

Phase equilibria in the system Ce–Ni–C at 800°C in the range 0–33.3 at.% Ce and new isostructural compounds $R_2Ni_5C_3$ ($R = Pr, Nd$)

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The phase equilibria in the ternary system Ce–Ni–C at 800°C in the range 0–33.3 at.% Ce were investigated by means of X-ray diffraction and energy-dispersive spectroscopy. Three ternary, CeNiC₂, Ce₂Ni₅C₃, and Ce₂Ni₂₂C_{2.75}, and five binary Ce–Ni and Ce–C compounds at 800°C were confirmed. Two new isostructural ternary compounds (structure type La₂Ni₅C₃, space group *P4/mbm*): Pr₂Ni₅C₃ ($a = 8.2888(1) \text{ \AA}$, $c = 3.95343(8) \text{ \AA}$) and Nd₂Ni₅C₃ ($a = 8.2810(2) \text{ \AA}$, $c = 3.9292(1) \text{ \AA}$), were synthesized and their crystal structures were refined. The compounds continue the isostructural series of $R_2Ni_5C_3$ ternary carbides with La₂Ni₅C₃-type structure.

Carbides / Phase equilibria / Crystal structure / Isostructural compounds

Introduction

The binary systems of carbon with rare-earth and transition elements have been widely investigated. However, ternary R – T – C systems (R = rare-earth element, T = transition element) have not yet been systematically investigated, although several ternary compounds of these systems, especially with light rare-earths, display interesting crystal structures, chemical bonding and physical properties.

The ternary systems (Y, La, Ce)–Ni–C have been investigated at 400°C in the full concentration range, and selected alloys examined at higher temperatures [1]. The ternary systems Gd–Ni–C and Y–Ni–C have also been investigated, the former at 600°C and the latter at 800°C [2,3]. Four ternary compounds have been reported to occur in the system Ce–Ni–C at 400°C: CeNiC₂ [1,4,5], \sim CeNi₃C₂ [1], CeNi₅C₄ [1], and Ce₂Ni₂₂C₃ [1,6]. Later, the compositions of the two ternary carbides \sim CeNi₃C₂ and Ce₂Ni₂₂C₃ were refined to Ce₂Ni₅C₃ [7,8] and Ce₂Ni₂₂C_{2.75} [9]. In addition, the ternary compounds CeNi₈C₂ and Ce₂Ni₅C₂ were synthesised at high pressures and temperatures [10,11]. Isostructural compounds $RNiC_2$ and $R_2Ni_{22}C_{2.75}$ (structure type CeNiC₂ and Ce₂Ni₂₂C_{2.75}, respectively) are known for almost all rare-earths. But ternary carbides $R_2Ni_5C_3$ (structure type La₂Ni₅C₃ [1,12]) have been synthesized and investigated only for $R = La$ and Ce.

In this work we report on the phase equilibria in the ternary system Ce–Ni–C at 800°C in the range 0–33.3 at.% Ce and on the new isostructural compounds $R_2Ni_5C_3$ ($R = Pr, Nd$) with La₂Ni₅C₃-type structures.

Experimental

0.5 and 1.0 g-alloys of different compositions of cerium, praseodymium, neodymium, nickel, and carbon, were prepared by arc-melting cold-pressed pellets of powders of the initial elements with purities not less than 99.9 wt.% (Alfa Aesar / Johnson Matthey) under argon atmosphere purified with Ti getter, on a water-cooled copper hearth, using a non-consumable tungsten electrode. During the melting procedure the weight losses were < 1.0 wt.% of the total mass of the ingots. The alloys were annealed in evacuated quartz ampoules at 800°C for 25 days.

Phase analysis of the alloys and crystal structure refinements (using Si as internal standard for refinement of the cell parameters, $a = 5.43075 \text{ \AA}$) were performed with the help of the WinXPOW [13] and WinCSD program packages [14], using powder X-ray diffraction (XRD) data obtained with DRON-3.0M (Cu $K\alpha$) and Stoe Stadi P (Cu $K\alpha_1$) powder diffractometers. Metallographic, qualitative and quantitative composition analyses of polished

samples were performed by energy-dispersive X-ray spectroscopy (EDX) with a scanning electron microscope REMMA-102-02. For metallographic and EDX analysis the alloys were embedded in Wood's metal (melting point 70°C). The embedded samples were polished on a wool cloth using abrasive materials with various grain sizes (0.5–5 μm) in dried paraffin oil. Surface cleaning and protecting of the polished samples were performed using petroleum ether.

Results and discussion

The isothermal section of the Ce–Ni–C phase diagram at 800°C in the range 0–33.3 at.% Ce determined in this work, and the previously reported section at 400°C [1], are shown in Fig. 1a and b, respectively. The alloys used for the investigation and their phase

composition according to the XRD and EDX analyzes are indicated in Fig. 1a. The existence of five binary compounds was confirmed: CeNi₅, Ce₂Ni₇, CeNi₃, CeNi₂ and α -CeC₂. The refined cell parameters are listed in Table 1. The lattice parameters of the binary Ce–Ni phases and α -CeC₂ in alloys of the binary and ternary systems are practically the same, *i.e.* the binary Ce–Ni compounds and α -CeC₂ do not dissolve carbon and nickel, respectively, at 800°C. Three ternary compounds exist in the system at 800°C: Ce₂Ni₂₂C_{2.75}, Ce₂Ni₅C₃, and CeNiC₂. Their crystal structure data are summarized in Table 2. The ternary carbide CeNi₅C₄, which was reported to occur at 400°C [1], was not observed at 800°C. The following three-phase regions: <CeNiC₂ + Ce₂Ni₅C₃ + CeNi₅C₄>, <CeNi₅ + Ce₂Ni₅C₃ + CeNi₅C₄>, <CeNi₅ + Ce₂Ni₂₂C_{2.75} + CeNi₅C₄> and <C + Ce₂Ni₂₂C_{2.75} + CeNi₅C₄>, which were reported to occur at 400°C [1], were not confirmed at 800°C.

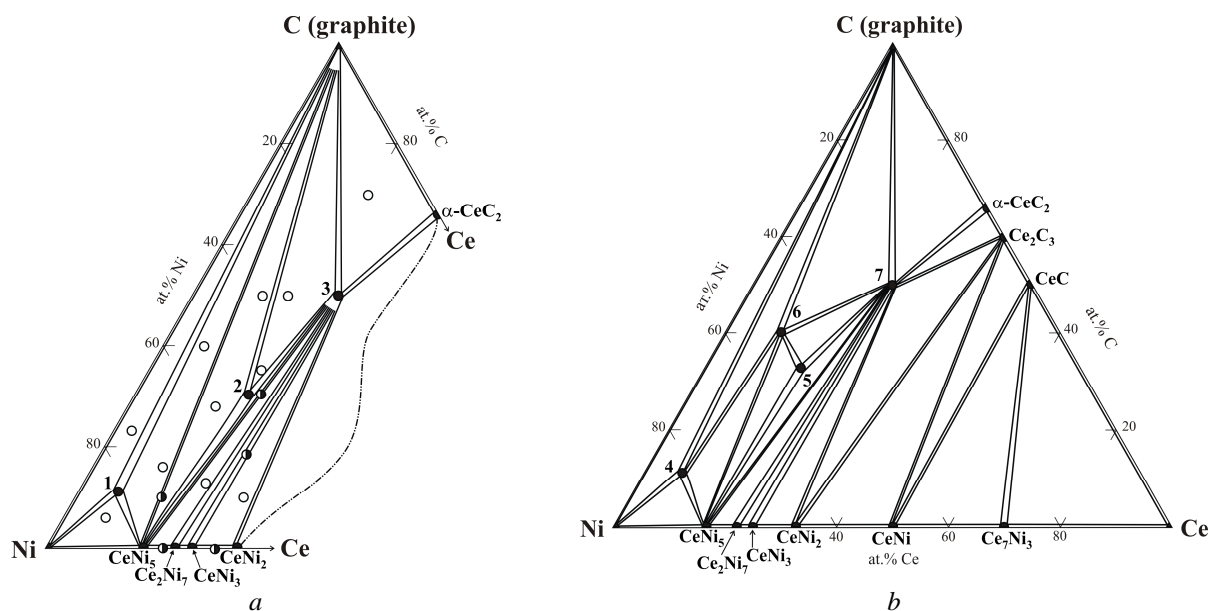


Fig. 1 Isothermal section of the Ce–Ni–C phase diagram at 800°C in the range 0–33.3 at.% Ce (a) and at 400°C [1] (b). The compositions of the alloys used in the investigation are indicated in (a) (○ – three-phase alloy, ◐ – two-phase alloys, ● – single-phase alloys). Ternary compounds: **1, 4** – Ce₂Ni₂₂C_{2.75}; **2** – Ce₂Ni₅C₃; **3, 7** – CeNiC₂; **5** – \sim CeNi₃C₂; **6** – CeNi₅C₄.

Table 1 Crystallographic data of α -CeC₂ and binary Ce–Ni phases in the Ce–Ni–C system at 800°C.

Compound	Structure type	Pearson symbol	Space group	<i>a</i> , Å	<i>c</i> , Å	<i>V</i> , Å ³	
α -CeC ₂	CaC ₂	<i>tI6</i>	<i>I4/mmm</i>	3.878(2)	6.487(2)	97.6(2)	a
				3.876(1)	6.485(3)	97.5(3)	b
CeNi ₂	MgCu ₂	<i>cF24</i>	<i>Fd-3m</i>	7.215(1)	–	375.56(1)	a
				7.214(2)	–	375.43(8)	b
CeNi ₃	CeNi ₃	<i>hP24</i>	<i>P6₃/mmc</i>	4.9639(3)	16.520(2)	352.53(9)	a
				4.9642(4)	16.522(2)	352.6(1)	b
Ce ₂ Ni ₇	Ce ₂ Ni ₇	<i>hP36</i>	<i>P6₃/mmc</i>	4.9412(6)	24.509(6)	518.2(3)	a
				4.9410(5)	24.511(4)	518.4(2)	b
CeNi ₅	CaCu ₅	<i>hP6</i>	<i>P6/mmm</i>	4.8872(4)	3.9999(3)	82.74(3)	a
				4.8870(2)	4.0041(6)	82.87(6)	b

^a ternary sample; ^b binary sample

The three-phase regions $\langle \text{CeNiC}_2 + \text{Ce}_2\text{Ni}_5\text{C}_3 + \text{C} \rangle$, $\langle \text{CeNi}_5 + \text{Ce}_2\text{Ni}_5\text{C}_3 + \text{C} \rangle$ and $\langle \text{C} + \text{Ce}_2\text{Ni}_{22}\text{C}_{2.75} + \text{CeNi}_5 \rangle$, which were observed at 400°C, are present also at 800°C. The stoichiometric compositions of the

binary and ternary compounds were confirmed by EDX analysis. Backscattered electron images of the alloys annealed at 800°C are shown in Fig. 2. Ternary compounds with the composition RNiC_2

Table 2 Crystallographic data of the ternary compounds in the Ce–Ni–C system at 800°C.

Compound	Structure type	Pearson symbol	Space group	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	<i>V</i> , Å ³	Ref.
CeNiC ₂	CeNiC ₂	<i>oS8</i>	<i>Amm2</i>	3.8755(3) 3.875	4.5490(4) 4.552	6.1623(5) 6.162	108.64(3) 108.7	^a [4,5]
Ce ₂ Ni ₅ C ₃	La ₂ Ni ₅ C ₃	<i>tP20</i>	<i>P4/mbm</i>	8.3033(4) 8.307	– –	3.9841(3) 3.979	274.68(4) 274.6	^a [6,7]
Ce ₂ Ni ₂₂ C _{2.75}	Ce ₂ Ni ₂₂ C _{2.75}	<i>oS216</i>	<i>Cmce</i>	11.374(4) 11.373	15.006(3) 15.004	14.622(2) 14.625	2495.7(9) 2495.6	^a [8,9]

^a own results

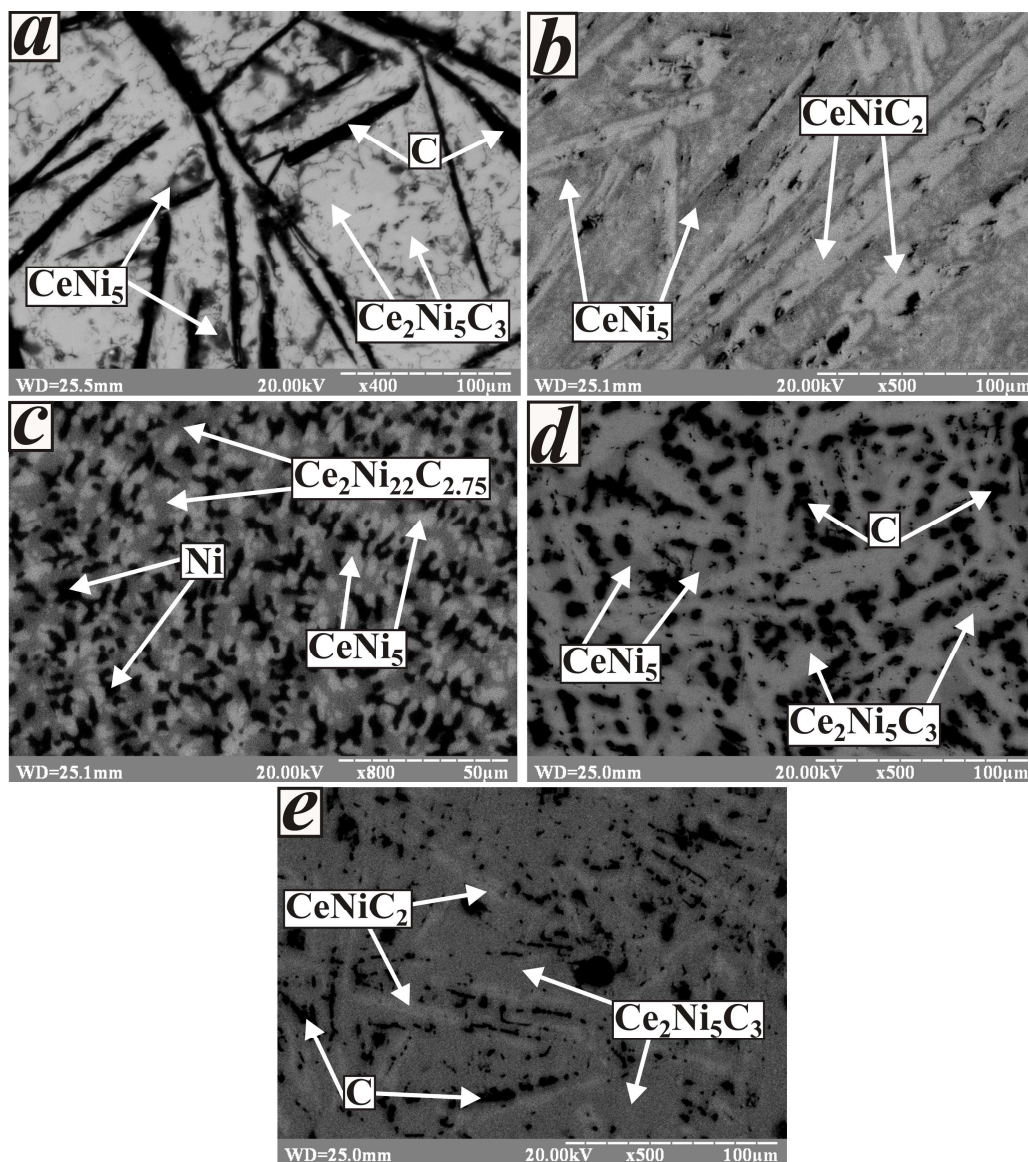


Fig. 2 Backscattered electron images of alloys annealed at 800°C : $\text{Ce}_{12}\text{Ni}_{38}\text{C}_{50}$ (a), $\text{Ce}_{21.8}\text{Ni}_{47.6}\text{C}_{30.6}$ (b, black inclusions are surface defects), $\text{Ce}_7\text{Ni}_8\text{C}_6$ (c), $\text{Ce}_{15}\text{Ni}_{57}\text{C}_{28}$ (d), $\text{Ce}_{19}\text{Ni}_{46}\text{C}_{35}$ (e). Composition of the phases is indicated according to the EDX analysis.

(CeNiC₂-type structure) occur also in the ternary systems (La, Ce, Y, Gd)–Ni–C. In the systems (La, Ce, Gd)–Ni–C, ternary carbides R₂Ni₂₂C_{3-x} with Ce₂Ni₂₂C_{3-x}-type structures exist too. However, ternary compounds R₂Ni₅C₃ with R = Y, Gd, or R₂Ni₂₂C_{3-x} with R = Y have not been reported.

Two new ternary carbides, Pr₂Ni₅C₃ and Nd₂Ni₅C₃, were synthesized by arc-melting cold-pressed pellets of powdered elemental components, and their crystal structures were determined. They are new

representatives of the isostructural series of R₂Ni₅C₃ ternary compounds with La₂Ni₅C₃-type structures, known up to now only for R = La and Ce. The new ternary carbides were observed in the as-cast and in the annealed (at 800°C) alloys of nominal composition R₂₀Ni₅₀C₃₀ (R = Pr, Nd). The crystal structures were refined by the powder XRD Rietveld method. The refined XRD profiles of the R₂₀Ni₅₀C₃₀ (R = Pr, Nd) alloys annealed at 800°C are presented in Fig. 3. Details of the refinements are summarized in Table 3.

Table 3 Details of the full-profile refinement of XRD patterns of Pr₂₀Ni₅₀C₃₀ and Nd₂₀Ni₅₀C₃₀ samples annealed for 25 days.

Phase	Pr ₂ Ni ₅ C ₃	Nd ₂ Ni ₅ C ₃
Content in sample, wt.%	84.33 ± 1.24	76.48 ± 1.04
Space group	<i>P4/mbm</i>	
<i>Z</i>	2	
<i>a</i> , Å	8.2888(1)	8.2810(2)
<i>c</i> , Å	3.95343(8)	3.9292(1)
<i>V</i> , Å ³	271.61(1)	269.45(2)
Calculated density, g cm ⁻³	7.4751(4)	7.6173(5)
Radiation; wavelength, Å	X-rays, Cu Kα ₁ ; 1.54056	
2θ, °; sin θ/λ, Å ⁻¹	110.64; 0.534	
<i>h k l</i>	0 ≤ <i>h</i> ≤ 5	0 ≤ <i>h</i> ≤ 5
	0 ≤ <i>k</i> ≤ 8	0 ≤ <i>k</i> ≤ 8
	0 ≤ <i>l</i> ≤ 4	0 ≤ <i>l</i> ≤ 4
Zero shift	-0.0001	-0.0008
Preferred orientation	1.39(2) [0 0 1]	1.37(2) [0 0 1]
<i>R</i> _B	3.75	5.46
<i>R</i> _p	3.28	2.84
<i>R</i> _{wp}	4.27	3.69
<i>R</i> _{exp}	3.94	3.57
<i>Goof</i>	1.084	1.034
Scale factor	0.175(3)	0.170(3)

Table 4 Atomic and isotropic displacement parameters for Pr₂Ni₅C₃ and Nd₂Ni₅C₃.

Atom	Wyckoff position	Site occupation	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso} , Å ²
Pr ₂ Ni ₅ C ₃						
Pr	4 <i>h</i>	1	0.3406(2)	<i>x</i> + ½	0	1.24(4)
Ni1	8 <i>i</i>	1	0.2125(4)	0.0775(4)	½	0.75(8)
Ni2	2 <i>b</i>	1	0	0	0	1.8(2)
C1	4 <i>g</i>	1 ^a	0	0	½	1.0 ^a
C2	2 <i>a</i>	1 ^a	0.060(2)	<i>x</i> + ½	½	1.0 ^a
Nd ₂ Ni ₅ C ₃						
Nd	4 <i>h</i>	1	0.3414(2)	<i>x</i> + ½	0	1.06(5)
Ni1	8 <i>i</i>	1	0.2120(5)	0.0774(5)	½	0.92(1)
Ni2	2 <i>b</i>	1	0	0	0	1.6(3)
C1	4 <i>g</i>	1 ^a	0	0	½	1.0 ^a
C2	2 <i>a</i>	1 ^a	0.060(3)	<i>x</i> + ½	½	1.0 ^a

^a constrained parameters

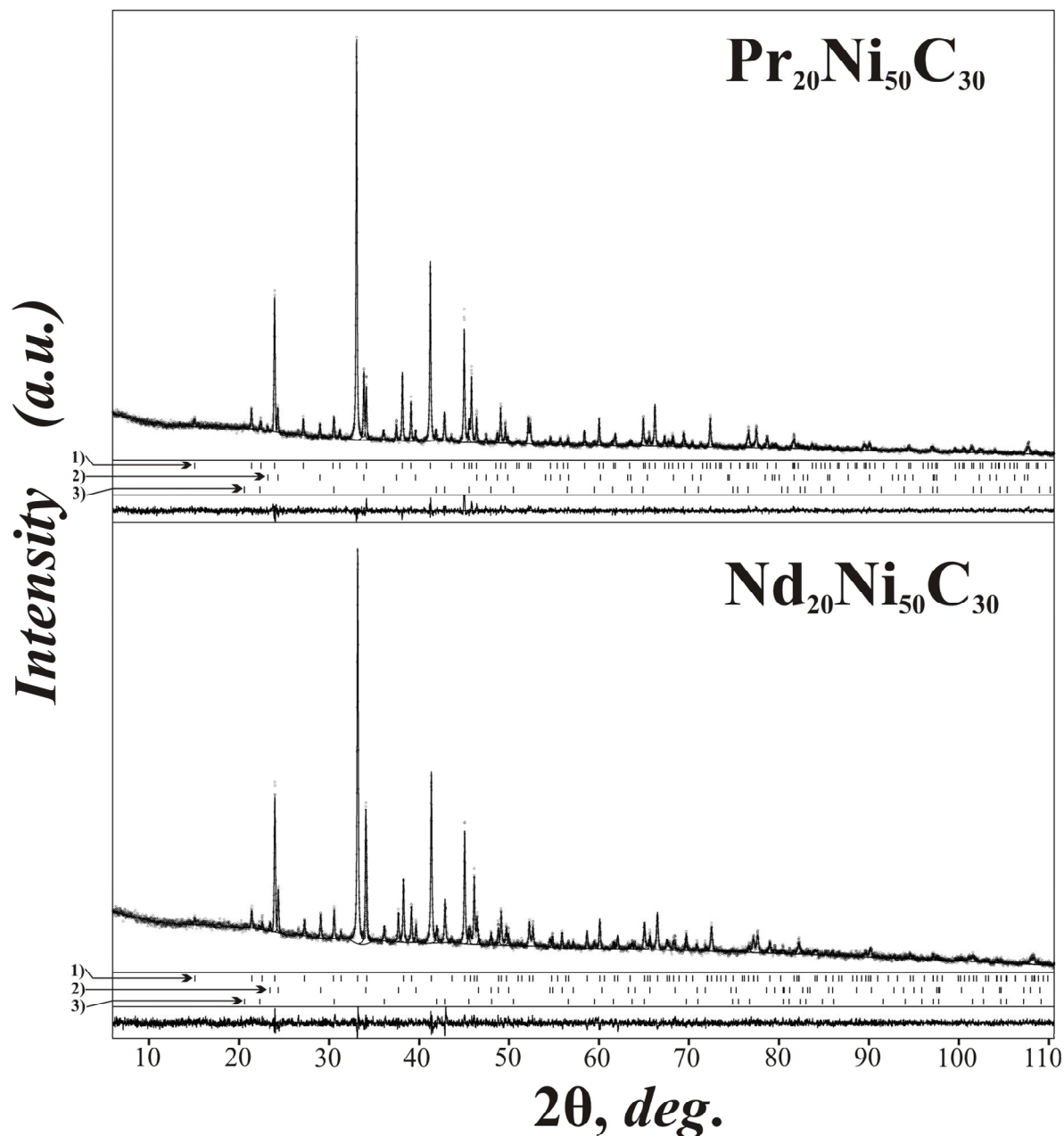


Fig. 3 Observed (dots) and calculated (line) profiles and their difference (bottom) for the XRD patterns of the $\text{Pr}_{20}\text{Ni}_{50}\text{C}_{30}$ (a) and $\text{Nd}_{20}\text{Ni}_{50}\text{C}_{30}$ (b) samples annealed at 800°C for 25 days. The Bragg positions are marked by vertical bars: 1) $\text{Pr}_2\text{Ni}_5\text{C}_3$ (a), $\text{Nd}_2\text{Ni}_5\text{C}_3$ (b); 2) PrNiC_2 (a), NdNiC_2 (b); 3) PrNi_5 (a), NdNi_5 (b).

Atomic and isotropic displacement parameters for the structures of $\text{Pr}_2\text{Ni}_5\text{C}_3$ and $\text{Nd}_2\text{Ni}_5\text{C}_3$ are listed in Table 4. The unit-cell content of the crystal structure and the coordination polyhedra of the atoms in the $R_2\text{Ni}_5\text{C}_3$ compounds ($R = \text{Ce}, \text{Pr}, \text{Nd}$) with $\text{La}_2\text{Ni}_5\text{C}_3$ -type structures are shown in Fig. 4. The interatomic distances calculated for the new ternary carbides are presented in Table 5. There are isolated carbon atoms (C1) and carbon pairs (C2–C2) in the crystal structure of the investigated isostructural compounds. The C–C

distances are 1.40(2) Å and 1.41(3) Å for $R = \text{Pr}$ and Nd , respectively. For the three ternary carbides $d_{\text{C-C}}$ takes values intermediate between the typical distances between carbon atoms in sp^3 - and sp^2 -hybridization. There are short Ni–C interatomic distances $d_{\text{Ni1-C1}}$ and $d_{\text{Ni1-C2}}$ in the investigated compounds. The values of $d_{\text{Ni1-C1}}$ and $d_{\text{Ni1-C2}}$ indicate covalent bonding between the atoms. However, the Ni2–C2 interatomic distances are almost equal to the sum of the atomic radii of the elements.

The variation of the cell volume within the series of $R_2Ni_5C_3$ ($R = La$ [1], Ce, Pr, Nd) compounds is shown in Fig. 5. The cell volumes are reduced from La to Nd, which reflects lanthanide contraction. The

cell parameters of the ternary compound $Ce_2Ni_5C_3$ did not change in the investigated three-component alloys that contained this carbide. Constant stoichiometric composition was also confirmed for $Ce_2Ni_5C_3$ in [8].

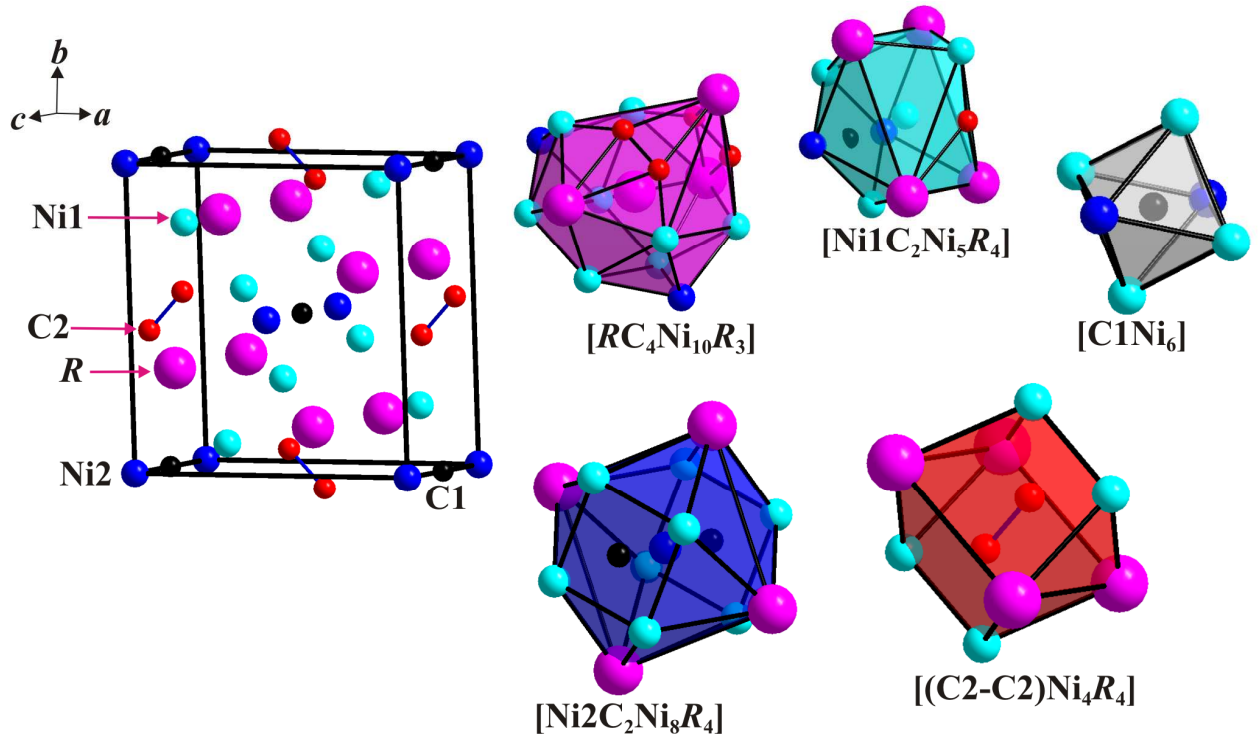


Fig. 4 Unit cell content and coordination polyhedra of the atoms in the crystal structure of the $R_2Ni_5C_3$ ternary compounds ($R = Ce, Pr, Nd$) with $La_2Ni_5C_3$ -type structure.

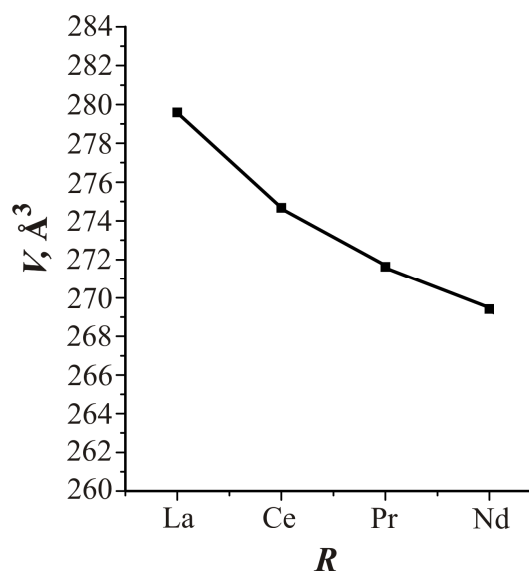


Fig. 5 Cell volumes for the series of carbides $R_2Ni_5C_3$ ($R = La$ [1], Ce, Pr, Nd).

Table 5 Interatomic distances (d , Å) and coordination numbers (CN) in the crystal structures of $\text{Pr}_2\text{Ni}_5\text{C}_3$ and $\text{Nd}_2\text{Ni}_5\text{C}_3$.

$\text{Pr}_2\text{Ni}_5\text{C}_3$			$\text{Nd}_2\text{Ni}_5\text{C}_3$		
Atoms	d	CN	Atoms	d	CN
Pr	– 4C2	2.81(1)	Nd	– 4C2	2.795(4)
	– 4Ni1	2.976(3)		– 4Ni1	2.971(3)
	– 4Ni1	2.982(3)		– 4Ni1	2.972(3)
	– 2Ni2	3.117(1)		– 2Ni2	3.117(2)
	– 1Pr	3.738(2)		– 1Nd	3.715(2)
	– 2Pr	3.954(1)		– 2Nd	3.929(1)
Ni1	– 1C1	1.875(3)	Ni1	– 1C1	1.869(4)
	– 1C2	1.89(2)		– 1C2	1.89(2)
	– 1Ni1	2.462(4)		– 1Ni1	2.466(5)
	– 2Ni1	2.651(4)		– 2Ni1	2.643(5)
	– 2Ni2	2.724(2)		– 2Ni2	2.712(3)
	– 2Pr	2.976(3)		– 2Nd	2.971(3)
	– 2Pr	2.982(3)		– 2Nd	2.972(3)
	Ni2	– 2C1		1.977(1)	Ni2
– 8Ni1		2.724(2)	– 8Ni1	2.712(3)	
– 4Pr		3.117(1)	– 4Nd	3.117(2)	
C1	– 4Ni1	1.875(3)	C1	– 4Ni1	1.869(4)
	– 2Ni2	1.977(1)		– 2Ni2	1.965(1)
C2	– C2	1.40(2)	C2	– C2	1.41(3)
	– 2Ni1	1.89(2)		– 2Ni1	1.89(2)
	– 4Pr	2.81(1)		– 4Nd	2.795(4)

Conclusions

The isothermal section of the Ce–Ni–C phase diagram at 800°C has been investigated in the range 0–33.3 at.% Ce. The binary compounds CeNi_5 , CeNi_2 , CeNi_3 , Ce_2Ni_7 , and $\alpha\text{-CeC}_2$ do not dissolve the third element. Three ternary compounds with constant compositions, CeNiC_2 , $\text{Ce}_2\text{Ni}_{22}\text{C}_{2.75}$, and $\text{Ce}_2\text{Ni}_5\text{C}_3$, occur in the system at 800°C. Two new ternary carbides, $\text{Pr}_2\text{Ni}_5\text{C}_3$ and $\text{Nd}_2\text{Ni}_5\text{C}_3$, with $\text{La}_2\text{Ni}_5\text{C}_3$ -type structure have been synthesized. The compounds were observed in the as-cast alloys and after homogenization at 800°C. They are new representatives of the isostructural series of carbides $R_2\text{Ni}_5\text{C}_3$. There are two types of carbon atoms in the crystal structure: isolated atoms and C_2 pairs.

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