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The isothermal section of Gd–Ni–Si system at 1070 K

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ABSTRACT

The Gd–Ni–Si system has been investigated at 1070 K by X-ray and microprobe analyses. The existence of the known compounds, *i.e.*: $GdNi_{10}Si_2$, $GdNi_8Si_3$, $GdNi_5Si_3$, $GdNi_7Si_6$, $GdNi_6Si_6$, $GdNi_4Si$, $GdNi_2Si_2$, $GdNiSi_3$, $Gd_3Ni_6Si_2$, GdNiSi, $GdNiSi_2$, $GdNi_{0.4}Si_{1.6}$, $Gd_2Ni_{2.35}Si_{0.65}$, Gd_3NiSi_2, Gd_3NiSi_3 and $Gd_6Ni_{1.67}Si_3$, has been confirmed. Moreover, five new phases have been identified in this system. The crystal structure for four of them has been determined: $Gd_2Ni_{16-12.8}Si_{1-4.2}$ (Th_2Zn_{17}-type), $GdNi_{6.6}Si_6$ ($GdNi_7Si_6$-type), Gd_3Ni_8Si (Y_3Co_8Si-type) and $Gd_3Ni_{11.5}Si_{4.2}$ ($Gd_3Ru_4Ga_{12}$-type). The compound with composition $\sim Gd_2Ni_4Si_3$ still remains with unknown structure. Quasi-binary phases, solid solutions, were detected at 1070 K to be formed by the binaries $GdNi_5$, $GdNi_3$, $GdNi_2$, GdNi, $GdSi_2$ and $GdSi_{1.67}$; while no appreciable solubility was observed for the other binary compounds of the Gd–Ni–Si system.

Magnetic properties of the $GdNi_6Si_6$, $GdNi_{6.6}Si_6$ and $Gd_3Ni_{11.5}Si_{4.2}$ compounds have also been investigated and are here reported.

1. Introduction

The study of the phase diagrams or isothermal cross-sections of rare earth (*R*) systems, along with the full characterization of the crystal structure of the compounds formed and the investigation of their magnetic properties, is an important step towards both fundamental and practical goals in the materials science, solid state chemistry and physics.

The isothermal section of Gd–Ni–Si at 870 K was early investigated by Bodak and Shvets [1–3]; the ternary compounds $GdNi_{10}Si_2$ [4], $GdNi_{6.72}Si_{6.28}$ [2], $GdNi_5Si_3$ [5], $GdNi_4Si$ [2], $GdNi_2Si_2$ [6], $GdNiSi_3$ [2], $GdNiSi_2$ [7], $Gd_3Ni_6Si_2$ [2], GdNiSi [2] and Gd_3NiSi_2 [8] were found to form in this ternary system at 870 K. Moreover, the occurrence of the quasi-binary systems $GdNi_{0.2}Si_{1.8}$ ($ThSi_2$-type, [1,2,9]), $GdNi_{0.4}Si_{1.6}$ (AlB_2-type, [1–3,9,10]), as well as Gd_2Ni_{17}-, $GdNi_5$-, Gd_2Ni_7-, $GdNi_3$- and $GdNi_2$-based solid solutions was reported [1–3,9]. The interactions in the Gd–Ni, Gd–Si and Ni–Si binary systems have been studied in detail and published in several works [1,3,9–29]. More recently, crystallographic data on new gadolinium nickel silicides have also been published: $GdNi_8Si_3$ ($GdNi_8Si_3$-type) [30], Gd_3NiSi_3 (Y_3NiSi_3-type) [31], $Gd_2Ni_{2.35}Si_{0.65}$ (Mo_2NiB_2-type) [32], $GdNi_4Si$ (YNi_4Si-type) [33], $GdNi_6Si_6$ (YNi_6Si_6-type) [34], $GdNi_7Si_6$ ($GdNi_7Si_6$-type) [35] and $Gd_6Ni_{1.67}Si_3$ ($Ce_6Ni_2Si_3$-type) [36]. The temperatures reported for the latter group of compounds are generally in the range 1070–1270 K; therefore, well above 870 K. Correspondingly, the magnetic properties of several of the ternary compounds pertaining to the Gd–Ni–Si systems were also deeply investigated [10,30,32,33,36–45].

A careful reinvestigation of the isothermal section of the Gd–Ni–Si system at 1070 K, together with an updated assessment of the existing phases, was considered necessary. The main motivation of the present work was to account for the great amount of additional data on the existing compounds in this system, with respect to the isothermal section reported at 870 K. Moreover, during this work the magnetic properties of some ternary rare earth nickel silicides have been also established.

The new identified compounds partially fill the gap in determining the presence and stoichiometry of rare-earth ternary compounds in isostructural rows. On the other hand, the results obtained from the magnetic measurements give supplementary information on the magnetic data of, and help to get better knowledge in, the *R*-Ni–Si ternary systems.

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2. Experimental details

Alloys with a total mass of 1–2 g were prepared by arc-melting in an electric arc furnace (90 V, 150 A) under argon (99.992 vol%) using a non-consumable tungsten electrode and on a water-cooled copper hearth. Pieces of gadoliniun (99.9 wt%), silicon (purity 99.99 wt%) and nickel (99.95 wt%) were used as starting components; all were commercial products. A titanium button was used as a getter during arc-melting; the alloys were remelted three times. The arc-melted samples were then annealed at 1070 K (±2 K) for 200–240 h in quartz ampoules closed under vacuum, then quenched in ice-water bath.

Phase analysis of the alloys was carried out using X-ray diffraction and electron microprobe analysis. The X-ray powder data were obtained by using a diffractometer Rigaku d/max-2500 (Cu-Kα radiation, 2θ range=5–120 and 10–80°, step 0.02°, 4–8 sec/step). The unit cell data were derived from the X-ray powder patterns, recorded at room temperature, using the Rietan program [46] in the isotropic approximation; the symmetry analysis was performed with the aid of the Bilbao Crystallographic Server [47]. An INCA-Energy-350 X-ray EDS spectrometer (Oxford Instruments) on a Jeol JSM-6480LV scanning electron microscope (20 kV accelerating voltage, 0.7 nA beam current and 50 μm beam diameter) was employed to perform quantitative microprobe analyses. Signals averaged over three points per phase gave estimated standard deviations of 1 at% for Gd (measured by L-series lines), 1 at% for Ni and 1 at% for Si (both measured by K-series lines).

The DC magnetization of polycrystalline samples was measured on a commercial SQUID magnetometer (Quantum Design) in the temperature range of 2–300 K and under an applied magnetic field up to 140 kOe. By fitting the paramagnetic susceptibility data to the Curie–Weiss law, the effective magnetic moments and paramagnetic Curie temperatures were obtained [48]. Magnetocaloric effect (MCE) has been calculated by the thermodynamic Maxwell equation [49], in terms of the isothermal magnetic entropy change, ΔS_m, using the magnetization *vs.* field data measured near the magnetic transition.

3. Results

3.1. Gd–Ni–Si system at 1070 K

Based on the X-ray and microprobe results obtained on nearly 40 samples (SEM micrographs of some of the representative samples are shown in Fig. 1), the isothermal section of the Gd–Ni–Si system at 1070 K was constructed (Fig. 2). The nominal composition of the prepared samples is shown as a dot (in light-gray color) in Fig. 2. The estimated equilibria are represented by dotted lines; these equilibria are named as “tentative”, as they were not

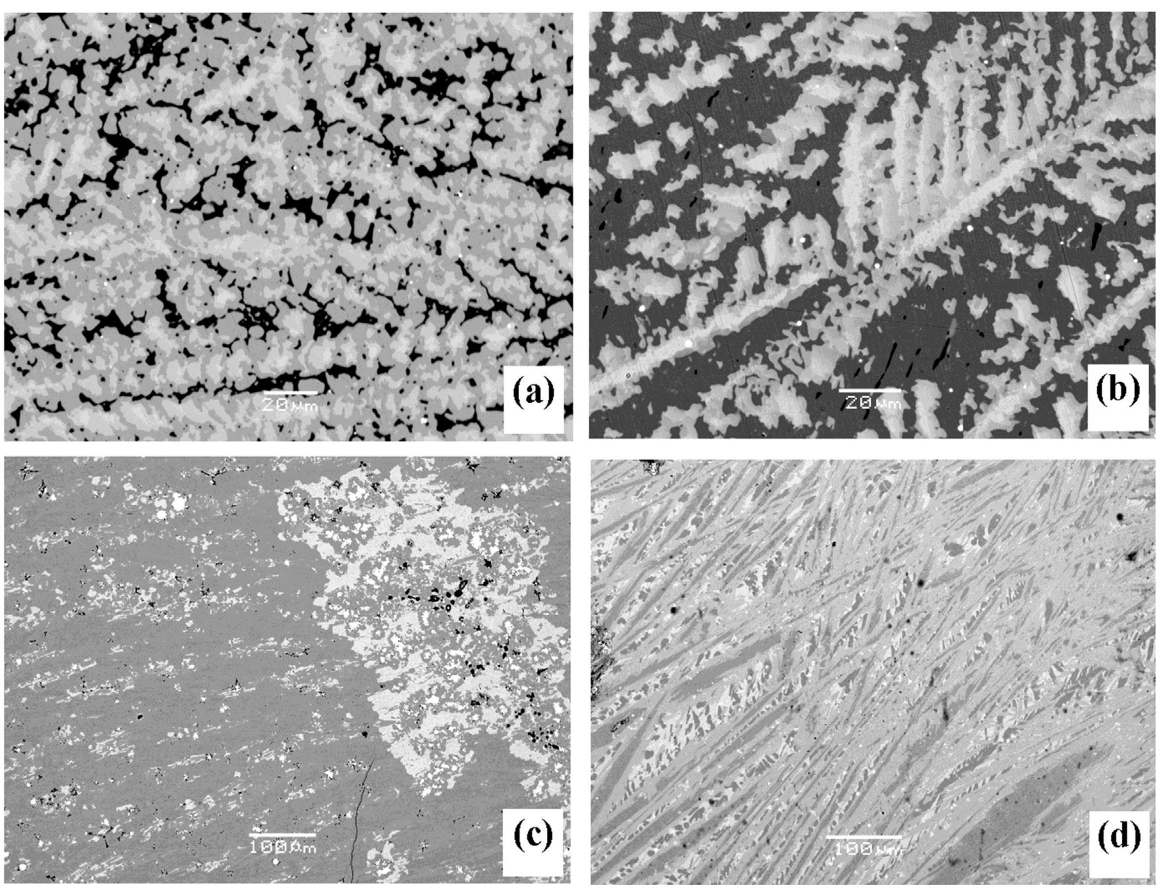

Fig. 1. Microstructure of some Gd–Ni–Si samples after annealing at 1070 K for a 200 h: (a) ‘$Gd_8Ni_{74}Si_{18}$’: $Gd_{11}Ni_{74}Si_{15}$ (Th_2Zn_{17}-type) (dark-gray), $Gd_8Ni_{77}Si_{15}$ ($ThMn_{12}$-type) (white-gray) and $Ni_{76}Si_{24}$ ($AuCu_3$-type) (black), (b) ‘$Gd_{12}Ni_{68}Si_{20}$’: $Gd_8Ni_{67}Si_{25}$ ($GdNi_8Si_3$-type) (dark), $Gd_{17}Ni_{67}Si_{16}$ (YNi_4Si-type) (white) and $Gd_{11}Ni_{65}Si_{23}$ (Th_2Zn_{17}-type) (dark-gray); (c) ‘$Gd_{25}Ni_{65}Si_{10}$’: $Gd_{33}Ni_{65}Si_2$ ($MgCu_2$-type) (white), $Gd_{28}Ni_{55}Si_{17}$ ($Ce_3Ni_6Si_2$-type) (gray) and $Gd_{25}Ni_{67}Si_8$ (Y_3Co_8Si-type) (dark-gray) and (d) ‘$Gd_{22}Ni_{48}Si_{30}$’: $Gd_{23}Ni_{44}Si_{33}$ (unknown) (dark-gray), $Gd_{28}Ni_{54}Si_{18}$ ($Ce_3Ni_6Si_2$-type) (gray) and $Gd_{17}Ni_{66}Si_{17}$ (YNi_4Si-type) (white).