

Phase equilibria in the Fe-rich alloys of the ternary system Nd–Fe–Si at 500 °C

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Abstract

The solid state phase equilibria and phase relationship at 500 °C in the Nd–Fe–Si ([Nd] ≤ 40 at.% and [Si] ≤ 40 at.%) ternary system were investigated mainly by X-ray powder diffraction, with the aid of differential thermal microanalysis and optical microanalysis techniques. The partial isothermal section at 500 °C of this system has been established. The existence of three binary compounds and two ternary compounds, namely β (NdFe₂Si₂) and γ (NdFeSi), was confirmed in this partial isothermal section. The β phase belongs to the tetragonal system with $a=0.4001$ nm and $c=1.0061$ nm. The γ phase is also a tetragonal system with $a=0.3921$ nm and $c=0.6942$ nm.

The partial section consists of five single-phase regions, ten two-phase regions and five three-phase regions. At 500 °C, the maximum solid solubility of Si in Nd₂Fe₁₇ is 12 at.%. The γ phase has a homogeneity range, while the β phase is a non-variable compound.

Keywords: Phase equilibria; Iron-rich alloys; Ternary systems

1. Introduction

The Fe–Si binary system was described in Ref. [1]. At 500 °C, the compounds in this system are α -Fe, α_1 (Fe₃Si, BiF₃ type), FeSi and FeSi₂. The Nd–Fe binary system was first studied by Terekhova et al. [2]. They claimed there are two binary compounds, Nd₂Fe₁₇ and NdFe₂, in this system. Schneider et al. [3] re-examined this system later. They were not able to confirm the existence of the compound NdFe₂. This result has been accepted by many scientists. The Nd–Si phase diagram is given by Ref. [4]. The compounds existing in this system are Nd₅Si₃, Nd₅Si₄, Nd₃Si₄, NdSi, Nd₂Si₃, and NdSi_x. Liu [5] investigated the phase diagram of the Nd–Fe–Cu ternary system. The phase diagram of the Nd–Fe–Si ternary system has not been reported. In this work, we studied this system at 500 °C.

2. Experimental details

Preparation of the alloy samples and other relevant experimental procedures were similar to those described in a previous paper [6]. The starting materials for synthesis of the alloys were from commercially available metals of high purity (Fe, 99.95%; Si, 99.99%; Nd,

99.9%). 88 alloy buttons were prepared. The weight loss was less than 0.5%, and the alloys did obviously not react with the alumina crucibles during melting because the melting time is so short in this system (about 30 s–1 min). Therefore, no chemical composition analysis was carried out.

The alloys which contained less than 20 at.% Nd were homogenized at 800 °C for 30 days and cooled at a rate of 10 K h⁻¹ to 500 °C, and they were kept at 500 °C for 7 days and then quenched into an ice–water mixture. The other alloys were homogenized at 650 °C for 40 days and cooled at a rate of 10 K h⁻¹ to 500 °C, kept at 500 °C for 7 days and then quenched into an ice–water mixture.

Samples for X-ray diffraction analysis were powdered and annealed at 500 °C for 5 days in small glass tubes in vacuum and were subsequently quenched into liquid nitrogen. X-ray diffraction analysis was performed using a Rigaku (3015) X-ray diffractometer with Mo K α radiation and Zr filters. By comparing and analysing the X-ray diffraction patterns of the samples annealed for different periods of time, it was shown that the phases in the alloys completely reached equilibrium and the equilibrium state of the sample at 500 °C was retained by the above heat treatment.

This partial isothermal section was mainly determined by X-ray diffraction analysis and was checked by optical microscopy.

3. Results

3.1. Phase analysis

From an analysis of the X-ray diffraction patterns of the samples, we have confirmed the existence of the binary compounds: α_1 , $\text{Nd}_2\text{Fe}_{17}$, and the ternary compounds NdFe_2Si_2 and NdFeSi in this partial isothermal section of the Nd–Fe–Si ternary system at 500 °C. Ternary single-phase material was obtained by preparing samples according to the compositions given above.

A comparison of the X-ray diffraction data of the single phases with their powder diffraction files (ASTM) led to good correspondence for α -Fe, α_1 and $\text{Nd}_2\text{Fe}_{17}$. Their crystal data were in agreement with those given in Refs. [1,2].

The X-ray diffraction pattern of NdFe_2Si_2 is indexed successfully on the basis of a tetragonal lattice with $a=0.4001$ nm and $c=1.0061$ nm. The systematic extinction is in agreement with that of space group $I4/mmm$. It is fundamentally in agreement with that reported in Ref. [7] which is tetragonal, space group $I4/mmm$, with $a=0.3992$ nm and $c=1.0070$ nm.

The indexing results for the compound NdFeSi are shown in Table 1. The compound is tetragonal with space group $P4/nmm$, $a=0.3921$ nm and $c=0.6942$ nm, in agreement with that of NdFeSi reported in Ref. [8], but not orthorhombic as reported in Ref. [9]. We think the orthorhombic phase is a high temperature phase.

Table 1
Diffraction data for NdFeSi

Line number	2θ	I/I_0	$\sin^2\theta_{\text{obs}}$	$\sin^2\theta_{\text{cal}}$	$h k l$
1	11.74	23.4	0.010 46	0.010 48	0 0 2
2	11.95	8.5	0.010 74	0.010 83	1 0 1
3	14.67	11.1	0.016 30	0.016 42	1 1 0
4	15.44	34.9	0.018 05	0.018 69	1 0 2
5	15.72	18.7	0.018 70	0.019 04	1 1 1
6	17.65	100	0.023 54	0.023 58	0 0 3
7	25.85	28.5	0.050 03	0.050 13	1 0 4
8	27.56	4.3	0.056 73	0.056 43	2 0 3
9	29.40	3.4	0.064 39	0.064 64	2 1 3
10	31.60	5.1	0.074 13	0.073 91	3 0 0
11	31.80	11.1	0.075 05	0.074 77	2 0 4
12	35.80	13.6	0.094 46	0.094 32	0 0 6
13	37.35	3.4	0.102 52	0.102 53	1 0 6
14	38.65	6.0	0.109 51	0.109 38	3 2 1

3.2. Isothermal section at 500 °C

By comparing and analysing the X-ray diffraction patterns of 88 samples and by identifying the phases in each sample, the isothermal section at 500 °C of the ternary Nd–Fe–Si ($[\text{Nd}] \leq 40$ at.% and $[\text{Si}] \leq 40$ at.%) system was determined. It is shown in Fig. 1 that this section consists of five single-phase regions, ten two-phase regions and five three-phase regions. The results obtained from optical observation of the representative samples supported those obtained by X-ray diffraction analysis. The microstructures of alloys 41 (Nd–86at.%Fe–9at.%Si, in the $\alpha + \text{Nd}_2\text{Fe}_{17}$ two-phase region) and 75 (Nd–52at.%Fe–27at.%Si, in the $\text{Nd}_2\text{Fe}_{17} + \beta + \gamma$ three-phase region) are shown in Figs. 2 and 3 respectively.

3.3. Solid solubility

The single-phase ranges in this isothermal section at 500 °C were determined by X-ray diffraction using the phase-disappearing method and by comparing the movement of the diffraction patterns of the single phases.

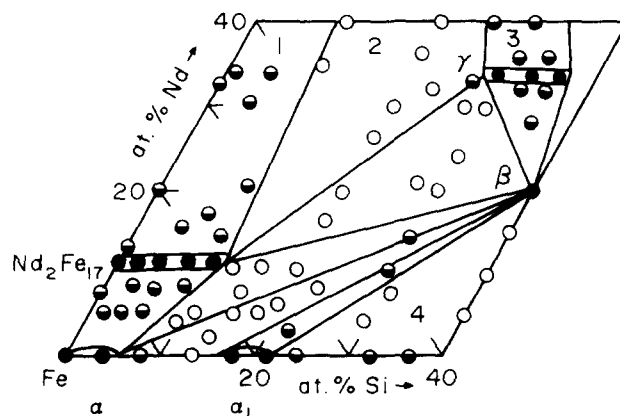


Fig. 1. Phase relationship of the Fe-rich portion of the Nd–Fe–Si system at 500 °C: ●, single-phase region; ◐, two-phase region; ○, three-phase region; 1, $\text{Nd}_2\text{Fe}_{17} + \text{Nd}$; 2, $\text{Nd}_2\text{Fe}_{17} + \text{Nd} + \gamma$ (NdFeSi); 3, $\gamma + \text{Nd}$; 4, $\alpha_1 + \beta$ (NdFe_2Si_2) + FeSi.



Fig. 2. Microstructure of alloy 41 (Nd–86at.%Fe–9at.%Si) in α -Fe + $\text{Nd}_2\text{Fe}_{17}$ (eutectic microstructure) two-phase region.



Fig. 3. Microstructure of alloy 75 (Nd-52at.%Fe-27at.%Si) in $\text{Nd}_2\text{Fe}_{17}$ (white needle) + β (light grey block) + γ (grey) three-phase region.

From X-ray diffraction analysis, we determined the single-phase region of $\text{Fe}_{17}\text{Nd}_2$, and NdFeSi to extend parallel to the Fe–Si boundary system. The maximum solubilities of Si in α -Fe and $\text{Fe}_{17}\text{Nd}_2$ at 500 °C are about 6 at.% and 12 at.% respectively. The single-phase ranges of α_1 and NdFeSi at 500 °C are approximately 16–24 at.% and 28–36 at.% respectively.

4. Discussion

The ranges of solid solution of α -Fe, α_1 , $\text{Fe}_{17}\text{Nd}_2$, and NdFeSi_{2-x} are parallel to the Fe–Si line. This means that the rare earth concentration remains fixed and Fe, Si can be mutually replaced to a certain degree in these phases.

De Mooij and Buschow [10] indicated that ternary compounds based on the tetragonal ThMn_{12} type structure were formed when rare earth elements are com-

bined with iron and elements M (M=Si, Ti, V, Cr, Mo, or W). They confirmed the compounds with Y and Gd rare earths. From an analysis of the X-ray diffraction of the samples near the composition of $\text{NdFe}_{10}\text{Si}_2$, we were not able to confirm the existence of a compound with ThMn_{12} -type structure. The phase in the sample of $\text{NdFe}_{10}\text{Si}_2$ is mainly $\text{Fe}_{17}\text{Nd}_2$, together with some α -Fe and β phases. We also were not able to confirm the existence of the compound NdFe_2 in this system.

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