Journal of Alloys and Compounds 704 (2017) 717–723

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

The Dy-Ni-In system at 870 K: Isothermal section, solid solutions, crystal structures

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ARTICLE INFO

Article history:
Received 27 October 2016
Received in revised form
31 January 2017
Accepted 3 February 2017
Available online 7 February 2017

Keywords:
Rare earth alloys and compounds
Intermetallics
Phase diagram
Crystal structure
X-ray diffraction
Magnetic measurements

ABSTRACT

Isothermal section of the Dy-Ni-In system at T = 870 K has been constructed. Twelve compounds exist in the system, namely: $DyNi_9In_2$, $Dy_4Ni_{10.80}In_{20.20}$, $DyNi_4In$, $DyNiIn_2$, $DyNi_{1-x}In_{1+x}$ (x = 0÷0.4), Dy_2Ni_2In, $Dy_2Ni_{2-x}In$ (x = 0.22), $Dy_5Ni_2In_4$, $Dy_{11}Ni_4In_9$, $Dy_6Ni_{2.34}In_{0.66}$, ~$Dy_{67}Ni_{22}In_{11}$ and $Dy_{13.60}Ni_{3.34}In_{3.06}$. Previously reported $Dy_{10}Ni_9In_{20}$ and $Dy_3Ni_2In_4$ compounds exist at higher temperature.

The Ni/In substitution was observed for $DyNi_{1-x}In_{1+x}$ (x = 0÷0.4) and the Dy/In for $Dy_{1-x}Ni_2In_x$ (x = 0÷0.5) solutions. Solid solution Dy_xNiIn_{1-y}, based on binary NiIn, extends up to 8 at.% Dy. Crystal structure of this solution at the composition $Dy_{0.13}NiIn_{0.93}$ was studied by single crystal and powder X-ray diffraction. Magnetic properties of numerous Dy-Ni-In compounds have been reviewed as well.

1. Introduction

The ternary systems *RE-T*-In (*RE* - rare earths, *T*-transition metal) are sufficiently rich in ternary compounds [1–3] which have attracted broad interest in recent years with respect to their interesting crystal chemistry and greatly varying physical properties. A comprehensive overview of the systems has been given in paper [4]. Whereas the systems with copper have been studied in detail, the investigation of other transition metal containing systems has not been fully completed. According to mentioned references, the Ni-containing ternary systems are mostly rich in ternary compounds among the concerned systems and nearly 150 $RE_xNi_yIn_z$ compounds are known. Isothermal sections of the phase diagrams have been constructed only for *RE*-Ni-In systems with *RE* = Ce, Tb, Er and Tm [5–8].

According to [1,4,9,10] twelve compounds are known in the system with dysprosium: $DyNi_9In_2$, $Dy_4Ni_{10.80}In_{20.20}$, $DyNi_4In$, $DyNiIn_2$, $Dy_{10}Ni_{9.32}In_{20}$, DyNiIn, Dy_2Ni_2In, $Dy_2Ni_{2-x}In$, $Dy_5Ni_2In_4$, $Dy_{11}Ni_4In_9$, $Dy_6Ni_{2.34}In_{0.66}$ and $Dy_{13.60}Ni_{3.34}In_{3.06}$.

The $Dy_3Ni_2In_4$ compound (= $DyNi_{0.67}In_{1.33}$) has recently been reported in Ref. [51] at 1020 K. It crystallizes with the hexagonal $Lu_3Co_2In_4$-type structure that is a superstructure to ZrNiAl type.

The latest data on the binary phase diagram and the compounds of Dy–In system were taken from Ref. [11], those of Dy-Ni from Ref. [12] and of Ni-In from Refs. [13,14].

In this paper we report on the isothermal section of the Dy-Ni-In phase diagram at 870 K. The particularities of crystal structure and physical properties of the ternary indides are discussed.

2. Experimental

For investigation of the interaction in the Dy-Ni-In ternary system 91 binary and ternary samples have been synthesized. The samples were prepared by arc melting under purified argon atmosphere (P = 50 kPa, sponged Ti was used as a getter) of the constituent components with certified purities of 99.8 wt. % for Dy, 99.92 wt. % for Ni and 99.99 wt. % for In. All buttons were re-melted twice to ensure homogeneity. The overall weight losses were generally less then 1 wt. % of starting weight near 1 g. The samples were annealed at 870 K for 720 h in evacuated quartz tubes and finally were quenched in cold water without breaking the tubes.

X-ray phase analysis was the main method for isothermal

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http://dx.doi.org/10.1016/j.jallcom.2017.02.023
0925-8388/

section construction. It was carried out using film data (Debye-Scherrer technique, RKD-57.3 cameras, CrK-radiation) and measurements using DRON-2.0 M (FeK_α-radiation) and STOE STADI P ($MoK_{\alpha1}$ and $CuK_{\alpha1}$ radiation) diffractometers. Indexing of the obtained diffraction data of the ternary samples was performed by comparison with calculated data using Powder Cell program [15].

Single crystals were studied using a Xcalibur diffractometer from Oxford Diffraction, equipped with a Sapphire2 CCD detector and an Enhance X-ray source option.

The Rietveld refinements of powder data were made using WinCSD [16] program package. The WinCSD was also used for single crystal structure refinement.

Metallographic and quantitative phase analyses were performed for selected samples using a Neophot 30 optical microscope and a REMMA-102-02 raster electronic microscope equipped with an energy dispersive X-ray analyzer (EDX).

Magnetic measurements were carried out using a vibrating sample magnetometer (VSM) option of the Quantum Design PPMS platform (Institute of Physics, Jagellonian University, Krakow, Poland). Measurement of ZFC (zero field cooling) magnetic susceptibility from 1.9 K up to 350 K in a magnetic field of 1 kOe was performed in order to determine phase transition temperatures, effective magnetic moment μ_{eff} and paramagnetic Curie temperature θ_p for $DyNi_4In$ compound.

3. Results and discussions

3.1. Isothermal section

The isothermal section of the phase diagram of Dy-Ni-In system at 870 K has been constructed for the first time and it is shown in Fig. 1.

At this temperature all binary compounds of Dy-In system [11]: Dy_2In (Ni_2In type), Dy_5In_3 (W_5Si_3), DyIn (CsCl), Dy_3In_5 (Pu_3Pd_5) and $DyIn_3$ ($AuCu_3$) have been confirmed. In Ni–In system [14] compounds: Ni_3In (Ni_3Sn type), Ni_2In (own structure), ζ–phase (high temperature modification of Ni_2In), $Ni_{13}In_9$ (In_9Pt_{13}), NiIn (CoSn), Ni_2In_3 (Al_3Ni_2) have been observed. Eight compounds of Dy-Ni system [12]: Dy_3Ni (Fe_3C), Dy_3Ni_2 (own structure), DyNi (FeB), $DyNi_2$ ($MgCu_2$), $DyNi_3$ ($PuNi_3$), Dy_2Ni_7 (Gd_2Co_7 type), $DyNi_5$ ($CaCu_5$) and Dy_2Ni_{17} (Th_2Ni_{17}) have been observed.

At 870 K the Dy-Ni-In system is characterized by the formation of twelve ternary compounds which are listed in Table 1 (the numbers of the compounds correspond to those of Fig. 1). One of those compounds of ~ $Dy_{67}Ni_{22}In_{11}$ composition has been revealed in this research.

The only two binary compounds $DyNi_2$ and NiIn dissolve significant amount of the third element. The single ternary phase of equiatomic composition forms extended homogeneity region. The particularities of the phase equilibria in the Dy-Ni-In ternary system at 870 K are described below.

3.2. $DyNiIn_2$ and $Dy_{10}Ni_9In_{20}$ compounds

Two compounds with very close stoichiometry $DyNiIn_2$ ($Dy_{25}Ni_{25}In_{50}$) and $Dy_{10}Ni_{9.32}In_{20}$ ($Dy_{25.4}Ni_{23.7}In_{50.9}$) have been reported in the literature. According to [20] the crystal structure of $DyNiIn_2$ was adopted to $MgCuAl_2$ and this of $Dy_{10}Ni_9In_{20}$ - to $Ho_{10}Ni_9In_{20}$ type [21]. At temperature of investigation only $DyNiIn_2$ has been confirmed. $Dy_{10}Ni_9In_{20}$ has been obtained in Ref. [21] by a special heat treatment (the sample was first heated to 1270 K within 5 h and held at that temperature for 5 h. Subsequently the temperature was lowered at a rate of 4 K/h to 1030 K, then at a rate of 20 K/h to 630 K, and finally cooled to room temperature within 5 h). The $Dy_{10}Ni_9In_{20}$ compound, probably, exists at higher temperature.

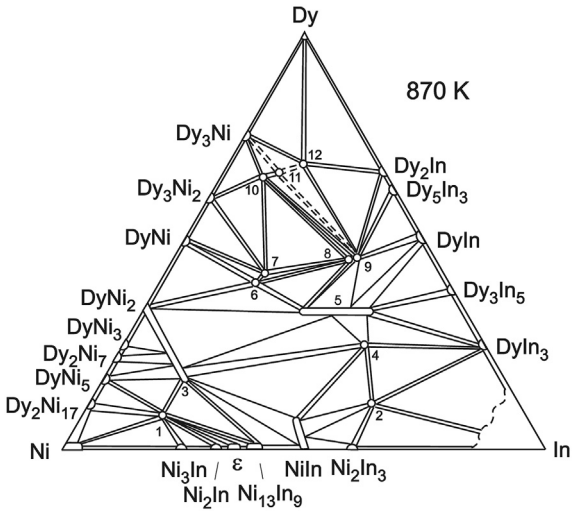

Fig. 1. Isothermal section of the Dy-Ni-In phase diagram at 870 K. The numbers of the compounds in figure correspond to those in Table 1.

3.3. Dysprosium-rich corner of the isothermal section

Three phases have been detected in region of high dysprosium concentration, more than 60 at. % Dy, namely: $Dy_6Ni_{2.34}In_{0.66}$ with crystal structure of Ho_6Co_2Ga type, $Dy_{14}Ni_3In_3$ - $Lu_{14}Co_2In_3$ type and ~ $Dy_{67}Ni_{22}In_{11}$ compound with unknown complex structure. According to EDX analysis composition of latter compound equals $Dy_{64.0}Ni_{19.3}In_{16.7}$.

3.4. $DyNi_{1-x}In_{1+x}$ solid solution

The first time DyNiIn compound was studied by Ref. [22] and it was adopted to Fe_2P type or its ordered derivative ZrNiAl. Later, it was established that this compound has homogeneous region, which can be described as $DyNi_{1-x}In_{1+x}$ ($x = 0 \div 0.4$). Substitution of nickel by indium (Fig. 2a) is accompanying by increasing of cell volume, according to atomic radii of elements [26], but if period *a* is increasing then period *c* is slightly decreasing [23]. Similar tendency was confirmed by single crystal investigation of $TmNi_{1-x-y}In_{1+x}$ structure [27]. According to it, the solid solution is characterized not only by occupation of 2*d* site of $P\bar{6}2m$ space group with Ni2/In2 mixture, but with partly occupation of 1*a* site with Ni1 atoms too.

3.5. $Dy_{1-x}Ni_2In_x$ ($0 \le x \le 0.5$) solid solution

$DyNi_4In$ was investigated for the first time in Ref. [19] and it was concerned as individual compound with the $MgCu_4Sn$ structure type. The systematic studies of the phase equilibria in this concentration region reveal solid solution between Laves phase $DyNi_2$ ($MgCu_2$ type) and $DyNi_4In$ ($MgCu_4Sn$ type, ternary derivative of $MgCu_2$) where substitution of rare earth atoms by indium in ¼ ¼ ¼ position occurs according to scheme: $8\,RENi_2 = RE_8Ni_{16} = RE_4RE_4Ni_{16} = RE_4In_4Ni_{16} = 4\,RENi_4In$. Lattice parameter decreases with small deviations from Vegard's rule up to the $DyNi_4In$ composition (Fig. 2b). In systems with Tb and Tm same solid solutions have been revealed [6,28]. For $ErNi_2$ – $ErNi_4In$ section two-phase equilibrium between two solid solutions has been noticed [7].