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Isothermal section of the Ni–Mn–In ternary system at 773 K

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ABSTRACT

The isothermal section of the Ni–Mn–In ternary system at 773 K was investigated and constructed using X-ray diffraction (XRD), and electron probe microanalysis (EPMA) techniques. The existence of 7 binary compounds and 2 ternary compounds was confirmed in the isothermal section. The six binary compounds Ni_2In_3 (Ni_2Al_3-type structure, space group P$\bar{3}$m1), NiIn (CoSn-type structure, space group P6/mmc), $Ni_{13}In_9$ ($Ni_{13}Ga_9$-type structure, space group C2/m), Ni_2In ($Co_{1.75}Ge$-type structure, space group $P6_3/mmc$), Ni_3In (Mg_3Cd-type structure, space group $P6_3/mmc$) and Mn_3In (Al_4Cu_9-type structure, space group P$\bar{4}$3m) in the sub-binary systems Ni–In and Mn–In are stoichiometric compounds, the homogeneity ranges of which are negligible. While the five single phase regions in the Ni–Mn binary system show a more or less homogeneity ranges formed by replacement of Mn for Ni. The homogeneity ranges of the ternary compounds T1 (Ni_2MnIn) and T2 (Mn_3Ni_2In) at 773 K were determined.

1. Introduction

Recently, the Heusler-type Ni–Mn–In shape memory alloys have attracted considerable attention due to their multi-functionalities [1], such as large magnetocaloric effect (MCE) [2], large magnetic-field-induced strain (MFIS) [3,4], giant magnetoresistance effect [5,6], and high magnetothermal conductivity [7]. All of these properties originate from the magnetic field-induced structural transformation from a high temperature high symmetry cubic structure (ferromagnetic austenite) to a low temperature orthorhombic structure (paramagnetic/antiferromagnetic martensite) with lesser crystal symmetry [8–11], which offers the possibility of application in high-performance actuators [12], environment-friendly magnetic refrigerators [13], etc. The martensitic transformation temperatures of these alloys are drastically decreased by application of a magnetic field and magnetic-field-induced reverse transformation, namely, metamagnetic phase transition, occurs near the martensitic reverse transformation start temperature Ms [14,15]. Although many interesting properties accompanying this unique transformation listed above have been reported, few research of phase diagram covering the whole range in the Ni–Mn–In ternary system has been established. Although Miyamoto et al. [16] have investigated the isothermal section at 850 °C and 700 °C recently, information about the phase diagram at 773 K is unknown.

The most reliable Ni–Mn [17–20], Mn–In [21] and Ni–In [22,23] phase diagrams have been published. The phase diagram of the Ni–Mn system was early investigated by many groups. Tsiuplakis and Kneller [17] investigated the Mn–Ni system in detail, in which eight intermetallic compounds Mn_3Ni, Mn_2Ni, MnNi(η), MnNi(η′), MnNi(η″), $MnNi_2$(ξ), $MnNi_2$(ξ′), and $MnNi_3$ were found. Later, Coles [18] reinvestigated the equiatomic region of the Mn–Ni system and stated that it is impossible to have so many stable phases suggested by Tsiuplakis and Kneller [17] at the equiatomic composition between 480 and 630 °C. In Coles's [18] and Ding's experiment [20], only one phase existed in the equiatomic region between 500 °C and 650 °C. According to Guo's work [19], there are four compounds in Ni–Mn binary system: αMnNi (B2-type structure), βMnNi ($L1_0$-type structure), $MnNi_2$ and $MnNi_3$, in which only βMnNi compound is stable at 773 K. For the Mn–In binary system, there is only one stoichiometric compound Mn_3In. The Ni–In system was compiled by Massalski [22] in 1990 and completely revised by Durusssel [23] in 1997. In Ref. [22], the proposed inter-mediate compounds, except for Ni_2In, show a detectable, more or less homogeneity range. While in Durusssel's work [23] it is proved that only three observed intermetallic compounds are nonstoichiometric: Ni_2In (high temperature form), $Ni_{13}In_9$ and NiIn (high temperature form), while the other intermetallic compounds are stoichiometric: Ni_3In, Ni_2In (low temperature form), NiIn (low temperature form), Ni_2In_3 and Ni_3In_7 in this system. The existence of two ternary compounds Ni_2MnIn and Mn_3Ni_2In in the Ni–Mn–In system has ever been reported

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[16,24]. Crystallographic data for the intermetallic compounds relevant to this study are mainly taken from Ref. [25] and listed in Table 1.

The aim of present work is to establish complete isothermal sections in the Ni–Mn–In system at 773 K by analyzing equilibrated ternary alloys using electron probe microanalysis (EPMA), X-ray diffraction (XRD) and differential scanning calorimetry (DSC). It is expected that this study will give further insights into the Ni–Mn–In ternary system for practical applications.

2. Experimental procedure

Polycrystalline Ni–Mn–In alloys were prepared by arc melting using a non-consumable tungsten electrode and a water-cooled copper tray in pure argon atmosphere. The nickel, manganese and indium metals with purity higher than 99.9% were used as starting materials. Titanium was used as an oxygen getter during the melting process. The samples were re-melted three times to ensure complete fusion and composition homogeneity. Ninety-two alloy buttons were prepared. The weight loss of the samples for phase analysis is less than 0.5 wt.%. The melted buttons were sealed in evacuated quartz tubes, and then put in a resistance furnace for homogenizing annealing at different temperatures in order to reach a good homogenization. The homogenization temperature of the alloys was chosen on the basis of the binary phase diagrams of the Ni–Mn, Ni–In and Mn–In systems and the result of differential thermal analysis (DTA) of some typical ternary alloys. The homogenization annealing was performed at 773 K for 60 days for the In-rich alloys with Ni and Mn less than 40 at.%, while at 873 K for 15 days for other alloys, which were cooled to 773 K and then kept at 773 K for 30 days. All alloys were quenched in liquid nitrogen after homogenization process at 773 K. Most samples were cut into two parts for X-ray powder diffraction and metallographic investigations.

The samples for X-ray diffraction were ground in an agate mortar into powder of micrometer size. The phases in the samples were identified by means of X-ray powder diffraction (XRD) analysis mainly using a Bruker D8 Advance SS/18 kW diffractometer with Cu Kα radiation operated at 40 kV and 200 mA. The data were collected in the range of 2θ from 20° to 80° at a step of 0.02°. JADE 6.0 and Topas 3.0 softwares were used for phase analysis and structure refinement. After standard metallographic preparation, the microstructures and the equilibrium compositions of each phase were measured by EPMA (JXA-8530F, JEOL, Japan). Pure elements Ni, Mn and In were used as standards and the measurements were carried out at 20.0 kV.

3. Results and discussion

3.1. Phase analysis and microstructures

X-ray diffraction analysis of the alloys in the boundary binary systems, Ni–Mn, Ni–In and Mn–In, in this work confirmed the existence of seven binary compounds, Mn_3In, Ni_2In_3, NiIn, $Ni_{13}In_9$, Ni_2In, Ni_3In and βNiMn at 773 K, which is in a good agreement with those reported in this systems [19,21,23]. Two ternary compounds, Ni_2MnIn and Mn_3Ni_2In, exist in the isothermal section at 773 K in this system. The existence of the ternary compound Mn_3Ni_2In which was first reported in 2013 by the Miyamoto's group [16] was also confirmed in our work. Most of the PDF files of the binary compounds mentioned above are available on JCPDS PDF cards (2004), except for the $Ni_{13}In_9$ and Mn_3Ni_2In compounds. The XRD patterns for the $Ni_{13}In_9$ and Mn_3Ni_2In compounds were calculated from their crystallographic data taken from Refs. [23,16] using the JADE 6.0 program for the phase analysis. Three typical XRD patterns for the samples on the boundary binary systems were shown in Fig. 1. We can see from Fig. 1 that the three alloys were located in the binary regions of Mn_3In + In, NiIn + Ni_2In_3 and NiIn + $Ni_{13}In_9$, respectively.

Phase identification was carried out based on the Rietveld refinement results and phase equilibrium composition determined by EPMA. The accuracy for the results of EPMA analyses was better than one percent. The Rietveld refinement results and the BSE (back-scattered electron) images for EPMA of selected five ternary Ni–Mn–In alloys are presented in Figs. 2–6, showing the phases and microstructures determined by the refinement results and EMPA analysis.

The Rietveld refinement results and BSE image of sample 44# ($Ni_{40}Mn_{20}In_{40}$), shown in Fig. 2, confirm that the alloy consists of the three phases: Ni_2MnIn, Ni_2In_3 and Mn_3Ni_2In, which was in a good agreement with that from EPMA analysis. The EPMA analysis results, presented in Table 2, indicate that the dark region was identified as Mn_3Ni_2In phase, the white region as Ni_2In_3 phase and the grey matrix as Ni_2MnIn phase, shown in Fig. 2(b).

The Rietveld refinement results of the XRD pattern and the BSE image for the sample 34# ($Ni_{20}Mn_{60}In_{20}$), presented in Fig. 3, shows that this alloy is located in the Mn_3In, β (Mn) and Mn_3Ni_2In three-phase region. The microstructure for the alloy is shown in Fig. 3(b). The EPMA analysis confirms that the dark region is the β (Mn) phase, the grey region is the Mn_3In phase and the light grey region is the Mn_3Ni_2In phase.

In the same way, it is verified that the $Ni_{60}Mn_{10}In_{30}$ alloy (at.%) shown in Fig. 4(a) and (b) is located in the Ni_2MnIn + Ni_2In two-phase region. For the $Ni_{35}Mn_{45}In_{20}$ alloy (at.%), we can see from Fig. 5(a) and (b) that Mn_3Ni_2In is the major phase, and Ni_2MnIn is the minor phase. Fig. 6(a) and (b) shows that $Ni_{20}Mn_{40}In_{40}$ (at.%) located in the Mn_3In + Mn_3Ni_2In + liquid (In-rich) three-phase region.

3.2. Isothermal section at 773 K

The phase equilibrium compositions related to the two ternary compounds Ni_2MnIn and Mn_3Ni_2In at 773 K determined by EPMA are listed in Table 2. By comparing and analyzing the XRD patterns and EPMA compositional results and identifying the phases in each sample, we have constructed the isothermal section of Ni–Mn–In ternary system at 773 K as presented in Fig. 7. The liquid boundary near In-rich side is indicated by dashed lines which hasnot been determined in this work. In the isothermal section, as shown in Fig. 7, fourteen three-phase regions, twenty-seven two-phase regions, and thirteen single-phase regions are existed in this present work. They are described as follows: the 13 single-phase regions are γ(Ni), βNiMn, γ(Mn), β(Mn), α(Mn), Mn_3In, Ni_2In_3, NiIn,

Table 1
Crystallographic data for the phases in the Ni–Mn–In ternary system.

Phase	Space group	Prototype	Lattice parameters				Refs.
			a (nm)	*b* (nm)	*c* (nm)	*β* (°)	
βMnNi	I4/mmm	In	0.3723	–	0.352		[25]
Mn_3In	$P\bar{4}3m$	Al_4Cu_9	0.942	–	–		[25]
Ni_3In	P63/mmc	Mg_3Cd	0.5332(2)	–	0.4234(2)		[25]
Ni_2In	P63/mmc	$Co_{1.75}Ge$	0.4171	–	0.5121		[25]
$Ni_{13}In_9$	C2/m	$Ni_{13}Ga_9$	1.4646	0.8329	0.8977	35.35	[25]
NiIn	P6/mmm	CoSn	0.4536(5)	–	0.4434(5)		[25]
Ni_2In_3	$P\bar{3}m1$	Ni_2Al_3	0.439	–	0.52		[25]
Ni_2MnIn	$Fm\bar{3}m$	Cu_2MnAl	0.608	–	–		[24]
Mn_3Ni_2In	$Fd\bar{3}m$	Mn_3Ni_2Si	1.1307	–	–		[16]