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Thermodynamic evaluations of the iron–lutetium and iron–thulium systems

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ABSTRACT

The iron–lutetium and iron–thulium binary systems needed to be reassessed after the previous thermodynamic evaluation by Konar (2012) [1] because significant discrepancies were observed with the experimental data. Furthermore new thermodynamic data were published in the meantime. In the present work, the modelings were carried out with the help of the CALPHAD (CALculation of PHAse Diagram) method. The seven intermediate phases $Fe_{23}Lu_6$, Fe_3Lu, Fe_2Lu, $Fe_{17}Tm_2$, $Fe_{23}Tm_6$, Fe_3Tm and Fe_2Tm in these two binary systems have been treated as stoichiometric compounds while the $Fe_{17}Lu_2$ substoichiometric intermetallic compound in Lu, in the Fe–Lu binary system which has a homogeneity range, was treated by a two-sublattice model with convenient substitution in each sublattice (Sundman et al., 1985 [2]). A solution model has been used for the description of the liquid phase and the (Fe), (Lu) and (Tm) solid solutions. The excess term of the Gibbs energy of the solution phases was assessed with the Redlich–Kister (Redlich and Kister, 1948 [3]) polynomial equation. The calculations based on the thermodynamic modeling are in good agreement with the phase diagram data and experimental thermodynamic values available in the literature.

1. Introduction

Binary TM–RE (TM=transition metal, RE=heavy rare earth) alloys are interesting from a fundamental point of view to study the influence of the structural disorder on the basic magnetic properties. Moreover, the RE–TM–M (M=Ti, V) ternary systems attract much attention due to the novel structure and properties of the compounds and solid solutions formed in these systems [4–6]. For example, the ternary solid solutions $REFe_{2-x}M_x$, $RECo_{2-x}M_x$, $RE_2Fe_{17-x}M_x$, etc., based on the RE–Fe and RE–Co binary compounds are very attractive due to their hydrogen absorption capacity and particular magnetic properties [7–9]. To understand the physical properties and the technological applications of these compounds, it is necessary to obtain a better knowledge of the thermodynamic properties of these technically relevant systems. In order to aid the aforesaid objective, computational thermodynamics serve as a powerful instrument. Computational thermochemistry based on the CALPHAD method is a modern tool that helps to obtain quantitative data to guide the development and optimization of materials processing.

2. Evaluation of data from literature

2.1. Phase diagrams

2.1.1. The Fe–Lu system

The early publication on the iron–lutetium phase diagram known to the present authors is the one by Kolesnichenko et al. [10] who carried out thermal analyses and X-ray studies on alloys made of 99.9 at% Fe and 99.2 at% Lu. According to him, there are four intermetallic compounds: $Fe_{17}Lu_2$, $Fe_{23}Lu_6$, Fe_3Lu and Fe_2Lu. The existence and the structures of $Fe_{17}Lu_2$, $Fe_{23}Lu_6$ and Fe_2Lu had already been reported by Kripyakevich and Frankevich [11], Skrabek [12], Dwight [13] and Givord et al. [14]. The expected fourth compound was discovered by [10] and assigned the Ni_3Pu structure [14]. [10] investigated the $Ni_{17}Th_2$ structure in the Iron-Lutetium system by X-ray and neutron diffraction; he found that the composition extends from $Fe_{8.5}Lu$ to $Fe_{9.5}Lu$.

The melting point of lutetium observed by [10], i.e. 1650 °C, is lower than the value suggested by Hultgren et al. [15], 1662 °C. A α/β transformation was not observed by [10], but a high-temperature β phase was identified by Spedding and Daane [16]. A transformation temperature α/β has therefore been estimated about 1600 °C.

The phase diagram thus obtained by [10] has been redrawn by Kubaschewski [17] in Fig. 1a. Author information has been taken from Okamoto [18] to draw Fig. 1b.

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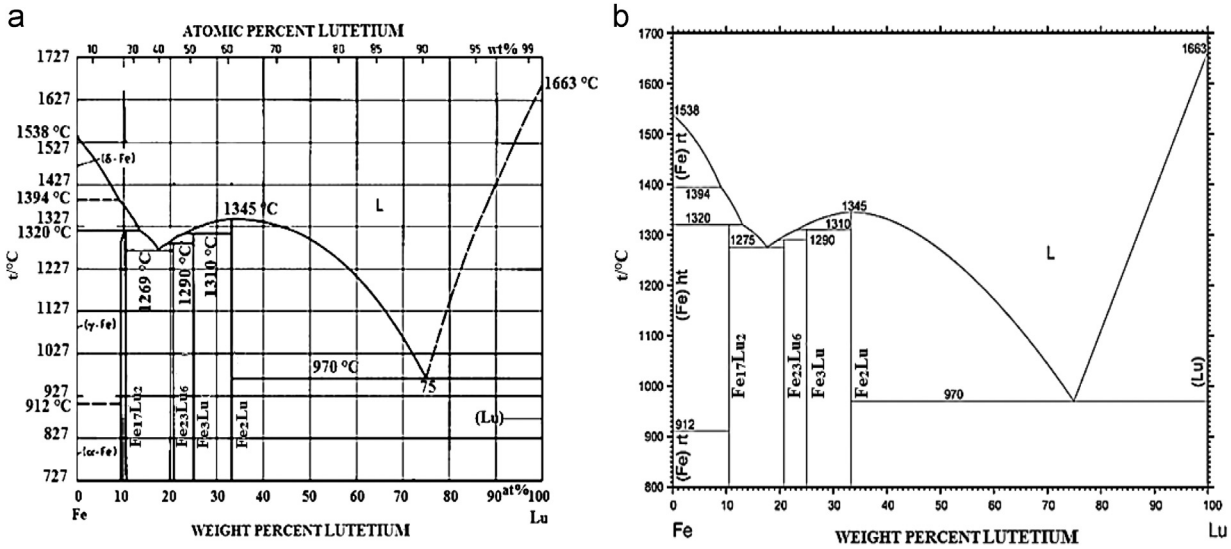

Fig. 1. Fe–Lu. Phase diagrams: (a) [18] and (b) [17].

Table 1
Fe–RE: system: crystal structures of the phases.

Phase	Composition at% RE	Symbol used in Thermo-Calc datafile	Pearson symbol	Space Group	Structure	Phase modeling	Model used	Ref.
δFe	0	BCC_A2	*cI2*	$Im\bar{3}m$	W	$(Fe,RE)_1:(Va)_1$[a]	SM	[20]
βFe	0	FCC_A1	*cF4*	$Fm\bar{3}m$	Cu	$(Fe, RE)_1:(Va)_{0.5}$[a]	SM	[20]
αFe	0	BCC_A2	*cI2*	$Im\bar{3}m$	W	$(Fe, RE)_1:(Va)_3$[a]	SM	[20]
$Fe_{17}RE_2$_LT	9.5 to 10.5 10.5	$Fe_{17}RE_2$	*hP38*	$P6_3/mmc$	$Ni_{17}Th_2$	$(Fe)_{17}:(Fe,Lu)_2$ $(Fe)_{17}:(Tm)_2$	TSMS TSM	[10,11,14]
$Fe_{23}RE_6$	20.6	$Fe_{23}RE_6$	*cF116*	$Fm\bar{3}m$	$Mn_{23}Th_6$	$(Fe)_{23}:(RE)_6$	TSM	[42,43,50]
Fe_3RE	25	Fe_3RE	*hR12*	$R\bar{3}m$	Ni_3Pu	$(Fe)_3:(RE)$	TSM	[10,42]
Fe_2RE	33.3	Fe_2RE	*cF24*	$Fd\bar{3}m$	Cu_2Mg	$(Fe)_2:(RE)_1$	TSM	[13,20,21,42,40,44,45,52]
(αRE)	100	HCP_A3	*hP2*	*P6₃/mmc*	Mg	$(Fe,RE)_1:(Va)_{0.5}$[a]	SM	[17,20]
(βRE)	100	–	–	–	–	–	SM	[20]

Models used: SM: Solution Model, TSM: Two Sublattices Model, and TSMS Two Sublattices Model with Substitution in one sublattice.

[a] Va = Vacancy

According to [19,20], Fe_2Lu which has a cubic structure melts congruently at 1345 °C and the remaining compounds, Fe_3Lu (rhombohedric), $Fe_{23}Lu_6$ (cubic), and $Fe_{17}Lu_2$ (hexagonal) form by peritectic reactions at 1310, 1290, and 1320 °C, respectively. The Fe–Lu system has two eutectic reactions at 970 °C and 27 at% Fe and at 1275 °C and 82 at% Fe. The alloys containing $\leq$ 10.6 at% Lu has a polymorphous transition at 915 °C: $Fe_{17}Lu_2$_LT ↔ $Fe_{17}Lu_2$_HT. γ–Fe to δ–Fe phase transition of Fe is unaffected by Lu. From the results reported by [10,17,19] no solubility of Lu in αFe, γFe and δFe was observed.

The crystallographic data of the Fe_pRE_q intermediate phases are listed in Table 1.

2.1.2. The Fe–Tm system

The iron–thulium phase equilibria have been determined by Kolesnichenko et al. [10]. The phase diagram information was taken by Kubaschewski [17] and Okamoto [18,19] and represented in their respective phase diagram compilations, shown in Fig. 2a and b.

The phase diagram reported by Kolesnichenko et al. [10] by X-ray diffraction and thermal analysis consists of four intermetallic compounds, Fe_2Tm and $Fe_{23}Tm_6$ with cubic structure and Fe_3Tm and $Fe_{17}Tm_2$ with rhombohedric and hexagonal structures. The existence and structure of Fe_2Tm, $Fe_{23}Tm_6$ and $Fe_{17}Tm_2$ had already been reported by Kripyakevich and Frankevich [11], Skrabek [12] and Haszko [21]. In addition, [10] found the expected 4th compound, Fe_3Tm, by thermal analysis and X-ray diffraction, alloys being made from 99.98 at% Fe and 99.9 at% Tm. Fe_2Tm melts congruently at 1300 °C and the remaining compounds Fe_3Tm, $Fe_{23}Tm_6$ and $Fe_{17}Tm_2$ form by peritectic reactions at 1280, 1270, and 1300 °C, respectively. The system forms two eutectic reactions at 1037 °C and 27 at% Fe and at 1255 °C and 82 at% Fe [10]. The compilation by Kubaschewski [17] shown in Fig. 2a was reported later in Massalski [20].

The melting point of Tm of 1547 °C [10] agrees with the value accepted by Hultgren et al. [15]. A α/β transformation of Tm has apparently not been found and has therefore been estimated at 1510–1520 °C. Furthermore, αTm is unaffected by Fe.

2.2. Thermodynamic and magnetic data

Germano et al. [22,23] by adiabatic calorimeter and Tereshina et al. [24] by using a PPMS magnetometer machine (Physical Properties Measurement System by Quantum design, USA) have determined the heat capacity for the Fe_2Lu, Fe_2Tm and $Fe_{17}Lu_2$