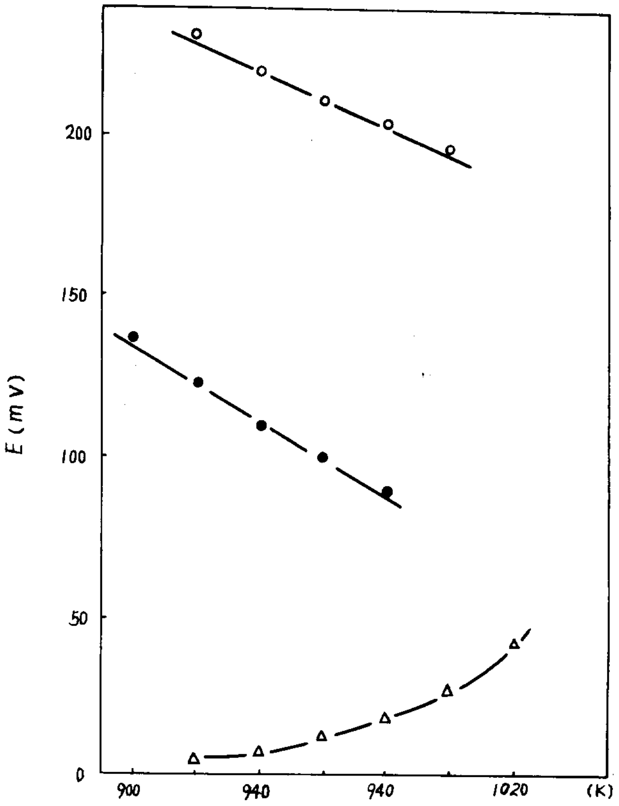

Fig. 2. Variation in cell e.m.f. with temperature for the three cells: ○, La, $LaF_3|CaF_2|La_2Fe_{14}B$, LaF_3; ●, Ce, $CeF_3|CaF_2|$-$Ce_2Fe_{14}B$, CeF_3; △, for cell, Y, $YF_3|CaF_2|Y_2Fe_{14}B$, YF_3.

$$a_{[\mathrm{Re}]\mathrm{Re_2Fe_{14}B}} = \exp(-nFE/RT) \qquad (8)$$

where $a_{[\mathrm{Re}]\mathrm{Re_2Fe_{14}B}}$ is the activity of rare earth in $\mathrm{Re_2Fe_{14}B}$.

The results of e.m.f. measurements, $\Delta G_{[\mathrm{Re}]}$ and $a_{[\mathrm{Re}]}$ calculations from eqns. (7) and (8) are listed in Table 1.

The compound's stability can be estimated by the data determined in the present experiments, which are expressed as the temperature dependences of the Gibbs free energy change of cell reactions and of the activities of various rare earth metals in the intermetallic compound as shown in Figs. 3 and 4. It may be seen that

TABLE 1. Results of E measurements and ΔG and $a_{[\mathrm{Re}]}$ calculations

Re	T (K)	E (mV)	$-\Delta G_{[\mathrm{Re}]}$ (J)	$a_{[\mathrm{Re}]} \times 10^3$
La	920	231.82	67103	0.1549
	940	220.14	63722	0.2877
	960	211.47	61212	0.4669
	980	204.60	59224	0.6970
	1000	196.97	57015	1.0513
Ce	900	136.57	39532	5.076
	920	123.23	35670	9.434
	940	110.85	32087	16.478
	960	99.90	28917	26.701
	980	89.71	25967	41.292
Y	920	5.70	1650	806.0
	940	7.39	2113	760.6
	960	12.10	3502	644.8
	980	18.35	5311	521.0
	1000	25.42	7358	412.7
	1020	41.42	11989	243.2

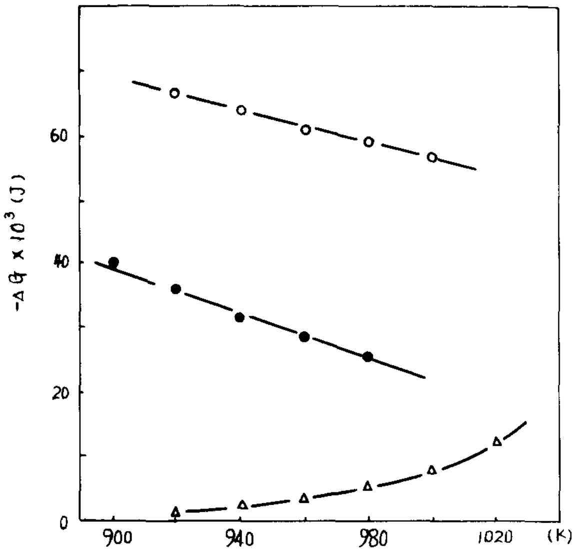

Fig. 3. Variation in Gibbs' free energy change of cell reaction with temperature: ○, cell reaction $\mathrm{La(s)} \rightarrow [\mathrm{La}]_{\mathrm{La_2Fe_{14}B}}$; ●, cell reaction $\mathrm{Ce(s)} \rightarrow [\mathrm{Ce}]_{\mathrm{Ce_2Fe_{14}B}}$; △, cell reaction $\mathrm{Y(s)} \rightarrow [\mathrm{Y}]_{\mathrm{Y_2Fe_{14}B}}$.

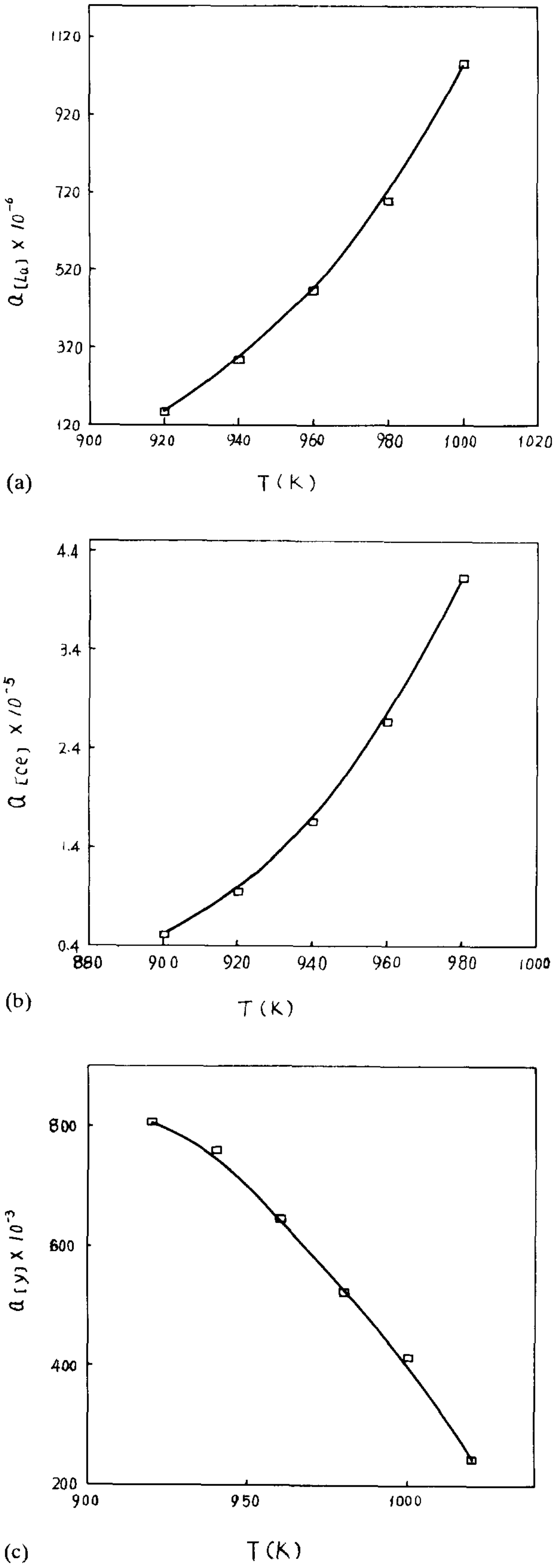

Fig. 4. Variation in activity of rare earth in intermetallic compound $\mathrm{Re_2Fe_{14}B}$ with temperature: (a) $\mathrm{La_2Fe_{14}B}$; (b) $\mathrm{Ce_2Fe_{14}B}$; (c) $\mathrm{Y_2Fe_{14}B}$.

the stability of the compounds $La_2Fe_{14}B$ and $Ce_2Fe_{14}B$ is higher than that of $Y_2Fe_{14}B$ and decreases with increasing temperature. However, the stability of the compound $Y_2Fe_{14}B$ increases with temperature; that may be due to the difference in chemical properties and needs to be studied further.

Since no information is available in the literature on the thermodynamic properties of the intermetallic compounds $Re_2Fe_{14}B$, the present results could not be compared with other data.

Acknowledgment

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References

1 D. Givord, M. S. Li, J. M. Moreau, R. Perrier, Da la Bathie and E. Du Tremlet de Lacheisserie, *Physica B, 130* (1985) 323.

2 R. Grossinger, P. Obitsch, X. K. Sun, R. Eibler, H. R. Kirchmayr, F. Rothwarf and H. Sassik, *Mater, Lett., 2* (1984) 539.

3 K. H. J. Buschow, *J. Less-Common Met., 118* (1986) 323.

4 K. H. J. Buschow, *J. Less-Common Met., 135* (1987) 39.

5 H. Fujii, H. Nagata, Y. Uwatoko, T. Okamoto, H. Yamamoto and M. Sagawa, *J. Magn. Magn. Mater., 70* (1987) 331.

6 X. Xu, G. Li, H. Yu and C. Wang, *J. Less-Common Met., 175* (1991) 271.