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Testing of Electron Beam Technique for NiC Coating Deposition

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Nanoscaled NiC powder is obtained by mechanical alloying of two equiatomic charges of Ni–carbon nanotubes and Ni–graphite in a high-energy planetary ball mill. Crystal structure of this carbide is a modified ZnS sphalerite type. Powder of NiC carbide is compacted by cold pressing at a pressure of 0.2 GPa, and the material obtained is used as a target for coating deposition by an electron beam technique. Thin films are deposited either on substrates from silicon wafer or fused glass. The phase composition of as-deposited coatings and after annealing at 900°C is studied. As shown, an annealing in air up to 900°C does not lead to cracking or peeling of the coatings from the substrate.

Key words: NiC monocarbide, mechanical alloying, electron beam, thin film, X-ray diffraction.

Нанорозмірний порошок монокарбіду NiC одержано методом механохемічної обробки двох еквіатомних сумішей Ni–ВНТ та Ni–графіту у високоенергетичному планетарному кульовому млині. Показано, що криста-

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лічна структура цього карбіду є модифікованою структурою типу ZnS сфалерит. Одержаний порошок карбіду NiC був скомпактований методом холодного пресування під тиском 0,2 ГПа, а одержаний до цього матеріял був використаний для електронно-променевого нанесення тонких покриттів на підложжя з пластин кремнію або топленого скла. Вивчено фазовий склад одержаних покриттів як у вихідному стані, так і після їх відпалу до 900°C. Показано, що ступінчастий відпал на повітрі до 900°C не веде до розтріскування або відлущення виготовлених покриттів від підложжя.

Ключові слова: NiC монокарбід, механічне леґування, електронно-променева технологія, тонка плівка, рентґенівська дифракція.

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1. INTRODUCTION

Synthesis of new materials with attractive functional characteristics as well as a development of nanostructured coatings based on them is one of the most important tasks of the material science. NiC coatings are quite interesting to study since NiC thin films obtained by sputtering or laser deposition methods [1–4] have high hardness (up to 14 GPa) and high visible-light transmittance (up to 98%).

Such an attractive combination of mechanical and electrophysical properties of NiC coatings could be very promising for the creation of transparent thin film electrodes in solar cells or photoelectric sensors.

Improvement of the target material plays an important role in deposition process since the properties of a coating is generally determined by the phase composition and the features of phase crystal structure. That's why in recent years our research is focused on a development of novel materials by mechanical alloying of the nickel powder and CNT (carbon nanotubes) in a high-energy ball mill.

So, as a result of processing of the charge Ni–CNT (3:1) we synthesized new nanoscaled carbide NiC_x with a modified ZnS-sphalerite type structure [5], while the Authors of Ref. [6] as a result of processing of the charge Ni–Graphite (3:1) have synthesized a powder, the dominant phase of which is the well-known Ni_3C carbide. Here, we present the results of our research, which include the synthesis and crystal structure study of the carbides formed in Ni–CNT (1:1) and Ni–Graphite (1:1) systems as well as fabrication the coatings from the materials prepared. Moreover, the technique of coating deposition from these materials is tested.

2. EXPERIMENTAL DETAILS

Two equiatomic mixtures of initial powders containing 50 at.% of Ni

metal (99.9% wt. purity, particle size is less than 80 μm) and 50 at.% of multi-walled CNT (production of LLC 'TM Spetsmash', Kyiv, particle size is about 10–20 nm) or 50 at.% of graphite (spectral purity 99.99%, particle size is less than 50 μm) are sealed into two steel vials for further cyclic processing in a high energy planetary ball mill (15 min of treatment and 30 min of cooling) in argon atmosphere.

The 11 steel balls (15 mm of diameter) are used for the processing of the charge; the balls to powder weight ratio is equal to 40:1. Temperature in the reaction zone did not exceed 100°C rotation speed of the vials is 1480 rpm.

Study of the phase composition of milling products and refinement of the crystalline structure of the carbides obtained is carried out by X-ray diffraction method. XRD spectra are collected by an automated DRON-3M diffractometer (CuK_α radiation, a discrete mode: the scanning interval $2\theta = (15–100)°$, the step scan is 0.05°, counting time per step at 3 s). Analysis and interpretation of the XRD data obtained is provided by an original software package, which includes a complete set of standard Rietveld procedures [7]. The Vickers microhardness tests have performed with PMT-3 apparatus at room temperature. All samples are preliminary polished by diamond paste. The load of 150 *g* is applied to the sample for 15 s. Number of indentations per one sample is 50.

3. RESULTS AND DISCUSSION

Results of XRD phase analysis show that the 60 min milled test samples are two-phased for both charges (Ni–CNT and Ni–Graphite). Each of them contains additional cubic phase NiC_x with a significantly higher lattice parameter except the initial nickel powder (a = 0.3522(3) nm). With further milling (120 min and more) the NiC_x phase becomes the only constituent of the test samples. Moreover, its lattice parameter gradually increases with the processing time increasing (Fig. 1).

Structural calculations, performed for final milling products of Ni–CNT and Ni–Graphite charges treated 750 min in a ball mill, confirmed, in generally, our earlier results on the formation under mechanical alloying the NiC_x carbide with a defective ZnS sphalerite type structure [5]. But the best match between experimental and calculated intensities (improvement of the reliability factor) is obtained for a model, in which carbon atoms are slightly shifted from 4(c) (1/4 1/4 1/4) position, inherent to cubic ZnS-type structure, towards the centre of the f.c.c. crystal lattice (1/2 1/2 1/2). So, the result of the crystal structure modelling and refinement for the NiC_x carbide, synthesized by mechanical alloying of the both Ni–C charges (1:1), are listed in Table 1, Fig. 2 illustrates the atomic arrangement in this structure.

Analysis of the results of structural calculations indicates that after

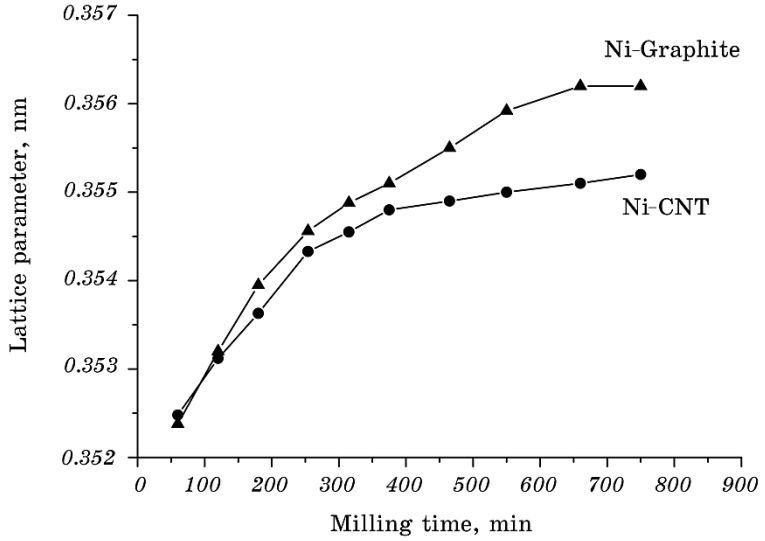

Fig. 1. Dependences of the lattice parameters of the NiC_x carbides forming at mechanical alloying of the equiatomic Ni–CNT and Ni–Graphite charges in a ball mill.

750 min of processing in a ball mill of both Ni–CNT and Ni–Graphite charges, the obtained milled powder products are NiC carbide with almost stoichiometric composition (Table 1).

However, the saturation of the NiC carbide by carbon does not reach 50 at.% for the Ni–CNT charge. But, on the contrary, in the case of the

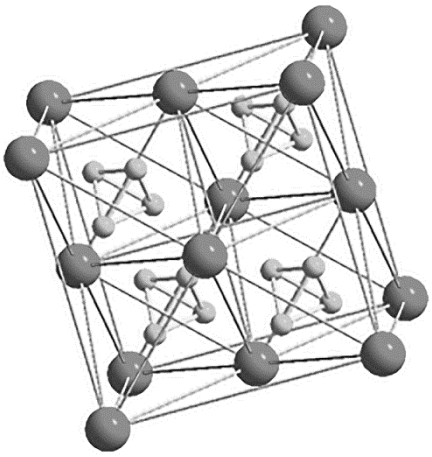

Fig. 2. Crystal structure of the NiC carbide. Nickel atoms are marked as dark grey circles, carbon atoms are marked as light grey circles.

Ni–Graphite charge the saturation of NiC carbide by carbon obtained by processing is somewhat higher. The final lattice parameters of these carbides are also different (Table 1).

The final powder products, obtained after 750 min of processing of both charges in a ball mill, are cold pressed under pressure of 0.2 GPa. XRD study has not revealed any significant changes in crystallographic parameters of NiC carbide after compacting. The Vickers hardness *HV* of the samples compacted is somewhat higher than the hardness of nickel powder compressed under similar condition. Namely, *HV* is equal to 0.93 GPa for a sample obtained from Ni–CNT charge; *HV* is equal to 0.85 GPa for the sample compressed from Ni–Graphite charge, and *HV* reaches 0.64 GPa for the initial nickel powder compressed.

NiC thin films (a film thickness is about 200 nm) are deposited either onto silicon substrate or fused glass wafers by electron beam technique using a compressed sample of NiC as a target material. A target is heated up to 1500°C, the substrate is held at room temperature.

XRD study revealed that the diffraction patterns of the coatings obtained are either X-ray amorphous ones or contain very weak single diffraction peak belonging to nickel metal (Fig. 3, *b*), the lattice parameter of which cannot be determined correctly. Diffraction halo on a diffractogram of the coating studied in the region of $2\theta \approx (19–27)°$ indicates the presence of X-ray amorphous component (Fig. 3, *b*). X-ray

TABLE 1. Crystal data for NiC carbides formed in the equiatomic Ni–CNT and Ni–Graphite mixtures after 750 min of milling.

Atom	Site	Site occ.	*X*	*Y*	*Z*
NiC carbide formed in the Ni–CNT mixture					
Ni	4*a*	1.00(1)	0	0	0
C	16*e*	0.23(1)	0.338(1)	0.338(1)	0.338(1)
Space group			*F*43*m* (No. 216)		
Lattice parameter *a*, nm			*a* = 0,3552(1)		
Total isotropic *B* factor, nm^2			$B = 2.88(2)\cdot10^{-2}$		
Calculated content, at.%			52.1(3) Ni + 47.9(3) C		
Reliability factor			$R_I = 0.003$		
NiC carbide formed in the Ni–Graphite mixture					
Ni	4*a*	1.00(1)	0	0	0
C	16*e*	0.27(5)	0.332(5)	0.332(5)	0.332(5)
Space group			*F*43*m* (No. 216)		
Lattice parameter *a*, nm			*a* = 0,3562(2)		
Total isotropic *B* factor, nm^2			$B = 3.09(9)\cdot10^{-2}$		
Calculated content at.%			47.7(3) Ni + 52.3(3) C		
Reliability factor			$R_B = 0.011$		

data also indicate that the remains of the material in an evaporator consist of NiC_x carbide ($a \approx 0.355$ nm) with some amount of graphite phase (Fig. 3, *a*). It should also be noted that the additional reflection with $d \approx 0.2712$ nm ($2\vartheta \approx 33.0°$), which is present on some diffraction patterns (Fig. 3, *b*), obviously belongs to $NiCO_3$ oxycarbide, which is formed on the surface of the coating. Upon annealing of the coatings up to 600°C $NiCO_3$ oxycarbide decomposes into NiO oxide and CO_2 gas (Fig. 3, *c*) (decomposition temperature of $NiCO_3$ is known to be about 400°C). Reflections of both oxides and graphite disappear from diffraction patterns after cleaning the surface of the coatings with a soft cloth.

If we do not take into account the surface phenomena such as formation and decomposition of $NiCO_3$ oxycarbide, then stepwise annealing in air up to 900°C (with expose at each temperature for 1–2 hours) does not lead to any cracking or peeling of thin coatings from the substrate, which certifies a good adhesion in the substrate-coating zone.

Thus, NiC carbide is synthesized by mechanical alloying for the first time. The powder material obtained is compacted by cold pressing and then successfully tested as a target material for its deposition on silicon or fused glass wafers substrates.

It should be noted that in addition to the attractive physical proper-

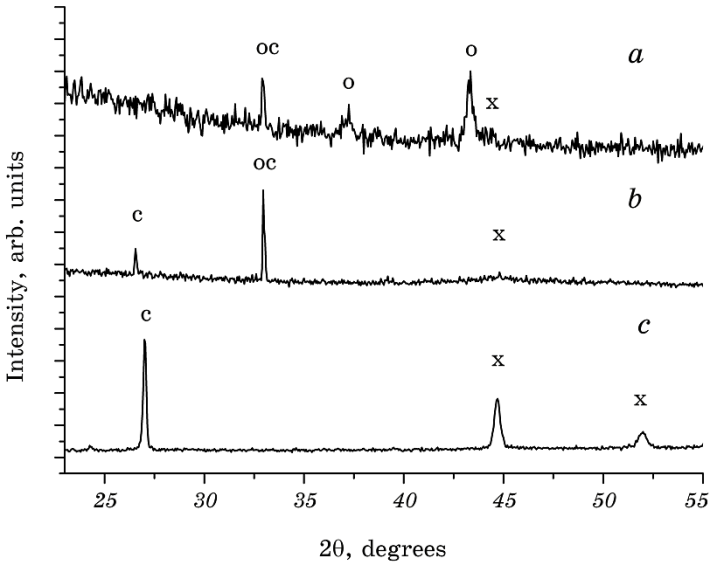

Fig. 3. Fragments of XRD patterns of the coating deposited from NiC compressed powder: after annealing at 800°C (*a*); as deposited (*b*); fragment of XRD pattern of the residual material (*c*). Reflections of Ni metal are marked as 'x', graphite reflections are marked as 'c', $NiCO_3$ and NiO phases are marked as 'oc' and 'o', respectively.

ties of NiC-based single layer coatings [1–4], it seems to be quite prospective the development of the multilayer coatings such as Ti/NiC and TiSiC/NiC [8–10]. Taking into account the achievements of the authors of this article in the field of mechanochemical synthesis of the binary carbides of transition metals [11], our attempts will to be further focused on synthesis of the multicomponent carbides in order to test them as coatings for various functional purposes.

4. CONCLUSIONS

The nanoscale powder of equiatomic NiC carbide is synthesized by mechanical alloying in a high-energy planetary ball mill using two powder mixtures containing 50 at.% of Ni, as well as 50 at.% of CNT or 50 at.% of graphite. It is shown that the composition of this carbide is close to stoichiometric, and its crystal structure is a modified ZnS sphalerite-type structure. The NiC carbide powders are compacted by cold pressing at a pressure of 0.2 GPa. Materials compacted are used for their deposition on substrates of a silicon wafer or fused glass by electron beam technique. The phase composition of the coatings obtained is studied both in the initial state and after their annealing up to 900°C.

REFERENCES

1. T. Ujvári, A. Tóth, G. J. Kovács, G. Sáfrán, O. Geszti, G. Radnóczi, and I. Bertóti, *Surf. Interface Analysis*, **36**, No. 8: 760 (2004).
2. H. Li, L. Guan, Y. Zhao, Z. Xu, J. Sun, J. Wu, and N. Xu, *Mater. Lett.*, **145**: 291 (2015).
3. G. Radnóczi, Gy. J. Kovács, G. Sáfrán, K. Sedlácková, O. Geszti, T. Ujvári, and I. Bertóti, *Metallic Materials with High Structural Efficiency* (Eds. O. N. Senkov, D. B. Miracle, and S. A. Firstov) (Dordrecht: Springer: 2004), p. 101.
4. Z. C. Hong and S. T. Shiue, *Thin Solid Films*, **618**: 21 (2016).
5. O. I. Nakonechna, N. N. Belyavina, M. M. Dashevskyi, A. M. Kuryliuk, and V. A. Makara, *Dopov. Nac. Akad. Nauk Ukr.*, No. 4: 50 (2019) (in Ukrainian).
6. V. K. Portnoi, A. V. Leonov, S. N. Mudretsova, and S. A. Fedotov, *Phys. Metals Metallogr.*, **109**, No 2: 153 (2010).
7. M. Dashevskyi, O. Boshko, O. Nakonechna, and N. Belyavina, *Metallofiz. Noveishie Tekhnol.*, **39**, No. 4: 541 (2017).
8. M. Braic, M. Balaceanu, A. C. Parau, M. Dinu, and A. Vladescu, *Vacuum*, **120**: 60 (2015).
9. H. Jiao, C. Yu, Z. Zhang, W. Li, Q. Huang, H. Chen, and Z. Wang, *Vacuum*, **155**: 49 (2018).
10. M. Khadem, O. V. Penkov, H. K. Yang, and D. E. Kim, *Friction*, **5**, No. 3: 248 (2017).
11. O. I. Nakonechna, M. M. Dashevskyi, O. I. Boshko, V. V. Zavodyanny, and N. N. Belyavina, *Prog. Phys. Metals*, **20**, No. 1: 5 (2019).