EFFECT OF BINDER WITH NANO NI ON MECHANICAL PROPERTIES 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.

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.

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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>
<thead>
<tr>
<th>Composition of the alloys’ binder, (wt. %)</th>
<th>ρadd., g/cm³</th>
<th>Size, Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 (7.5 Ni-2.5 Cr)</td>
<td>5.55</td>
<td>1..2 μm</td>
</tr>
<tr>
<td>18 (13.5 Ni-4.5 Cr)</td>
<td>5.63</td>
<td>1..2 μm</td>
</tr>
<tr>
<td>24 (18 Ni-6 Cr)</td>
<td>5.8</td>
<td>1..2 μm</td>
</tr>
<tr>
<td>10 (7.5 Ni (nano)b-2.5 Cr)</td>
<td>5.55</td>
<td>70 nm</td>
</tr>
<tr>
<td>18 (13.5 Ni (nano)b-4.5 Cr)</td>
<td>5.63</td>
<td>70 nm</td>
</tr>
<tr>
<td>24 (18 Ni (nano)b-6 Cr)</td>
<td>5.8</td>
<td>70 nm</td>
</tr>
</tbody>
</table>

*TiC-5WC-5NbC is the polycarbide basis in all alloys,

*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: \(a = 5 ± 0.25 \ mm, b = 5 ± 0.25 \ mm, c = 35 ± 1 \ mm\). Cylindrical specimen with diameter \(d = 8 ± 0.25 \ mm\) and height \(h = 16±1 \ mm\) 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-m$^{1/2}$, in the second case it was 6.7...8.1 MPa-m$^{1/2}$.

Due to metallographic and fractographic analysis it was found early [9] that alloys with nano Ni have more fine microstructure ($d = 0.7...1 \mu m$) compared to fine-grain Ni ($d = 1...2 \mu m$) 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](image.png)

**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, $K_{IC} 8 – 10 \text{ MPa} \cdot \text{m}^{1/2}$).

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

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, Rockwell hardness of 91,6, fracture toughness of 7,6 MPa $\cdot \text{m}^{1/2}$, 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

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Список використаної літератури


УДК 620.17

ВПЛИВ ЗВ’ЯЗКИ З НАНО НІ НА МЕХАНІЧНІ ВЛАСТИВОСТІ ТВЕРДИХ СПЛАВІВ НА ОСНОВІ ТІС

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, зносостійкості та термостійкості. Суттєвою перевагою цих сплавів є низька густина, що в 3 рази менша, ніж у вольфрамокобальтових твердих сплавах. 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°C/хв) в інтервалі температур від 600°C до температури спікання. Використання другого способу спікання дозволяло зменшити кількість ізольованих пор у сплавах, при цьому їх пористість зменшилася в 3 рази. Встановлено, що спікання при низьких температурах сплавів із нано Ni у зв’язці порівняно з дрібнодисперсним Ni призводить до зниження пористості та підвищення механічних властивостей. Винене фізико-механічні властивості сплавів з 10, 18 та 24% (мас.) нано Ni або дрібнодисперсного Ni відповідно. Виявлено, що використання нано-нікелю (70 нм) у порівнянні з дрібнодисперсним нікелем (1 – 2 мкм) дозволяє отримати дрібнозернисту 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 його спічкина в сплавах, спечених з нано Ni, зменшує втрати зносостійкості до 1040 МПа та коефіцієнта тріщиності до 7,6 МПа ∙м1/2. За рівнем фізико-механічних властивостей та областю використання досліджени сплави віднесено до груп P01–P25 відповідно до стандарту ISO.

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

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