



Phase equilibria in the Fe–Mn–Ce system at 900 °C



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ABSTRACT

Phase equilibria in the Fe–Mn–Ce system at 900 °C were studied using DTA, X-ray diffraction, SEM and electron probe microanalysis. Using the results an isothermal section at 900 °C for this system was constructed covering the whole concentration range. The stability of the ternary compounds Fe₁₁Mn₆Ce₂ (τ_1) and Fe₅Mn₇Ce (τ_2) at 900 °C, identified previously, was confirmed. The ternary compound τ_1 is located along a line with a constant Ce concentration of 9.6 at.% and its homogeneity range extends from 20 up to 34 at.% Mn at 900 °C. The ternary compound τ_2 is located along a line with a constant Ce concentration of 8 at.%. Its homogeneity range extends from 35 up to ~70 at.% Mn at 900 °C. The phases β Fe₁₇Ce₂ and Fe₂Ce, both of which dissolve appreciable quantities of Mn, are located along lines with constant concentrations of Ce of 10.8 and 33 at.%, respectively. The solubilities of Mn in β Fe₁₇Ce₂ and Fe₂Ce were established to be 18 and ~28 at.%, respectively.

At 900 °C the liquid phase is stable in the Fe–Mn–Ce system. The isothermal section is characterized by eight three-phase regions: (α Fe) + (γ Fe,Mn) + (β Fe₁₇Ce₂), (γ Fe,Mn) + (Fe₂Ce) + (β Fe₁₇Ce₂), (γ Fe,Mn) + (Fe₂Ce) + τ_1 , (γ Fe,Mn) + τ_1 + τ_2 , τ_1 + τ_2 + (Fe₂Ce), (γ Fe,Mn) + (β Mn) + τ_2 , L + (β Mn) + τ_2 and L + τ_2 + (Fe₂Ce) plus the corresponding two-phase regions.

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1. Introduction

Fe–Mn alloys have many attractive properties, such as shape memory properties, mechanical properties, electrical and magnetic properties etc. The Laves phases RFe₂ (where R is a rare-earth element) exhibit novel magnetic properties arising from the interaction between the localized 4f electrons and the itinerant 3d electrons. Intermetallic compounds RFe₂ are very attractive materials due to their hydrogen absorption capacity [1]. Intermetallic compounds R₂Fe₁₇ have high magnetic moments and relatively low Curie temperatures. The Curie temperatures T_c can be increased by minor partial substitution of iron by aluminum, silicon, gallium, manganese, cobalt, and other elements, as well as by the introduction of hydrogen, nitrogen, or carbon atoms [2,3]. The R₂Fe₁₇ compounds thus modified can be used to manufacture strong and relatively cheap permanent magnets. Because of the very small difference between the atomic radii of Fe and Mn, the solid solubility range of Mn in the Fe₂Ce and Fe₁₇Ce₂ is wide in the Fe–Mn–Ce ternary system. These factors are important and can

improve the performance of materials. The performance of materials depends not only on the properties of the single-phases in the materials, but is also influenced by the interaction of the various phases in the materials and the concentration of third element in solid solution. Consequently, the study of the phase diagrams of alloy is an effective way by which one might find new materials and improve the original materials.

Recently, phase equilibria in the Fe–Mn–Ce system covering the range of melting and solidification were studied by us [4]. Liquidus and solidus projections for this system over the whole concentration range were constructed. The ternary compounds Fe₁₁Mn₆Ce₂ (τ_1) (structure type Th₂Ni₁₇, hP38-P6₃/mmc, 194, $a = 0.8502$, $c = 0.8381$ nm [4]) and Fe₅Mn₇Ce (τ_2) structure type ThMn₁₂, tI26-I4/mmm, 139, $a = 0.8480$ – 0.8491 and $c = 0.8354$ – 0.8365 nm [4], identified previously [5,6], were found to melt incongruently by peritectic reaction: $P_1: L + (\gamma\text{Fe,Mn}) + (\text{Fe}_2\text{Ce}) \rightleftharpoons \tau_1$ and $P_2: L + (\gamma\text{Fe,Mn}) + \tau_1 \rightleftharpoons \tau_2$ at 974 and 953 °C, respectively [4]. The ternary compound τ_1 is located along a line with a constant Ce concentration of 10.5 at.% and its homogeneity range extends from 20 up to 36 at.% Mn at the solidus temperature. The ternary compound τ_2 is located along a line with a constant Ce concentration of 8 at.%. Its homogeneity range extends from 35 up to 78 at.% Mn at the solidus temperature. The solubilities of Mn in β Fe₁₇Ce₂ and

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Fe₂Ce were established to be 18 and 33 at.%, respectively. A previous experimental investigation of the Fe–Mn–Ce system had been carried out by Kalychak et al. [5]. Isothermal sections at 600 °C and 400 °C (600 °C up to 33.3 at.% Ce, 400 °C above 33.3 at.% Ce) were suggested on the basis of light microscopy investigations and X-ray analysis of annealed samples. In this paper we present our experimental study, using SEM, EPMA and X-ray diffraction, of phase equilibria in the Fe–Mn–Ce system over the whole concentration range at a temperature 900 °C.

The boundary binary systems accepted in this work were discussed in Ref. [4].

2. Experimental

2.1. Sample preparation

The purity of the starting materials was Fe–99.99%, Mn–99.9% and Ce–99.8%. The alloys were melted in an arc-furnace with an unconsumable tungsten electrode on a water-cooled copper hearth in an Ar atmosphere 99.998% pure (pressure 80 kPa), purified by a Ti melt. To achieve homogeneity, the buttons were turned over and remelted six times. The ingot weights were typically 5 g and the weight losses did not exceed 0.2%. For each of these samples, an area scan was performed using microprobe examination. Good correspondence with the composition of initial mixtures was obtained. Therefore, the composition of the samples was taken according to their nominal composition.

The alloys, placed in an Al₂O₃ crucible, were subjected to homogenization heat treatment at 900 °C for 15–30 h. The annealing experiments were performed in a tube furnace with (Nabertherm RHTV 120/300/1700) with a temperature accuracy of ± 3 °C under an argon atmosphere 99.998% pure. After annealing, the samples were quenched on air to retain the equilibrium microstructures.

The samples were studied by the methods of differential thermal analysis (DTA), optical microscopy (OM), scanning electron microscopy (SEM), electron probe microanalysis (EPMA) and X-ray diffraction (XRD).

2.2. Microstructure analysis

Metallographic specimens for microscopic examination were prepared by a grinding-and-polishing machine (Struers Labopol-5). Firstly, the grinding procedure was carried out using SiC-paper and then diamond discs with grain sizes of 9 and 1 microns. Diamond suspension or spray was applied at regular intervals during the preparation. The microstructure of the alloys was examined using optical microscopy (OM) (Olympus-GX71F-5) and by scanning electron microscopy (SEM) using a TESCAN VEGA LMH microscope with a LaB₆ cathode and an energy dispersive X-ray microanalysis system – Oxford Instruments Advanced AZtecEnergy. Both back-scattered electron and secondary electron imaging were used in the analysis. An electron microprobe analysis (EPMA) was carried out on all phases using a four-crystal wave spectrometer (the analyzed particle size was larger than 2 μ m). The acceleration voltage used for the EPMA was 20 kV. The error of measurement in determining the concentration of elements using X-ray analysis was 0.1% wt.

2.3. Differential thermal analysis

Phase transition temperatures were measured with the DSC LABSYS and SETSYS evo Setaram. Pure metal standards, Sn, Al, Cu, and Ag, were used for calibration. DTA experiments were carried out in a closed Al₂O₃ crucible under a continuous flow of argon on the as-cast samples and some alloys after homogenization heat treatment at 900 °C/15–30 h. The heating and cooling rate was

5 °C/min. The temperatures of the invariant reactions were determined from the onset. Data for the phase transition temperatures were determined from the heating curves. The liquidus temperatures on heating were evaluated from the peak maximum, those on cooling from the corresponding onset. On the whole, pronounced supercooling effects were not observed for the investigated alloys, and the liquidus temperatures for most alloys were therefore taken from the corresponding cooling curve since thermal effects on cooling are shown more clearly.

2.4. X-ray diffraction analysis

X-ray diffraction (XRD) analysis was applied to determine the phase composition of the alloys using CuK α radiation operated at a voltage of 40 kV, a current of 40 mA and filtered with a Ni-crystal monochromator. XRD measurements were performed using a multipurpose X-ray diffractometer (Bruker-AXS D8 Discover). A parallel beam with a divergence of 0.03° is formed using the mirror of Gobel. The reflected intensity of the beam was measured using LYNXEYE position sensitive detector (angular resolution of 0.015°). Indexing of the reflections was performed with the WinXPOW and PowderCell software products.

3. Results and discussion

The alloys were studied after annealing at 900 °C for 15–30 h. The phase compositions of the studied alloys and the EPMA results are given in Table 1. The isothermal section of the Fe–Mn–Ce system at this temperature was constructed and shown in Fig. 1. In Table 1 these data are presented following refinement using a least-squares method. These results are also shown in Fig. 1. A few measurements for each phase were performed by using the microprobe method. The microstructures of some of the annealed samples are presented in Fig. 2. The lattice parameters of the solid phases are shown in Table 2.

The binary compound Fe₁₇Ce₂ occurs in two crystalline modifications: rhombohedral (ht) (Zn₁₇Th₂-type structure, *hR57-R-3m*, 166) and hexagonal (rt) (Ni₁₇Th₂-type structure, *hP38-P6₃/mmc*, 194). The transition temperature has not been established. We observed only the high-temperature modification of this compound in our work. The low temperature modification, α Fe₁₇Ce₂, with a hexagonal Ni₁₇Th₂-type structure [12] had also not been observed in Refs. [5,9,11]. Since β Fe₁₇Ce₂ (ht) and the ternary compound τ 1 have different crystal structures they do not form a continuous solid solution. The homogeneity ranges, representing the solubility of Mn in the binary compounds β Fe₁₇Ce₂ and Fe₂Ce, are significant. The maximum manganese content in the phase β Fe₁₇Ce₂ reaches ~18 at.% as discussed in Ref. [4]. The alloys with 74Fe–15.5Mn–10.5Ce (#24) and 72Fe–17.5Mn–10.5Ce (#25) according to SEM, EPMA and XRD data contain mainly the (β Fe₁₇Ce₂)-phase and a small amount of the (γ Fe,Mn) phase (Tables 1 and 2, Figs. 1, 2a and 3a). The homogeneity range of this phase is located along the line of constant Ce concentration of 10.8 at.% (Table 1). The Laves Fe₂Ce-phase dissolves up to ~28 at.% Mn. This results from the mutual substitution of Fe and Mn atoms. The homogeneity range of this phase is located along the line of constant Ce concentration of 33 at.% (Table 1). Maximum solubility of Mn in Laves Fe₂Ce-phase was determined via intersecting isopleths. The isopleths were constructed mainly according to DTA data.

The stability of the ternary compounds Fe₁₁Mn₆Ce₂ (τ ₁) and Fe₅Mn₇Ce (τ ₂) at 900 °C was confirmed [4–6]. As found in the establishment of the solidus surface, both ternary compounds, τ ₁ and τ ₂, have significant linear homogeneity ranges, and the phases are located along the lines with constant concentrations of Ce of 9.6 and 8 at.% respectively. The homogeneity range of the τ ₁-phase

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