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Letter

Thermodynamic studies of $YFe_{12-x}V_x$ and $SmFe_{12-x}V_x$ alloys

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Abstract

The Invar alloys of $YFe_{12-x}V_x$ (x = 1.6, 2.0, 2.4, 2.8, 3.2) and $SmFe_{12-x}V_x$ (x = 2.4, 2.8) were prepared. The activity and the relative partial molar Gibbs free energy of the yttrium and samarium in the alloys were determined by the e.m.f. method using a single crystal of CaF_2 as a solid electrolyte at temperatures of 920–1020 K and 900–1000 K respectively.

1. Introduction

It has been discovered recently that some rare earth containing alloys with Laves phase structure, *e.g.* $NaZn_{13}$ type [1, 2], $Nd_2Fe_{14}B$ type [3–5] and $ThMn_{12}$ type [6–8] structures, exhibit higher Curie transition temperature and Invar-like characteristics in their thermal expansion behaviour. In order to investigate the relationship between thermodynamic properties and thermal expansion behaviour of these kinds of alloys, the thermodynamic properties of $La(Fe_xAl_{1-x})_{13}$ alloys was studied by the previous work [9].

The purpose of this work was to study the thermodynamic properties of yttrium in $YFe_{12-x}V_x$ (x = 1.6, 2.0, 2.4, 2.8, 3.2) and samarium in $SmFe_{12-x}V_x$ alloys (x = 2.4, 2.8) using the e.m.f. method; a single crystal of CaF_2 was used as a solid electrolyte.

The galvanic cell used can be expressed as

$$\text{Mo}|\text{Y}, \text{YF}_3|\text{CaF}_2|\text{YF}_3, \text{YFe}_{12-x}\text{V}_x|\text{Mo} \quad (920\text{–}1020\ \text{K})$$

and

$$\text{Mo}|\text{Sm}, \text{SmF}_3|\text{CaF}_2|\text{SmF}_3, \text{SmFe}_{12-x}\text{V}_x|\text{Mo} \quad (900\text{–}1000\ \text{K})$$

The half-cell reaction on the left-hand side is

$$\text{Re(s)} - 3\text{e}^- + 3\text{F}^- \longrightarrow \text{ReF}_3\text{(s)}$$

and the half-cell reaction on the right-hand side is

$$\text{ReF}_3\text{(s)} + 3\text{e}^- \longrightarrow [\text{Re}]_{\text{alloy}} + 3\text{F}^-$$

The overall cell reaction is

$$\text{Re(s)} \longrightarrow [\text{Re}]_{\text{alloy}}$$

The relative partial molar free energy $\Delta\bar{G}_{Re}$ of the rare earth in $ReFe_{12-x}V_x$ is equal to the free energy change ΔG of the cell reaction, *i.e.*

$$\Delta\bar{G}_{[\text{Re}]} = \Delta G = -3FE$$

where E is the e.m.f. and F is the Faraday constant. If pure rare earth solid phase is chosen as the standard state, the activity of the rare earth is unity; then

$$\Delta\bar{G}_{[\text{Re}]} = RT \ln a_{[\text{Re}]}$$

$$a_{[\text{Re}]} = \exp(-3FE/RT)$$

where $a_{[\text{Re}]}$ is the activity of yttrium in $YFe_{12-x}V_x$ alloys and samarium in $SmFe_{12-x}V_x$ alloys.

2. Experimental details

2.1. Materials

2.1.1. Source materials

CaF_2 single crystals (15 mm × 5 mm) were obtained from the Institute of Optical Research, Academia Sinica.

YF_3 and SmF_3 were prepared from Y_2O_3 (better than 99.95%) and Sm_2O_3 (better than 99.95%) with NH_4HF_2 (AR) according to the following reaction.

$$\text{Re}_2\text{O}_3\text{(s)} + 6\text{NH}_4\text{HF}_2\text{(s)} = 2\text{ReF}_3\text{(s)} + 6\text{NH}_4\text{F(s)} + 3\text{H}_2\text{O(g)}$$

All the obtained ReF_3 were identified by X-ray diffraction analysis. The iron was 99.93% pure and deoxidized by hydrogen at 1550 °C for 10 h; the vanadium was more than 99.95% pure; the yttrium and samarium were more than 99.5% pure.

2.1.2. Preparation of $ReFe_{12-x}V_x$

$YFe_{12-x}V_x$ with x = 1.6, 2.0, 2.4, 2.8, 3.2 and $SmFe_{12-x}V_x$ with x = 2.4, 2.8 were obtained by melting the elements in water-cooled copper crucibles in a small arc furnace with a magnetic stirring apparatus. $Zr_{84}Al_{16}$ alloy was placed in one of the crucibles to decrease the oxygen potential in the chamber; first the yttrium and samarium were purified in this arc furnace. The furnace was evacuated and then ultrapure argon was introduced; the details of the procedure were described in the previous paper [9].

The obtained alloys were wrapped in molybdenum foil and sealed in a quartz tube filled with ultrapure

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TABLE 1. Results of e.m.f. measurements on cells

Alloy	E.m.f.s (mV) for the following temperatures						
	900 K	920 K	940 K	960 K	980 K	1000 K	1020 K
$YFe_{10.4}V_{1.6}$		4.86	6.15	8.16	11.29	16.04	23.34
$YFe_{10}V_{2.0}$		5.84	7.66	10.02	13.30	18.79	27.57
$YFe_{9.6}V_{2.4}$		10.88	17.53	25.40	33.45	44.30	60.13
$YFe_{9.2}V_{2.8}$		12.92	18.34	27.36	40.78	53.91	67.94
$YFe_{8.8}V_{3.2}$		6.30	8.18	12.51	17.49	23.68	34.39
$SmFe_{9.6}V_{2.4}$	233.4	224.0	211.4	197.4	182.1	174.1	
$SmFe_{9.2}V_{2.8}$	214.1	202.7	188.5	176.4	164.6	155.2	

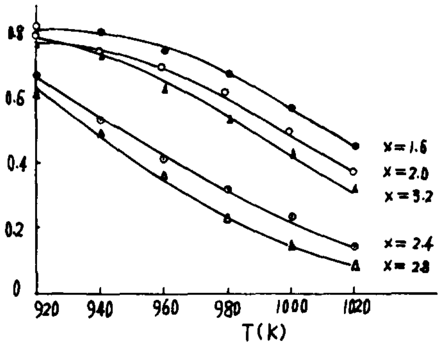

Fig. 1. Activity of yttrium in $YFe_{12-x}V_x$ as a function of temperature.

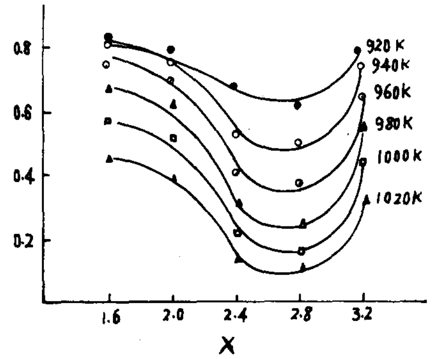

Fig. 2. Activity of yttrium of a function of composition.

argon; pieces of $Zr_{84}Al_{16}$ were put on the end of the tube to absorb traces of oxygen. Homogenization of the alloys was carried out by heating at 850 °C for 500 h. The samples of the alloys were powdered in methylbenzene and then were examined by X-ray diffraction analysis and scanning electron microscopy.

2.2. *Cell assembly*

Reference electrode, ReF_3, and rare earth powders were mixed in a weight fraction ratio of 2:8 in an argon-filled glove-box and pressed into pellets of diameter 10 mm and thickness 3 mm thick; one rounded end of 0.5 mm molybdenum wire was pressed to the pellet to provide a good contact.

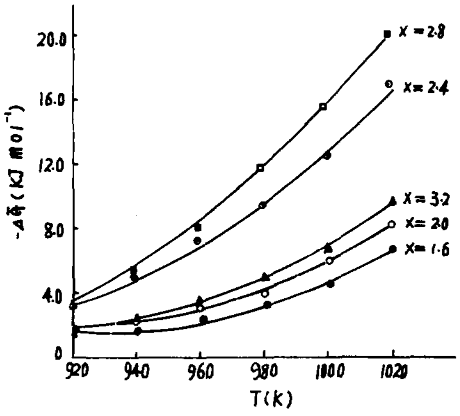

Fig. 3. Partial molar free energy of yttrium in $YFe_{12-x}V_x$ as function of temperature

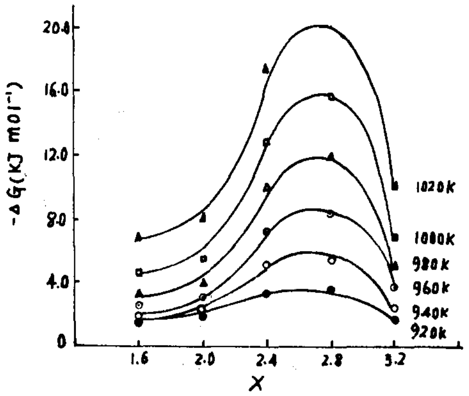

Fig. 4. Partial molar free energy of yttrium as a function of composition.

For the research electrode $ReFe_{12-x}V_x$ alloy powders were mixed with ReF_3 powder also in the weight fraction ratio of 2:8 and pressed together with molybdenum wire to the same size as above.

All the pellets of an electrode were wrapped in molybdenum foil and sealed in a quartz tube, which was filled with ultrapure argon and then annealed at 600 °C for 24 h.

The cell assembly was same as in the previous paper [9], which were assembled in a quartz tube filled with ultrapure argon.

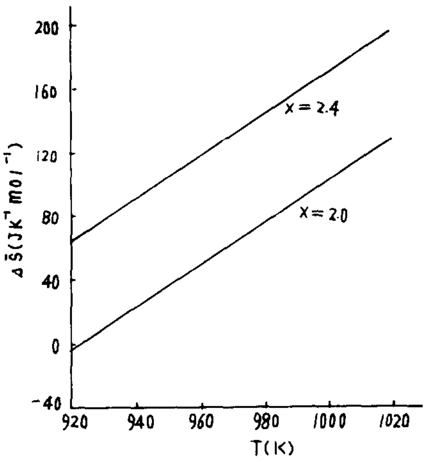

Fig. 5. Partial molar entropy of yttrium in $YFe_{12-x}V_x$ as a function of temperature.

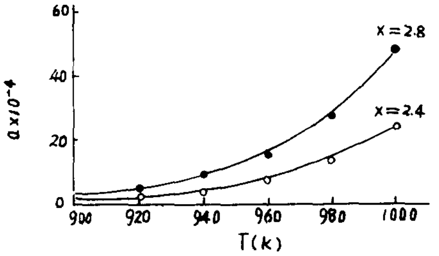

Fig. 6. Activity of samarium in $SmFe_{12-x}V_x$ as a function of temperature.

The quartz tube was placed in a special rounded furnace and shielded with a molybdenum cylinder, which was grounded. Pt–PtRh(10%) thermocouples were used for temperature measurement and control; the temperature was controlled to an accuracy of ±1 K.

2.3. *E.m.f. measurement*

The e.m.f.s of the cells were measured using a Keithley 610C solid state electrometer (10^{14} Ω) with a Keithley 192 high input digital voltmeter ($>10^{12}$ Ω) which was switched to the solid electrometer to display the e.m.f. values. The experiments were taken from low temperature to high temperature and then from high to low temperature. When the temperature was constant after 1–4 days the e.m.f. values obtained were reproducible to within ±1 mV; the reversibility of the cell was ascertained in each case by momentarily polarizing the electrode and observing with an *X–Y* recorder that the original e.m.f. was restored.

After the experiments all the single crystals of CaF_2 were clear; no reaction was found between electrodes and solid electrode.

3. Results and discussion

The results of e.m.f. measurements on cells with different compositions for $YFe_{12-x}V_x$ and $SmFe_{12-x}V_x$ alloys at different temperatures are listed in Table 1.

From the results of e.m.f. measurements the regression equations were obtained by using multinomial regression analysis and from which the curves of activity and partial molar free energy of yttrium in $YFe_{12-x}V_x$ as a function of temperature and composition were obtained as shown in Figs. 1–4. There are only two curves for the molar entropy of yttrium in alloys with $x = 2.0$ and $x = 2.4$, which are shown in Fig. 5; the other compositions exhibit similar tendencies.

The activity and partial molar free energy of yttrium in $YFe_{12-x}V_x$ alloys show that the yttrium should not be stable in the alloys, which may be easy to oxidize.

The same method as above was used to obtain the activity of samarium in $SmFe_{9.6}V_{2.4}$ and $SmFe_{9.2}V_{2.8}$ as a function of temperature and the results are shown in Fig. 6. This shows that the activities of samarium in these two alloys were smaller so that the two alloys are stable.

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