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Features of cubic Ni_3C and NiC carbides obtained by HT-HP sintering

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In this work NiC carbides were manufactured by HP-HT sintering of mechanically alloyed charges of the elemental Ni–carbon nanotubes (CNT) or Ni–Graphite. Structural features of the materials obtained were characterized by X-ray diffraction and scanning electron microscopy. X-ray diffraction studies have revealed that the crystal lattice of nickel carbide obtained from mechanically alloyed Ni–CNT charge is supplemented with additional Carbon atoms from the graphite shell of the high-pressure cell at HT-HP sintering. On the other hand, nickel carbide fabricated from mechanically alloyed Ni–Graphite charge retains its composition. It is shown that materials studied in this work demonstrate an advanced value of microhardness (up to 7 GPa).

Keywords: mechanical alloying; nanoscale material; x-ray diffraction; crystal structure; microhardness.

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Introduction

Mechanical alloying (mechanochemical synthesis) as a solid state powder processing technique, allows production of homogeneous nanoscale intermetallics, oxides, carbides or composite materials starting from blended elemental powder mixtures [1-3]. In addition to obtaining material in a nanocrystalline state, the advantages of this method include obtaining metastable supersaturated solid solutions.

The nickel carbide could be found at catalytic reactions [4], carbon nanowhiskers and nanotubes [5]. The Ni_3C carbide is a metastable compound obtained by different techniques, including nonequilibrium methods, such as carbon ion implantation into Ni [6], diffusion reactions of nickel and amorphous carbon films [7, 8], chemical synthesis [9], and plasma deposition [10]. Besides, the $Ni_{1-x}C_x$ blends ($x = 0.10–0.90$) were first obtained by reaction milling of elemental powders of Ni and carbon black by T. Tanaka et al. in [11].

We have successfully applied mechanical alloying to obtain a number of carbides using elemental transition *d*-metal powders and multiwalled carbon nanotubes (CNT) as charge components. As a result, nanoscaled TiC, ZrC, HfC, VC, NbC, TaC monocarbides [12, 13], Mo_2C, W_2C, WC carbides [14], Fe_3C [15] and Co_3C [16] were synthesized.

As for nickel carbide, the authors of [17] suggested that the hexagonal nickel carbide can be considered as a metastable Ni–C solid solution, where changes in the stacking sequence of metallic (Ni) layers are similar to the $\alpha \rightarrow \beta$ transition in Co. Resembling assumption that Ni_3C is a solid solution based on *hcp* Ni, rather than the intermetallic compound, is presented in [18, 19] considering the fact that, as a result of mechanical alloying, this phase exists over a wide composition range and has a simple symmetry. V.K. Portnoi et.al. [20] have mechanochemically obtained hexagonal Ni_3C. Authors [20] have mentioned that the mechanically alloyed carbide has a lower unit cell; i.e., it is in a compressed state of stress. The lattice parameter of the carbide formed at mechanical alloying are $a = 0.2610–0.2637$ nm and $c = 0.4306–0.4324$ nm [20]. Nevertheless, we have synthesized a novel NiC_x carbide with defective ZnS-sphalerite crystal structure by mechanical alloying of Ni-CNT and Ni-Graphite charges of (3:1) composition [21].

We have also shown that the existence region of this cubic nickel carbide expands at least to the NiC equiatomic composition, undergoing certain structural transformations [22, 23].

The aim of this work is to study the crystal structure and microhardness of compact samples obtained by the reaction sintering under high pressure and high temperature from mechanically alloyed Ni-C powder.

I. Experimental details

Mechanically alloyed NiC powders obtained from Ni-C charge of (3:1) and (1:1) compositions [22, 23] were sintered by high temperature –high-pressure (HP-HT) technique. The toroid-type high pressure apparatus was applied to create the pressure of 7.7 GPa and temperature of 1500–2200 °C (the powder wrapped into the AlN foil was heated in a high pressure cell for 40 s).

The crystal structure of sintered samples was studied by X-ray diffraction methods on the test samples selected after every 30-60 min of milling. XRD data was collected with DRON-3M or with Shimadzu XRD-6000 automatic diffractometers (CuKα radiation) in a discrete mode under the following scanning parameters: observation range $2\theta = (10–100)°$, step scan was 0.05° and counting time per step was 3 s. The original software package [24, 25], including full complex of standard Rietveld procedures, has been used for analysis and interpretation of the X-ray diffraction patterns obtained, namely, determination of both peak positions and integral intensities of the Bragg's reflections by means of full profile analysis; carrying out qualitative and quantitative phase analysis using PDF data for phase identification and the least square method for lattice parameters refinement; testing of the structure models and refining crystal structure parameters (including coordinates of atoms, atomic position filling, texture, etc.); calculation of the parameters of the real structure of the individual phases (coherent block sizes and microdeformation values).

SEM exanimation of the samples was carried out using JEOL JAMP-9500F field emission auger microprobe (10kV), which offers the flexibility of optional analysis functions such as an energy-dispersive X-ray spectroscopy (EDS).

The Vickers microhardness tests have performed with PMT-3 apparatus at room temperature. All samples were preliminary polished by diamond paste. The load of 150 g was applied to the sample for 15 s. Number of indentations per one sample was 50.

II. Results and discussion

According to XRD analysis all sintered samples are single-phase (Fig. 1). However, the calculation of the crystal structure shows that if the elemental composition of sintered samples obtained from the Ni-Graphite (1:1) charge completely corresponds to the initial charge content, then the crystal lattice of NiC obtained from the Ni-CNT charges is supplemented by additional Carbon atoms from the graphite shell of the reaction medium. As a result, the carbon content in nickel carbide obtained could reach 60 at. % of C. XRD data on the crystal structure of carbide phases obtained at mechanical alloying are shown in Table 1, the sintering conditions of these powders, as well as data on the crystal structure of the phases in sintered materials are listed in Table 2.

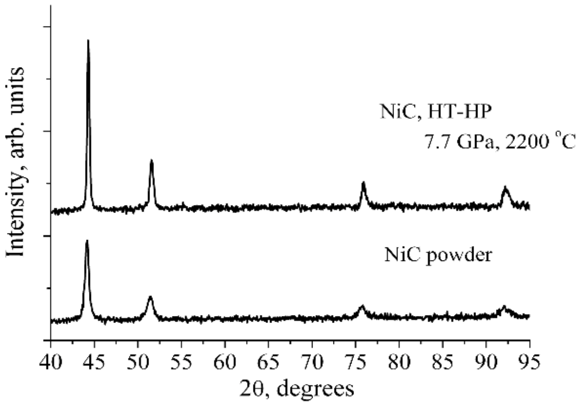

Fig. 1. Diffractograms of mechanically alloyed Ni-Graphite (1:1) charge and a sample sintered from it.

SEM images (Fig. 2) demonstrate a rather high density of the obtained composites, besides, the graphite shell residue is visible on the surface (dark inclusions up to 5 μm in size). It should also be noted that the residue of graphite was detected by XRD studies of some sintered samples. The size of the coherent scattering blocks in the obtained composite materials is 20-30 nm.

Ability of the mechanically alloyed Ni-C charge to consolidate with the formation of a dense material with smooth surface (Fig. 2) contributed to obtaining correct data on the microhardness of the samples produced (Table 2). Analysis of the results obtained shows that samples of mechanically alloyed Ni-CNT charge when HP-HT sintered demonstrate higher microhardness (Table 2). Moreover, during HT-HP sintering of the samples, an additional amount of Carbon from the graphite shell of the high-pressure cell was dissolved in the crystal structure of nickel carbide obtained from Ni-CNT charge, which obviously affected the microhardness of the compacts (Table 2, Fig. 3).

Table 1.

Crystal data of phases formed in mechanically alloyed Ni–CNT and Ni–Graphite powders.

Material	Charge	Phase	Lattice parameter (nm)	Phase composition (at.%)	
				Ni	C
Ni	Ni	Ni	0.3525(1)	100	-
Ni_3C	Ni–CNT (3:1)	Ni_3C ZnS-sphalerite type	0.35492(5)	77.2(5)	22.8(5)
NiC	Ni–Graphite (1:1)	NiC own type	0.35622(5)	50.0(4)	50.0(4)
NiC	Ni–CNT (1:1)	NiC own type	0.35524(4)	51.0(4)	49.0(4)

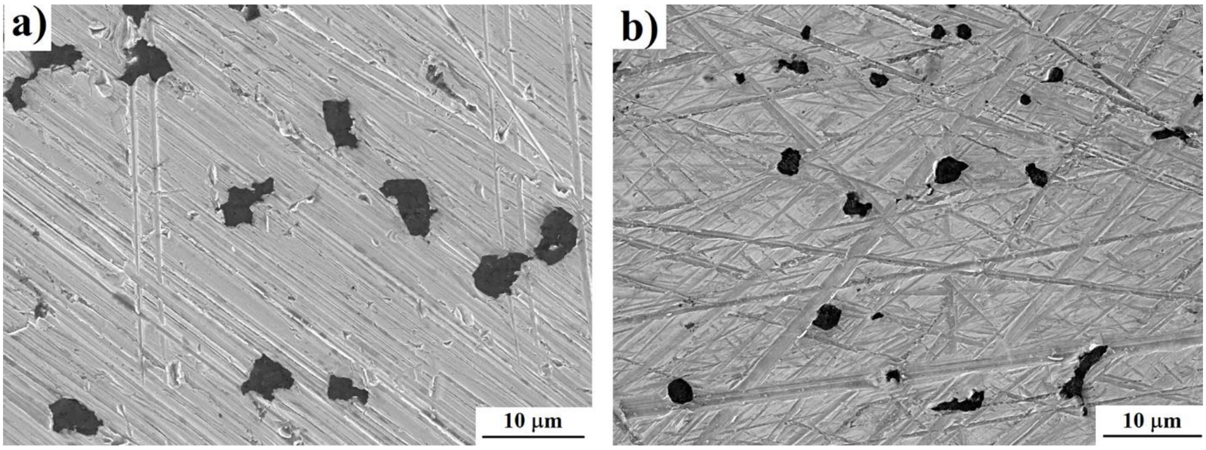

Fig. 2. SEM images of HT-HP sintered (7.7 GPa and 1850 °C) samples: (*a*) Ni-graphite (1:1); (*b*) Ni–CNT (1:1). x2000.

Table 2.

Crystal data of phases and microhardness of sintered samples.

HT-HP sintering conditions	Phase	Lattice parameter (nm)	Phase composition (at.%)		Microhardness (GPa)
			Ni	C	
Ni charge					
0.02 GPa, 1500 °C	Ni	0.3525(1)	100.0	-	0.99(3)
Ni-CNT (3:1) charge					
7.7 GPa, 1200 °C	Ni_3C ZnS-sphalerite type	0.35441(4)	72.6(4)	27.4(4)	6.4(1)
7.7 GPa, 1500 °C		0.3548(1)	65.4(5)	34.6(5)	6.6(3)
7.7 GPa, 2000 °C		0.3554(2)	52.2(4)	47.8(4)	6.8(3)
Ni-graphite (1:1) charge					
0.02 GPa, 1500 °C	NiC of own type	0.3578(1)	51.6(6)	48.4(6)	1.30(2)
7.7 GPa, 1850 °C		0.3550(1)	50.2(5)	49.8(5)	4.47(5)
7.7 GPa, 2200 °C		0.3554(1)	50.1(5)	49.9(5)	3.94(6)
Ni-CNT (1:1) charge					
0.02 GPa, 1500 °C	NiC of own type	0.3552(1)	48.6(4)	51.4(4)	1.42(2)
7.7 GPa, 1850 °C		0.3547(1)	41.0(5)	59.0(5)	6.05(8)
7.7 GPa, 2200 °C		0.3545(1)	40.3(5)	59.7(5)	4.75(6)

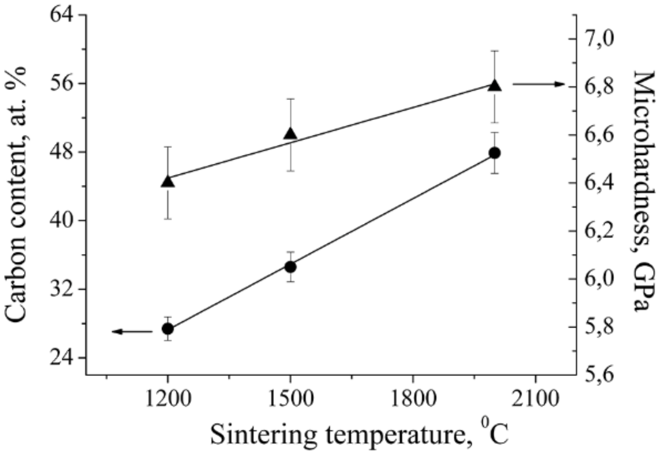

Fig. 3. Microhardness of HT-HP sintered Ni-CNT (3:1) samples and a carbon content in a charge.

Generally, the microhardness of the HT-HP sintered nickel carbide s likely to be affected by the crystal structure features. Thus, as we showed previously [21, 22], the crystal structure of Ni_3C carbide obtained from a (3:1) Ni-C is characterized by the statistical arrangement of Carbon atoms in the centers of the tetrahedral voids of the original Ni lattice. However, in the crystal structure of nickel monocarbide formed from equiatomic Ni-C charge, the available carbon atoms are slightly shifted from the centers of the tetrahedral voids of Ni lattice

Table 3.

Crystal data of the nickel carbide obtained (space group *F-43m* (no.216))

Atom	Position	Occ.	*X*	*Y*	*Z*	Atom	Position	Occ.	*X*	*Y*	*Z*
Ni-CNT (3:1) charge											
Mechanically alloyed nickel carbide						HT-HP (7.7 ГПа, 2000 °C) sintered sample					
Ni	*4a*	1.00(1)	0	0	0	Ni	*4a*	1,00(1)	0	0	0
C	*4c*	0.91(1)	0.25	0.25	0.25	C	*4c*	0.91(1)	0.25	0.25	0.25
Lattice period (nm)			*a* = 0.35492(5)			Lattice period (nm)			*a* = 0.3554(2)		
Temperature factor, nm^2			*B* = 2.15(2)$\cdot 10^{-2}$			Temperature factor (nm^2)			*B* = 1.25(2)$\cdot 10^{-2}$		
Phase content			77.2(5)Ni + 22.8(5)C			Phase content			52.2(3)Ni + 47.8(3)C		
Reliability factor			R_I = 0.003			Reliability factor			R_I = 0.023		
Ni-BHT (1:1) charge											
Mechanically alloyed nickel carbide						HT-HP (7.7 ГПа, 2200 °C) sintered sample					
Ni	*4a*	1.00(1)	0	0	0	Ni	*4a*	1,00(1)	0	0	0
C	16*e*	0.24(2)	0.342(5)	0.342(5)	0.342(5)	C	*16e*	0.37(5)	0.332(5)	0.332(5)	0.332(5)
Lattice period (nm)			*a* = 0.35524(4)			Lattice period (nm)			*a* = 0,3545(1)		
Temperature factor (nm^2)			*B* = 1.68(3)$\cdot 10^{-2}$			Temperature factor (nm^2)			*B* = 3.09(9)$\cdot 10^{-2}$		
Phase content			51.0(4) Ni + 49.0(4) C			Phase content			40.3(3) Ni + 59.7(3) C		
Reliability factor			R_B = 0.008			Reliability factor			R_B = 0.011		

towards the centers of its octahedral voids.

These two types of characteristic arrangement of Carbon atoms in mechanically alloyed nickel carbide (Fig. 4), are stored at HP-HT sintering, as evidenced by the results of studying the crystal structure of this samples (Table 3).

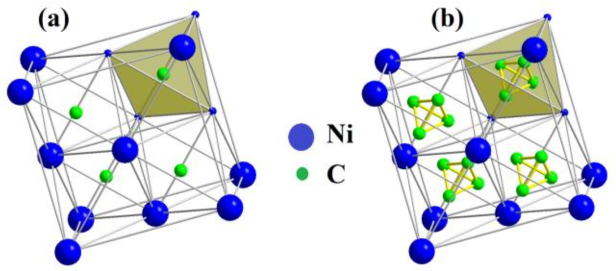

Fig. 4. Crystal structure of fcc Ni_3C (*a*) and NiC (*b*) and coordination polyhedra.

Conclusions

Study of the crystal structure and microhardness of HT-HP sintered nickel carbide has revealed the following.

1. Mechanically alloyed NiC powder is well consolidated with the formation of a dense single-phase material.

2. Mechanically alloyed NiC generally retains its crystal structure at HT-HP sintering. NiC crystal lattice of NiC obtained from Ni–CNT charge is supplemented with additional Carbon atoms from the graphite shell of the high pressure cell.

3. Sintered NiC obtained from Ni–CNT charge demonstrates higher hardness compared to that obtained from Ni–Graphite charge.

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Властивості кубічних карбідів Ni_3C та NiC одержаних методом HT-HP спікання

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Досліджено фазовий склад та мікротвердість компактних матеріалів, отриманих консолідацією методом реакційного спікання в умовах високих тисків та температур (тиск 7.7 ГПа, температура 1200-2200 °C) фінальних продуктів механохімічного синтезу шихти Ni-C (де C – графіт або вуглецеві нанотрубки, ВНТ) складів (3:1) та (1:1). Показано, що порошкові продукти, що містять карбід нікелю Ni_3C (кристалічна структура ZnS-сфалерит) або карбід нікелю NiC (власний структурний тип), при їх HT-HP спіканні утворюють щільний однофазний матеріал, кристалічна структура карбіду нікелю в якому в цілому відповідає кристалічній структурі карбіду нікелю в розмеленій шихті. Проте дослідження методом рентгенівської дифракції показало, що в умовах HT-HP реакційного спікання кристалічна ґратка карбіду нікелю, отриманого за участю ВНТ, доукомплектовується додатковою кількістю вуглецю, наявного в графітовій оболонці комірки високого тиску, в той час як карбід нікелю, отриманий з шихти Ni–графіт, свій склад при спіканні зберігає. Показано, що серед вивчених в роботі матеріалів найбільше значення мікротвердості (до 7 ГПа) притаманне тим, що були отримані HT-HP спіканням розмеленої шихти Ni-ВНТ.

Ключові слова: механічне легування; наноструктурний матеріал; рентгенівська дифракція; кристалічна структура; мікротвердість.