Вісник Тернопільського національного технічного університету
Scientific Journal of the Ternopil National Technical University
2018, № 3 (91)
ISSN 2522-4433. Web: **visnyk.tntu.edu.ua**

UDC 620.17

EFFECT OF BINDER WITH NANO NI ON MECHANICALPROPERTIES OF TIC BASED HARD ALLOYS

Halyna Kramar; Lyudmyla Bodrova; Yaroslav Kovalchuk; Sergiy Marynenko; Ihor Koval

Ternopil Ivan Puluj National Technical University, Ternopil, Ukraine

Summary. *Titanium carbide based hard alloys with nickel-chromium binder possess high hardness, wear and heat resistance. In order to improve physical and mechanical properties of alloys the polycarbide basis TiC-5WC-5NbC and Ni (nano Ni)-Cr binder were used. The physical and mechanical properties of the alloys with 10, 18 and 24% (wt) of the binder, which contained 7,5, 13,5 and 18% (wt) of nano Ni or fine grained Ni respectively, were studied. It is found that the use of nano nickel (70 nm) compared to fine nickel (1..2 μm) allows to obtain lower porosity, more fine-grained microstructure (d = 0,7..1 μm) and higher physical and mechanical properties of the alloys by 10..15%. Binder with nano Ni prevents formation of carbide skeleton and the nano Ni content increase results in the hardness, micro hardness, transverse rupture strength and fracture toughness increase.*

Key words: *mechanical properties, hard alloy, nano nickel, titanium carbide, hardness, fracture toughness.*

Received 13.10.2018

Statement of the problem. TiC based hard alloys are successfully used as substitutes of WC-Co hard alloys for cutting structural and alloyed steels and non-ferrous metals because they possess high hardness, wear resistance and satisfactory strength [1 – 3]. The alloys have three times lower density compared to common WC-Co alloys. Main applications of the titanium carbide based hard alloys with nickel-chromium binder are semi-finishing and finishing machining. Various carbides and metal binders are used as initial materials in TiC based hard alloys to improve mechanical properties, but their fracture toughness is lower enough. Potential possibilities of hard alloys significantly increased when new technological methods of structure forming based on application of nanopowder and nanotechnologies have appeared.

Analysis of the available investigations. It is known [4] that adding of nanopowders to ordinary powders makes it possible to obtain high level of the properties. Reduced by 4...7% porosity of powdered products and decreased by *150…200°C* sintering temperature result in the strength and plastic properties improvement. The prevention of recrystallization process, optimization of compaction pressure by the criteria of minimum carbide grain sizes and maximum density of the alloy are of great importance for alloys with nano Ni addings. However, obtaining of high-density compacts is a significant problem as nanopowders are poorly pressed because of the adhesive interaction between particles, the value of which increases rapidly with the particle size decrease [5]. Previous studies [1] observed that the optimal compaction pressure is *150 MPa*. Then samples pressed at such a pressure must be sintered under special thermal-kinetic parameters [6].

An important issue during the alloys with nanoscale powders sintering is to preserve their fine-grained structure at the final stages of sintering [7, 8]. High-speed sintering (HSS) was used to resolve this issue. The applied new technology has certain features aimed at solving the problem of structural heterogeneity formation and liquidating or minimizing the number of isolated pores.

The aim of this paper is to investigate the effect of Ni(nano Ni) on the physical and mechanical properties of the TiC-WC-NbC-Ni-Cr hard alloys.

Statement of the task. Research the using of polycarbide base and Ni(nano Ni)-Cr binder in the alloys for increasing hardness which is higher than of common alloys and to obtain higher fracture toughness and transverse rupture strength.

Materials and experimental procedure. TiC-5WC-5NbC with Ni(nano Ni)-Cr binder (ratio of Ni(nano Ni):Cr = 3:1) in the alloys were used. The physical and mechanical properties of the alloys with 10, 18 and 24% *(wt)* of the binder, which contained 7,5, 13,5 and 18% *(wt)* of nano Ni or fine-grained Ni respectively, depending on the sintering temperature in vacuum, were studied. The hard alloys were manufactured by the common technology of the powder metallurgy. The grinding of powder mixture was carried out in the ethyl medium in a ball mill for *72 hours*. A 5% solution of synthetic rubber was used as plasticizer. Sintering was realized by two ways: vacuum double-stage sintering (DSS) with slow heating in temperature interval of the plasticizer decomposition and HSS during which alloys were heated at a speed of *°C/min* in the range from *600°C* to sintering temperature. The sintering was carried out at the temperatures of *1300°C*, *1350°C* and *1400°C* for *20 min*.

The chemical composition of the alloys' binder, density of the alloys and sizes of the initial Ni (nano-Ni) powders are shown in Table 1.

Table 1

Chemical composition of the alloys' binder, density of the alloys and size of the Ni powder

Composition of the alloys' binder, *(wt. %)*[a]	$\rho_{add.}$, g/cm^3	Size, Ni
10 (7.5 Ni-2.5 Cr)	5,55	1..2 μm
18 (13.5 Ni-4.5 Cr)	5,63	1..2 μm
24 (18 Ni-6 Cr)	5,8	1..2 μm
10 (7.5 Ni (nano)[b]-2.5 Cr)	5,55	70 *nm*
18 (13.5 Ni (nano)[b]-4.5 Cr)	5,63	70 *nm*
24 (18 Ni (nano)[b]-6 Cr)	5,8	70 *nm*

[a]*TiC-5WC-5NbC is the polycarbide basis in all alloys,*
[b]*Nano Ni is produced by National University of Science and Technology «MISiS».*

The mechanical properties of the alloys: hardness by Rockwell and Vickers, transverse rupture strength σ_{trs} and compression strength σ_{cs} were determined at the room temperature according to the standard methods. Vickers hardness was measured by applying a load of *300 N* (ISO 3878). Fracture toughness (K_{IC}) was calculated after microscopic investigation of the indentations and cracks. Transverse rupture strength σ_{trs} was determined by the method of three-point bend on specimen with following dimensions: $a = 5 \pm 0{,}25$ *mm*, $b = 5 \pm 0{,}25$ *mm*, $c = 35 \pm 1$ *mm*. Cylindrical specimen with diameter $d = 8 \pm 0{,}25$ *mm* and height $h = 16 \pm 1$ *mm* were used to determine the compression strength σ_{cs}. Density was measured by hydrostatic weighing. Porosity was determined by the metallographic method.

Results and discussion. The reproducibility of mechanical properties and preserving them at a high level are very important features in hard alloys manufacturing. Such characteristics as transverse rupture strength and compression strength have considerable variability of results.

Dependencies of the mechanical properties on the content of Ni and nano Ni and sintering technology are shown in Figure 1. It is found that with the increase of Ni content the transverse rupture strength increases in both cases. For alloys with fine-grained Ni it changes from *750* to *810 MPa*, whereas with nano Ni – from *880* to *980 MPa*. Alloys sintered by HSS have higher transverse rupture strength by 10…15%.

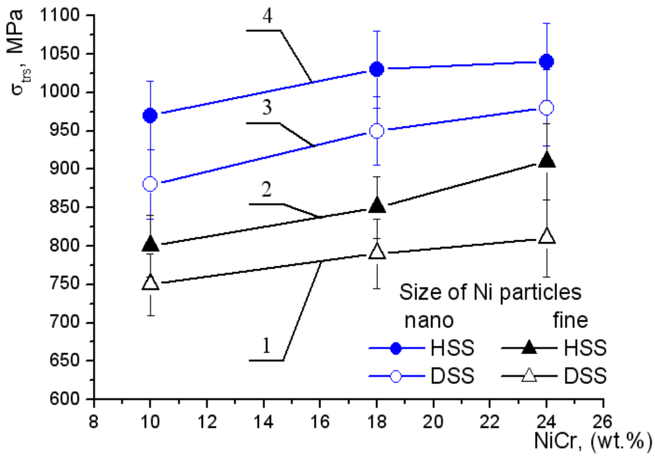

Figure 1. Effect of Ni (1, 2) and nano Ni (3, 4) content in the alloys on transverse rupture strength.
1, 3 – DSS; 2, 4 – HSS

Dependencies of transverse rupture strength and compression strength on temperature and technology of sintering and chemical composition of the hard alloys are shown in Figure 2. It was determined that the sintering temperature of *1350°C* and HSS are optimal for obtaining high level of these properties. For the hard alloys of all compositions sometimes significantly higher values of mechanical characteristics *(σ_{cs} = 3120 MPa, σ_{trs} = 1230 MPa)* were observed indicating the possibility of such properties improvement.

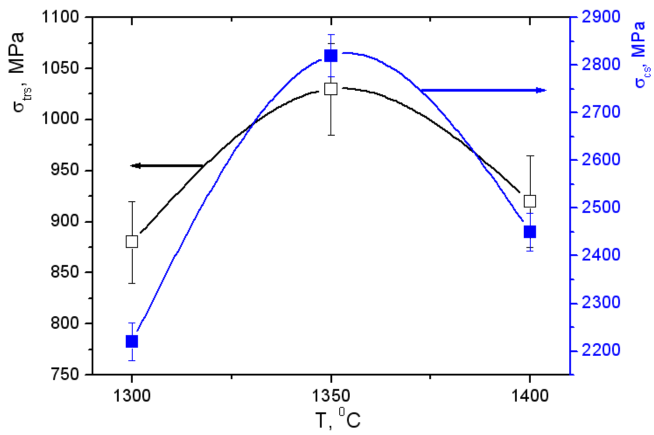

Figure 2. Dependencies of transverse rupture strength and compression strength on sintering temperature for Ti-5WC-5NbC-13,5 nano Ni-4.5Cr hard alloy (HSS)

Dependencies of physical and mechanical properties on the content of fine Ni and nano Ni in the alloys' binder are shown in Figure 3. Density of the alloys increases with increased nano Ni content for all sintering temperatures and both sintering technologies. The hardness has the similar behaviour – the increase of nano Ni content in the alloys results in the significant increase of their hardness and micro hardness apart from the alloy with *18 wt.%* nano Ni sintered at *1400°C* for which these properties slightly decrease. Increasing hardness of the alloys with nano Ni is probably connected with the fact that for the alloys with nano Ni solubility of the carbides' metals (Ti, Nb, W) increases in the binder [9] and the binder becomes more strengthened. For the alloy with *18 wt.%* nano Ni sintered at *1350°C* by HSS Vickers hardness is 13,3 GPa and Rockwell hardness is 91,6 HRA.

Hardness of the alloys with fine-grained Ni decreases with its increased content as well as for commercial alloys WC-Co, WC-TiC-Co, TiC-Ni-Mo [10, 11]. Moreover, it is known, that for commercial alloys factors that increase hardness cause the K_{1C} decrease. But in our case the use of nano Ni in the binder resulted in obtaining an opposite dependence. It was found that K_{1C} increases with increasing binder content without a loss in toughness along with the binder phase strengthening by Ti, W and Nb. The investigations testify that fracture toughness of hard alloys obtained by DSS and HSS technologies is significantly different: in the first case it was $6,2...7,5\ MPa{\cdot}m^{1/2}$, in the second case it was $6,7...8,1\ MPa{\cdot}m^{1/2}$.

Due to metallographic and fractographic analysis it was found early [9] that alloys with nano Ni have more fine microstructure (*d = 0,7…1 µm*) compared to fine-grain Ni (*d = 1…2 µm*) and hard alloy with *10 wt.%* binder (*7,5 wt.%* of nano Ni) is damaged by brittle mechanism but fracture of the hard alloy with *24 wt.%* binder (*18 wt.%* of nano Ni) is accompanied by appearance of micro viscous fracture elements.

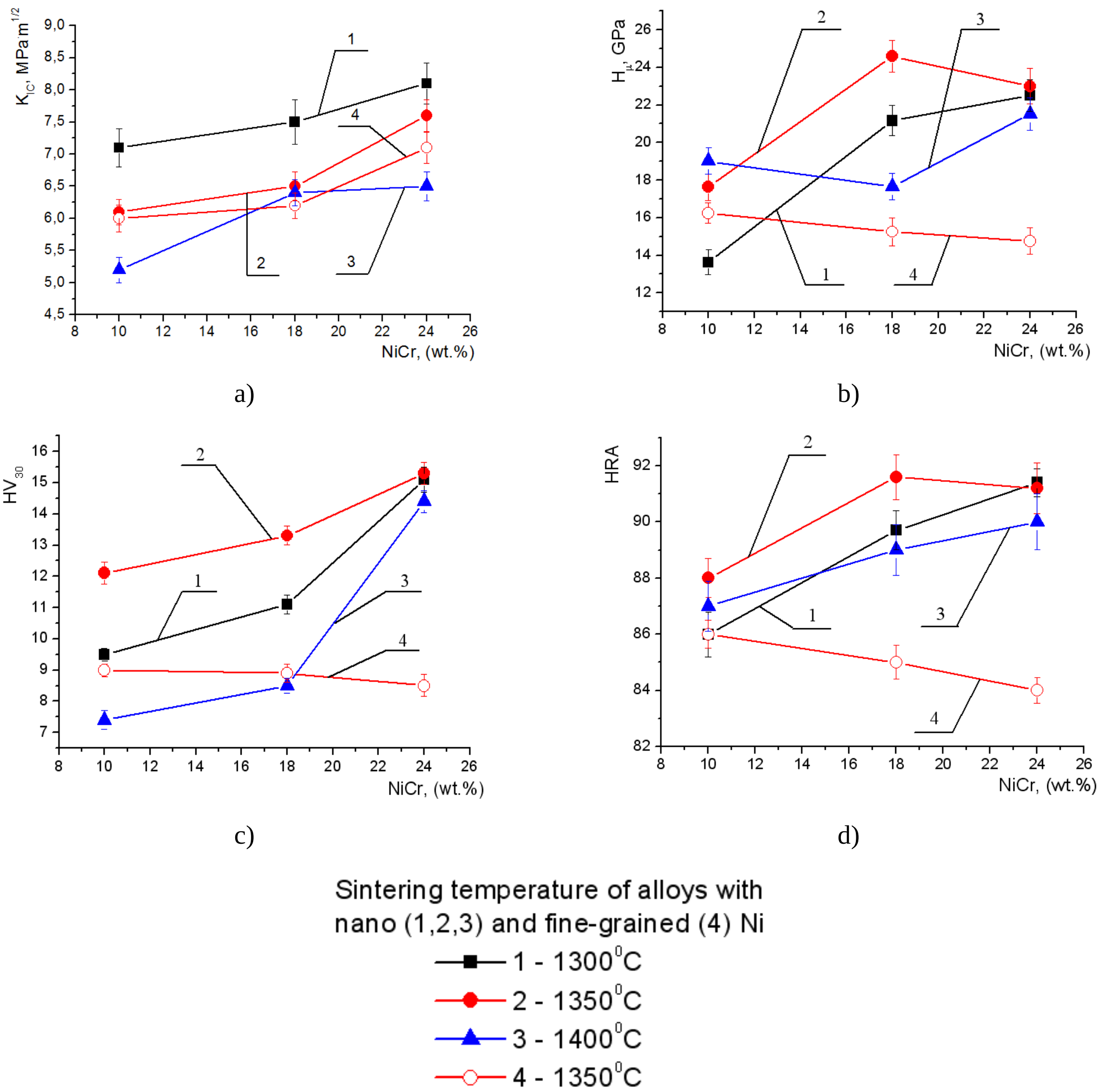

Figure 3. Dependencies of the alloys' mechanical properties (fracture toughness (a), microhardness (b), Vickers hardness (c), Rockwell hardness(d)) on Ni and nano Ni content and sintering temperature

Porosity of alloys with nano Ni changes from B 04 to A 02. It was found that at lower sintering temperatures the use of nano Ni compared to fine Ni allows to obtain lower porosity, more fine microstructure and, consequently, higher physical and mechanical properties of the alloys by 10..15%. It is known [5] that the use of nano components in alloys results in high stress and distortion of the crystal lattice, change in interatomic distances and appearance of significant atoms displacements at nonequilibrium boundaries of grains. The binder in the amount of up to 18% *(wt)* nano Ni uniformly surrounds carbide grains, prevents the formation of a continuous carbide skeleton and results in the increase of fracture toughness and transverse rupture strength. At the higher content of the nano structural component, the binder «islands» are formed and large conglomerates of carbide grains appear, resulting in the alloys mechanical properties decrease.

In general, alloys containing nano Ni, obtained by HSS, have a significantly higher fracture toughness and transverse rupture strength compared to alloys with fine grained Ni. Rockwell and Vickers hardness of them are at the same level compared to another polycarbide based and metallic binder of the alloys (Table 2). Fracture toughness of the developed hard alloys is higher than of the known free-tungsten hard alloys and their properties were comparable to commercial alloy (HV *14 – 15 GPa*, K_{1C} *8 – 10* $MPa{\cdot}m^{1/2}$).

Table 2

Physical and mechanical properties of hard alloys

Hard alloys	Sintering technology	HRA	HV_{30}	σ_{tr}, MPa	K_{IC}, $MPa{\cdot}m^{1/2}$
TiC-VC-NbC-WC-NiCr	DSS	89,6…91,4	16,9…17,2	780…800	7,6…7,8
TiC-WC-NbC-Ni-Cr	DSS	84…86	7,8…8,9	750…810	5,4...6,5
	HSS	87…90	8,5...9,0	800…910	6,0...7,1
TiC-WC-NbC-Ni(nano)-Cr	DSS	85,5…87	12,8…14,9	880…980	6,2...7,5
	HSS	89…91,6	13,4...15,8	950…1040	6,7...8,1
WC-TiC-Co[10]		90,2	17,0	1100	8…10
TiC-Ni-Mo[11]		91		1150	
Ti(C,N)-WC-Ni [12]			10,1		7,3
Ti(C,N)-WC-Co [13]			17,9	910	3,7

Results of the TiC- WC NbC based hard alloys with the Ni(nano-Ni)-Cr binder mechanical properties investigation testify that they may be used as tool materials for inserts, dies, press molds, wire dies. These alloys belong to P01-P25 according to ISO.

Conclusions. The alloys with 18% *(wt.)* and 24% *(wt.)* nano Ni content in the binder sintered by HSS at the temperature of *1350°C* possess high hardness with relatively high toughness. This alloys has the maximum Vickers hardness of *15,3 GPa*, Rockvell hardness of *91,6,* fracture toughness of *7,6* $MPa{\cdot}m^{1/2}$, transverse rupture strength of *1040 MPa* and compression strength of *2820 MPa*. Significant improvement in the mechanical properties of the alloy with nano Ni in the binder was observed compared to that of fine-grained Ni and their values are competitive with commercial alloys.

References

1. Bodrova L.G., Kramar G.M., Mul O.V., Koval I.V., Sushynskiy V.I. Effect of nano WC alloying additions on the Structure Formation of TiC-5VC-18NiCr Cermets. Proceeding World PM 2010. Vol. 3, pp. 479 – 484.
2. Bellosi A., Calravarini R., Faga M.G. and other. Characterisation and application of titanium carbonitride – based cutting tools. Jornal of Materials Processing Technology 143 – 144 (2003), pp. 527 – 532. www.elsevier/locate/jmatprotec/.
3. Rajabi A., Ghazali M., Daud A. Chemical composition, microstructure and sintering temperature modifications on mechanical properties of TiC-based cermet. Jornal Materials and Design 67 (2015). P. 95 – 106. www.elsevier.com/locate/matdes/.
4. Richter V., Poetschke J., Holke R., Michaelis A. Nanoscaled Hardmetals – Fiction or Reality? Proceedings of 18 Plansee Seminar 2013: International Conference on Refractory Metals and Hard Materials, Reutte, Austria, June 3 – 7, 2013, 19 p.
5. Gusev A.I., Rempel A.A. Nanokristallicheskiye materialy. M. Phizmashmet, 2000, 384 p. [In Russian].
6. Skorokhod V.V. Rapid rate sintering of dispersed systems: theory, processing and problems. Powder Metallurgy, 1999, No. 7 – 8, pp. 30 – 39.
7. Kramar H.M., Sushynskiy V.I., Isaev Ye.O. Osoblyvosti spikannya tverdykh splaviv na polikarbidniy osnovi z dribno- i nanodyspersnoyu zv'yazkoyu. Research Bulletin of NTUU “Kyiv Polytechnic Institute”, 2011, No. 6, pp. 96 – 101 [In Ukrainian].
8. Lisovsky A.F. Thermodynamics of Isolated Pores Filling with Liqued in Sintered Composite Materials. Metallurgical and Materials Transactions. 25 A. April, 1994, pp. 733 – 740.
9. L. Bodrova, G. Kramar, I. Koval, V. Sushynskyi, S. Marynenko, V. Bukhta. Microstructure and mechanical properties of hard alloys fabricated from starting nanopowder. Euromat 2011, 12 – 15 September, 2011, Montpellier, France.
10. Bodrova L.G., Kramar G.M., Marynenko S.Yu. [and other]. Novi vitchyznyani bezvol'framovi tverdi splavy z pidvyshchenymy ekspluatatsiynymy vlastyvostyamy. Instrumental'nyy svit, 2011. No. 1 – 2 (49 – 50). pp. 54 – 56 [In Ukrainain].
11. Panov V.S. Tekhnologiya i svoystva spechennykh tverdykh splavov i izdeliy iz nikh. M. MISiS, 2001, 428 p. [In Russian].
12. J. Jung. Effect of ultra-fine powders on the microstructure of Ti(C,N)-xWC-Ni cermets. Acta Materiala 52 (2004). 1379 – 1386. www. Actamat-journals.com.
13. Chao S, Liu N, Yuan Y.P, Han C.L, Xu Y.D, Shi M, Feng J.P. Microstructure and mechanical properties of ultrafine Ti (C,N)-based cermets fabricated from nano/submicro starting powders. Ceram Int 2005, 31, pp. 851-862.

Список використаної літератури

1. Bodrova, L.G. Effect of nano WC alloying additions on the Structure Formation of TiC-5VC-18NiCr Cermets [Text] / L.G. Bodrova, G.M. Kramar, O.V. Mul, I.V. Koval, V.I. Sushynskiy // Proceeding World PM 2010. – Vol. 3. – P. 479 – 484.
2. Bellosi, A. Characterisation and application of titanium carbonitride – based cutting tools / A. Bellosi, R. Calravarini, M.G. Faga and other. Jornal of Materials Processing Technology 143 – 144 (2003). – P. 527 – 532. – www.elsevier/locate/jmatprotec/.
3. Rajabi, A. Chemical composition, microstructure and sintering temperature modifications on mechanical properties of TiC-based cermet. – A review / A. Rajabi, M. Ghazali, A. Daud // Jornal Materials and Design 67 (2015). – 95-106. – www.elsevier.com/locate/matdes/.
4. Richter, V. Nanoscaled Hardmetals – Fiction or Reality? [Text] / Richter V., Poetschke J., Holke R., Michaelis A. // Proceedings of 18 Plansee Seminar 2013: International Conference on Refractory Metals and Hard Materials. – Reutte : Austria. – June 3 – 7, 2013. – 19 p.
5. Гусев, А.І. Нанокристаллические материалы [Текст] / А.І. Гусев, А.А. Ремпель // М.: Физмашмет. – 2000. – 384 с.
6. Skorokhod, V.V. Rapid rate sintering of dispersed systems: theory, processing and problems [Текст] / V.V. Skorokhod // Powder Metallurgy. – 1999. – № 7 – 8. – P. 30 – 39.
7. Крамар, Г.М. Особливості спікання твердих сплавів на полікарбідній основі з дрібно- і нанодисперсною зв’язкою [Текст] / Крамар Г.М., Сушинський В.І., Ісаєв Є.О. // Наукові вісті Національного технічного університету України «Київський політехнічний інститут». – 2011. – № 6. – С. 96 – 101.
8. Lisovsky, A.F. Thermodynamics of Isolated Pores Filling with Liqued in Sintered Composite Materials [Text] / A.F. Lisovsky // Metallurgical and Materials Transactions. 25 A. – April, 1994. – P. 733 – 740.

9. Microstructure and mechanical properties of hard alloys fabricated from starting nanopowder. [Text] / L. Bodrova, G. Kramar, I. Koval, V. Sushynskyi, S. Marynenko, V. Bukhta. Euromat 2011. – 12 – 15 September, 2011. – Montpellier : France.
10. Нові вітчизняні безвольфрамові тверді сплави з підвищеними експлуатаційними властивостями [Текст] / Л.Г. Бодрова, Г.М. Крамар, С.Ю. Мариненко [та ін.] // Інструментальний світ. – 2011. – № 1 – 2 (49 – 50). – С. 54 – 56.
11. Панов, В.С. Технология и свойства спеченных твердых сплавов и изделий из них [Текст] / В.С. Панов. – М. : МИСиС, 2001. – 428 с.
12. Jung, J. Effect of ultra-fine powders on the microstructure of Ti(C, N)-xWC-Ni cermets. – Acta Materiala 52 (2004) 1379 – 1386. – www.actamat-journals.com.
13. Microstructure and mechanical properties of ultrafine Ti (C,N)-based cermets fabricated from nano/submicro starting powders [Text] / Chao S., Liu N., Yuan Y.P., Han C.L., Xu Y.D., Shi M., Feng J.P. – Ceram Int 2005, 31. – P. 851 – 862.

УДК 620.17

ВПЛИВ ЗВ'ЯЗКИ З НАНО NI НА МЕХАНІЧНІ ВЛАСТИВОСТІ ТВЕРДИХ СПЛАВІВ НА ОСНОВІ TIC

Галина Крамар; Людмила Бодрова; Ярослав Ковальчук; Сергій Мариненко; Ігор Коваль

Тернопільський національний технічний університет імені Івана Пулюя, Тернопіль, Україна

Резюме. *Тверді сплави на основі карбіду титану з нікель-хромовою зв'язкою використовують як матеріал різальних інструментів при обробці вуглецевих та легованих конструкційних сталей і сплавів на основі кольорових металів завдяки їх високій твердості, зносо- та термостійкості. Суттєвою перевагою цих сплавів є низька густина, що в 3 рази менша, ніж у вольфрамокобальтових твердих сплавів. Однак для їх широкого впровадження необхідно підвищити міцнісні характеристики. Для покращення фізико-механічних властивостей сплавів на полікарбідній основі TiC-5WC-5NbC використовували Ni(нано Ni)-Cr як зв'язку та різні способи спікання у вакуумі – двостадійне з повільним нагріванням в інтервалі температур розкладу пластифікатора та спікання з високошвидкісним нагріванням (120°С/хв) в інтервалі температур від 600°С до температури спікання. Використання другого способу спікання дозволило зменшити кількість ізольованих пор у сплавах, при цьому їх пористість змінилася з В 04 до А 02. Встановлено, що спікання при нижчих температурах сплавів із нано Ni у зв'язці порівняно з дрібнодисперсним Ni призводить до зниження пористості та підвищення механічних властивостей. Вивчено фізико-механічні властивості сплавів з 10, 18 та 24% (мас.) зв'язки, які містять 7,5, 13,5 та 18% (мас.) нано Ni або дрібнодисперсного Ni відповідно. Виявлено, що використання нано-нікелю (70 нм) у порівнянні з дрібнодисперсним нікелем (1 – 2 мкм) дозволяє отримати дрібнозернистішу мікроструктуру (d = 0,7..1 мкм) та кращі фізико-механічні властивості сплавів на 10..15%. Зв'язка з нано Ni запобігає утворенню карбідного каркасу, а збільшення її вмісту у сплавах, спечених із високошвидкісним нагріванням до температури спікання 1350°С, призводить до підвищення твердості за Роквеллом до 91,6, твердості за Віккерсом до 15,3 ГПа, границі міцності на згин до 1040 МПа та коефіцієнта тріщиностійкості до 7,6 МПа·м$^{1/2}$. За рівнем фізико-механічних властивостей та областю використання досліджені сплави віднесено до груп Р01-Р25 відповідно до стандарту ISO.*

Ключові слова: *механічні властивості, нанонікель, карбід титану, твердість, тріщиностійкість.*

Отримано 13.10.2018