

Structure Formation of Polycarbide-Based TiC-VC(NbC)-WC/nano WC Hard Alloys

Cieto sakausējumu struktūru veidošanās uz polikarbīda TiC-VC(NbC)-WC/nano WC bāzes

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Abstract – The process of structure formation in the alloys of the system TiC-VC(NbC)-NiCr with the alloying additions of the fine or nano WC, depending on the chemical composition and sintering temperature using the optical microscopy, SEM and XRD analysis, is investigated in this paper. The core/rim structure alloys were found irrespective of the amount of tungsten carbide additions. The research suggests that the adding of nano WC causes decrease in carbide grains, redistribution of the elements in the core and rim, and decrease in sintering temperature by 50–100 °C.

Keywords – Alloying, core, hard alloys, inner rim, microstructure, nano additions, outer rim, titanium carbide, tungsten carbide.

I. INTRODUCTION

Tungsten carbide hard alloys are widely used as the instrumental material nowadays in metalworking, where they are sure to be the leaders thanks to their high cutting properties of hardness and wear resistance and as the structural material, in which their high static strength and heat resistance are realized.

During the first years of the application of tungsten carbide alloys, there arose the problem of replacing the expensive and scarce tungsten carbide by cheaper carbides, but the operation characteristics being not sufficient decreased. This resulted in the creation of new groups of hard alloys based on the system TiC-NiMo, TiC-NiCr, and Cr₃C₂-Ni; however, their strength was lower than that of tungsten-cobalt alloys [1]–[2].

Further investigations testified that the application of TiC alloyed by other carbides of transition metals is more effective; therefore, some grades of polycarbide-based TiC-VC, TiC-NbC, and TiC-VC-NbC alloys were created, and some of their grades have already been applied in industry [3]–[5]. The alloys of the TiC-VC- NiCr system sufficiently combine the availability of raw materials and the mechanical and operation properties. But WC is the best alloying carbide, which, being even in small amount, affects sufficiently the strength and viscosity of alloys [6]–[9]. The correlation between the grain size of the initial materials and the properties is known to be strong; therefore, the investigation of the effects of alloying carbides on the core/rim sizes of the structure and properties of alloys was of great interest. The

investigation of the effect of fine and nano alloying carbides WC on the properties of TiC-VC / (VC-NbC)-NiCr alloys is of special interest, as the cutting tools made of them have revealed high operation properties [10]–[12].

Taking into account that most of the mechanical and operation properties of hard alloys are structural-sensitive, the dependence of the microstructure on the amount of alloying fine and nano tungsten carbide and the sintering temperature as the principle technological factor of the effect on the structure formation of the TiC-VC/ (VC-NbC)-NiCr-based alloys, have been investigated in the paper.

II. MATERIALS AND METHODS

The TiC, VC, NbC, and WC carbides powder with the particle size of 1–2 μm and the binder metals containing the basic component of 99.8 % chromium and nickel were used for the investigation. The nano-powders of tungsten carbide were produced by the “Nanostructured and Amorphous Materials, Inc.” (Houston, USA).

Chemical composition of the initial materials is presented in Table I, and the chemical composition of nano WC certified by the producer is presented in Table II.

TABLE I
CHEMICAL COMPOSITION OF THE INITIAL MATERIALS

No.	Material	Chemical composition, % (weight)					Stoichiometric formula	Particle size
		Me	C _{total}	C _{free}	O	S		
1	Titanium carbide	79.8	19.5	0.27	0.31	<0.003	TiC _{0.96}	1–2 μm
2	Vanadium carbide	81.5	17.2	0.9	0.25	<0.003	VC _{0.88}	1–2 μm
3	Tungsten carbide	93.6	5.95	0.1	0.2	<0.003	WC _{0.97}	1–2 μm
4	Niobium	91.2	8.7	0.15	0.03	<0.003	NbC _{0.74}	1–2 μm
5	Nickel	99.8	0.03			<0.003		1–2 μm
6	Chromium	99.8	0.05			<0.003		1–2 μm
7	Tungsten nano-carbide	99.5	6.16	0.03	0.2	0.001		90–200 nm

The shape of nano WC particles is similar to spherical. The crystallographic lattice of nano WC is hexagonal; the specific density is 15.63 gr/cm^3 .

The alloys were obtained applying the common technology for manufacturing hard alloys, modified taking into account the peculiarities of the nano-powders application. The nano WC was added as the solution in the ethyl alcohol at the stage of alloy blending.

Alloys were sintered in a high-temperature furnace in vacuum $1.33 \times 10^{-2} \text{ Pa}$ at the temperature of $1300\text{--}1450^\circ\text{C}$.

TABLE II

CHEMICAL COMPOSITION OF NANO WC BEING CERTIFIED BY THE PRODUCER (NANOSTRUCTURED AND AMORPHOUS MATERIALS, INC., HOUSTON, USA)

Component	Content (% wt)	Component	Content (% wt)
C _{total}	6.16	K	0.005
C _{free}	0.03	Mn	0.0006
O	0.20	Mo	0.003
Al	0.0006	Na	0.0005
As	0.001	Ni	0.0006
Ca	0.0015	P	0.009
Co	0.0057	S	0.001
Cr	0.0065	Si	0.001
Cu	0.0006	Ti	0.001
Fe	0.01	V	0.0036

Previous investigations [13] have demonstrated that in all alloys, the content of metal binder was 13.5 Ni and 4.5 Cr (% wt).

Chemical composition of the investigated alloys is presented in Table III.

TABLE III

CHEMICAL COMPOSITION OF THE INVESTIGATED ALLOYS CARBIDE BASE

No.	Chemical composition (% wt)			
	TiC	VC	NbC	WC
1	72	5	–	5 nano
2	67	5	–	10 nano
3	62	5	–	15 nano
4	72	5	–	5
5	72	5	5	5
6	67	5	5	10
7	62	5	5	15

To carry out the investigations according to the described technology, a cylinder specimen of 8 mm in diameter and 8 mm in height and the specimens of $5 \times 5 \times 35 \text{ mm}$ were made.

The investigations of microstructure were carried out using the methods of XRD analysis, and optical and scanning electronic microscopy (SEM). The analysis of the alloys microstructure was performed according to the standard method of metallographic investigation of hard alloys. The microanalysis was performed using the optical microscope “Neofot-2” at a magnification of 100 and 2000, and the

scanning electronic microscope “Camsan 4DV” at a magnification of up to 5000.

Point analysis of the elements in phases and their linear distribution was performed using the semi-quantitative energy-dispersive microanalysis.

The XRD analysis was performed by using the diffractometer “DRON-4.0M” with the characteristic filtrated rays Fe K α . The diffractometer survey was taken according to the Bregg–Brentano scheme. To identify the phases, the database “Pearson’s Crystal Data” (structural characteristics of non-organic compounds) was used [14]. Specification of the structure parameters was performed according to the Rietveld method [15], which is based on the full-profile analysis without taking into account the integral intensity of the observed peaks taking advantage of the DBWS software [16].

III. RESULTS OF RESEARCH AND DISCUSSION

The investigations carried out testified that the core/rim structure of carbide grains is formed in all investigated alloys (Fig. 1). The core mostly consists of TiC, and the rim is a complex solid solution (Ti, V, Nb, W)C. It is known that the highest mechanical properties of the alloys correspond to the structural state when the thickness of the rim and core does not exceed $3 \mu\text{m}$ [17]. At larger core/rim sizes, the hardness and strength of alloys decrease.

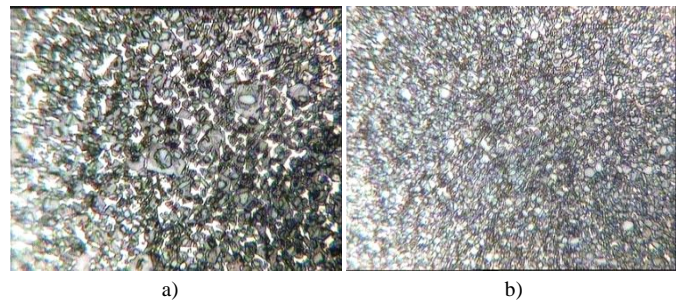


Fig. 1. Microstructure of alloys with additions of 5 % (wt) fine (a) and nano WC (b); sintering temperature – 1400°C .

The alloys with nano WC additions form a fine structure with the average grain $d = 0.76 \mu\text{m}$ already at the sintering temperature of 1350°C . At the same time, for the alloys with fine WC, the structure with the average grain $d = 1.2 \mu\text{m}$ was formed only at 1450°C (Fig. 2).

The adding of alloying additions WC causes the division of carbide rim into two parts: enriched (inner rim), and non-enriched (outer rim) of tungsten. Besides, the core/rim structure and the sizes of its sublayers (enriched and non-enriched by the tungsten) are changed.

In the structures of investigated alloys, the following structure components were found: binder (β), and three types of carbide grain: core (α) – inner rim (γ') – outer rim (γ); core (α) – rim (γ); homogeneous carbide grains (α') (Fig. 3).

The core is identified as the phase α containing typically the particles of the initial TiC being not changed under sintering. Besides titanium carbide, small amounts of V, Nb, Cr, and W are dissolved in it, which conform to the data of quantitative elements distribution in the structure components (Fig. 4).

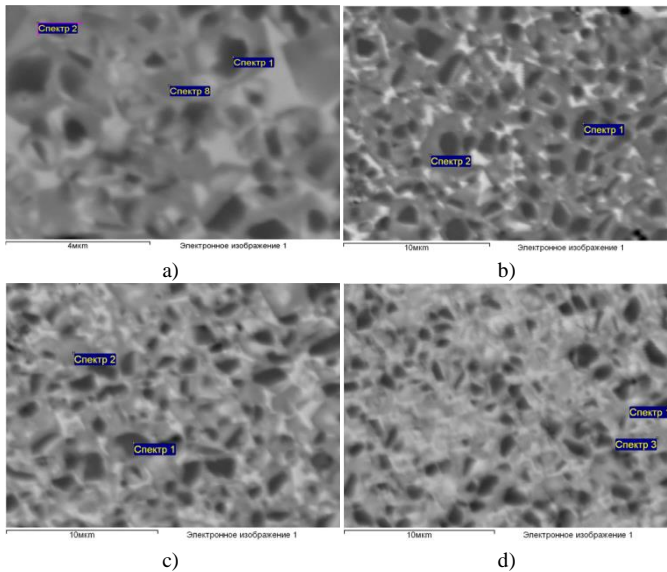


Fig. 2. Microstructure of alloys with additions of 5 % (wt) fine (a) and 5 % (b), 10 % (c), 15 % (d) (wt) nano WC; sintering temperatures – 1450 °C (a) and 1350 °C (b, c, d).

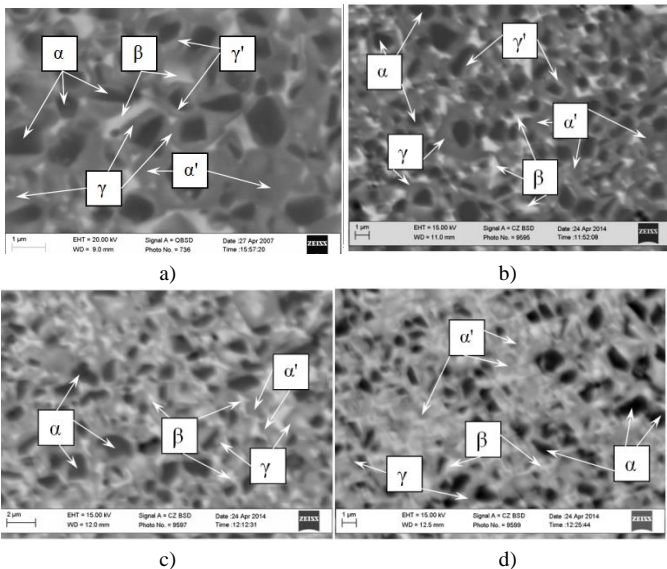


Fig. 3. Microstructure of alloys with additions of 5 % (wt) fine (a) and 5 % (b), 10 % (c), 15 % (d) (wt) nano WC with typical elements of structure: core (α), inner rim (γ'), outer rim (γ), homogeneous carbide grains (α'), and binder (β).

The inner rim γ' is a solid solution of the TiC-based metal alloying carbides and the binder metal – nickel and chromium. The inner rim is saturated by the tungsten and is like the barrier for the diffusion processes. But in the alloys with the 10 and 15 % wt of nano WC, the inner rim is not available or almost not noticed.

The outer rim γ (or the rim for the alloys with 10 and 15 % wt of nano WC) is a TiC-based solid solution with a smaller amount of alloying carbide metals, W in particular, which contains Ni and Cr as well.

The homogeneous carbide grains α' are of sufficiently smaller sizes (0.1–0.3 μm) and of the highest titanium content at a small amount of the binder metal.

The binder β is identified as the nickel-based solid solution of titanium, vanadium, niobium, tungsten, and chromium.

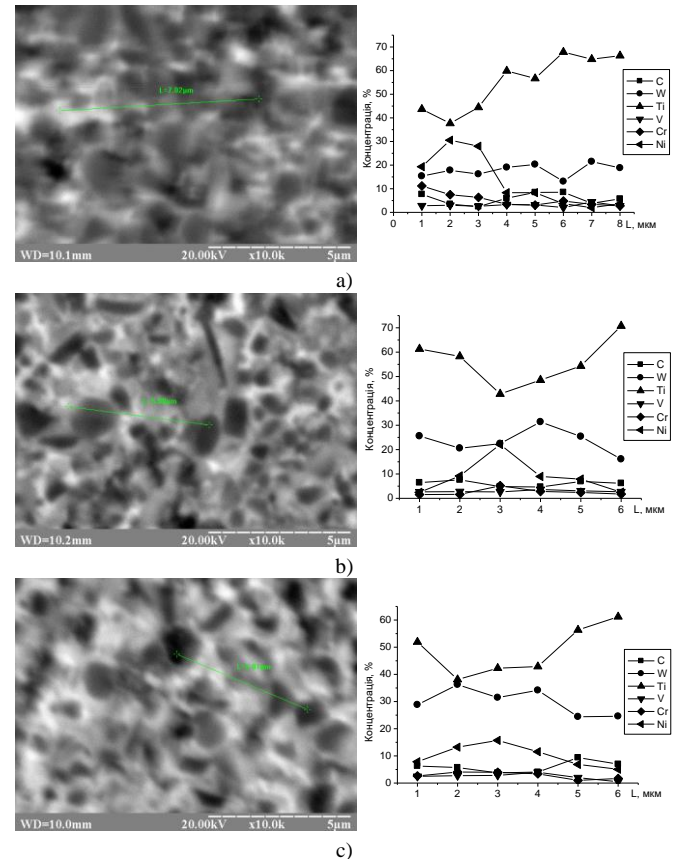


Fig. 4. Microstructure and elements distribution along the line of alloys with additions of 5 % (a), 10 % (b), and 15 % (c) (wt) nano WC; sintering temperature – 1300 °C.

Using the semi-quantitative energy-dispersive microanalysis, the chemical composition of the alloys structure elements was found: the core (Fig. 5) (spectrum 1 in Fig. 2), rims (Fig. 6) (spectrums 2, 3, and 8 in Fig. 2), and the binder (Fig. 7).

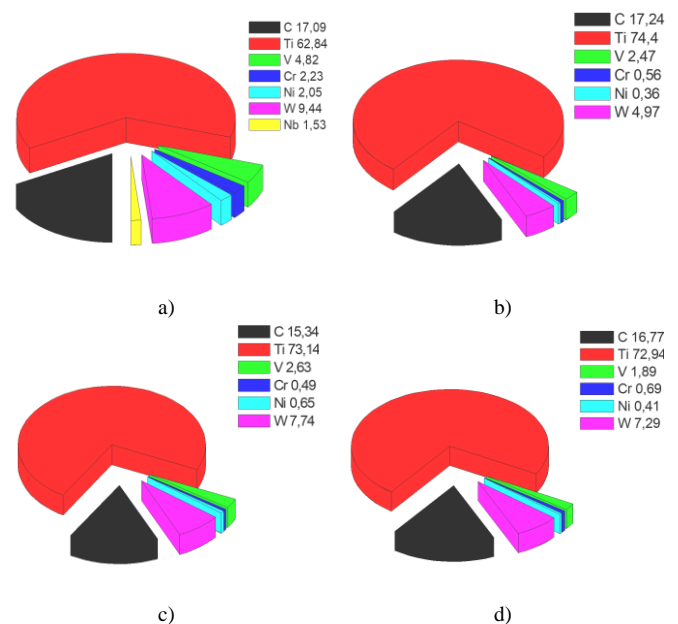


Fig. 5. Chemical composition in the spectrum 1 of the core being alloyed by the 5 % (wt) fine WC (a), 5 % (b), 10 % (c), and 15 % (d) (wt) nano WC; sintering temperature – 1350 °C.

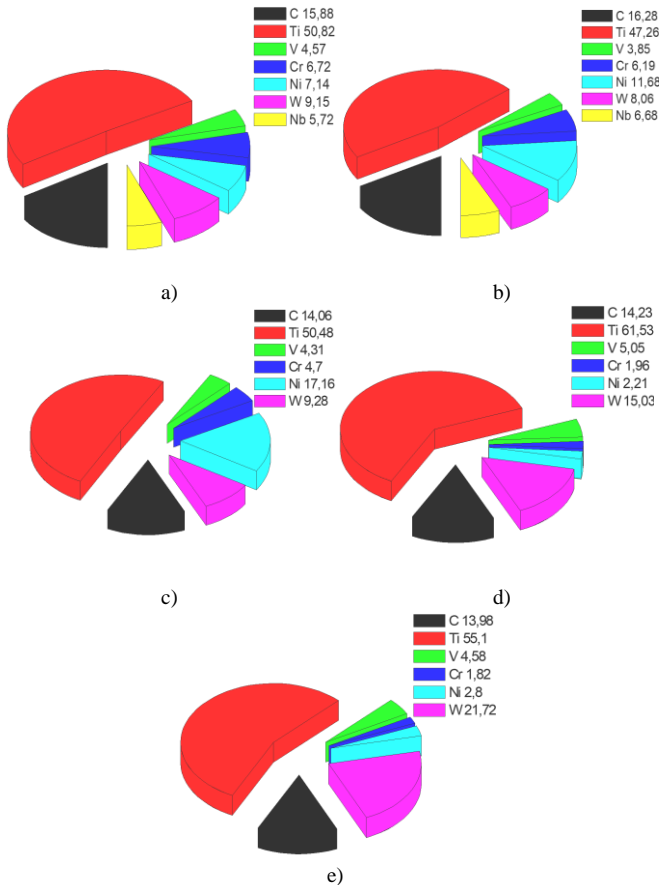


Fig. 6. Chemical composition in the spectrums 2, 3, and 8 of the outer rim (a) and inner rim (b) being alloyed by 5 % (wt) fine WC, and the rim being alloyed by 5 % (c), 10 % (d), and 15 % (e) (wt) nano WC; sintering temperature – 1350 °C.

Despite the available inner rim in the alloys alloyed by the 5 % nano WC (wt), we failed to determine its chemical composition, as the distribution ability of the microscope was bigger than the size of its rim.

When the amount of nano WC is increased, the percentage of W in the core increases from 4.97 to 7.74 % (wt), Ti being decreased from 74.4 to 72.94 % (wt). In the rim, the percentage of W increases from 9.28 to 21.72 and Cr decreases from 4.7 to 1.82 % (wt).

The results of the semi-quantitative energy-dispersive microanalysis showed that the data on the element distribution testified that the content of tungsten on the outer rim of the solid solution rim is equal to 6.65 % (wt), and on the inner rim, adjusting to the carbide core, Ti is 17.85 % (wt).

The adding of the WC alloying additions causes some balance of the tungsten concentration in the complex solid solution of carbides and an increased homogeneity within both the rim and the core.

Thus, it is shown that the adding of the WC alloying additions in the amount of 10 % (wt) and more increases the balance of the tungsten concentration in the rim of the complex solid solution of carbides.

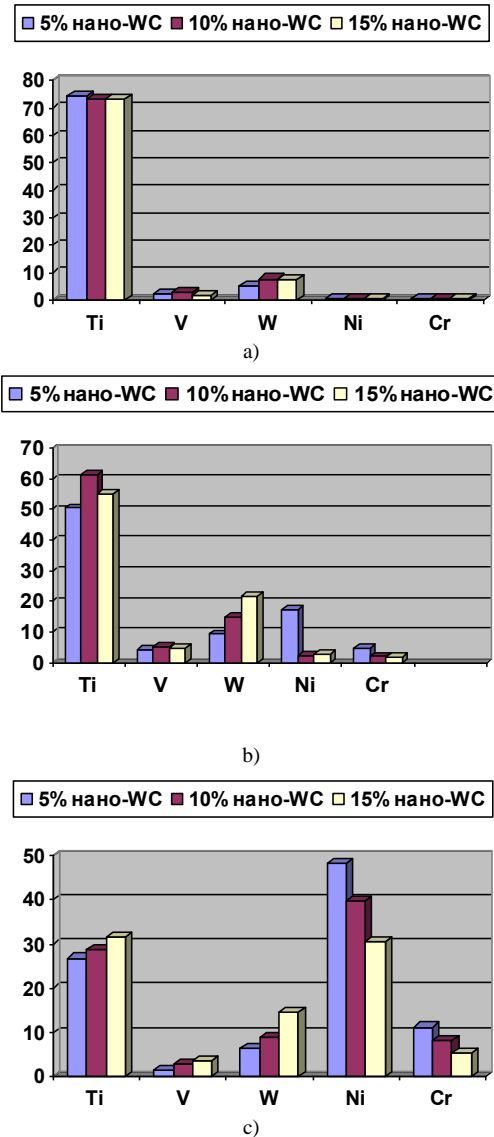
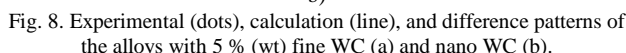


Fig. 7. Chemical composition of the alloys structural components being alloyed by nano WC: a – core; b – rim; c – binder; sintering temperature – 1350 °C.

Using the XRD analysis (Fig. 8), the main phases of the investigated alloys were determined: in the alloys being alloyed by nano WC, irrespective of its content and sintering temperature, the main phases are the solid solution (Ti, V, Nb, and W) C, $\text{Ni}_{0.75}\text{Cr}_{0.25}$ and Cr with the cubic structures of NaCl, Cu and W (the Pearson symbol c12; space group $Im-3m$), correspondingly, and in the alloys being alloyed by the fine WC – (Ti, V, Nb, and W) C, $\text{Ni}_{0.5}\text{Cr}_{0.5}$, Cr and the tracks of Cr_3C_2 and Cr_{23}C_6 . It should be noted that the composition of the phase (Ni, Cr) in this specimen is described by the formula $\text{Ni}_{0.5}\text{Cr}_{0.5}$, which is testified by the lattice parameters ($a = 0.36012(6)$ nm), which differ greatly from the parameter of the phase unit cell $\text{Ni}_{0.75}\text{Cr}_{0.25}$ ($a = 0.35807(9)$ – $0.35632(5)$ nm).

The increase of the W dissolution in the TiC phase testifier well the change of the unit cell. In the solution with 5 % nano WC (wt), the lattice parameter equals $a = 0.43148(7)$ nm.



IV. CONCLUSION

The change in sintering temperature from 1300 °C to 1450 °C results in the formation of the fine structure of alloys at 1350 °C for the alloys with the nano WC, and at 1450 °C for the alloys being alloyed by the fine WC. The decrease in sintering temperature by 50–100 °C allows decreasing the power expenditures of the manufacturing process.

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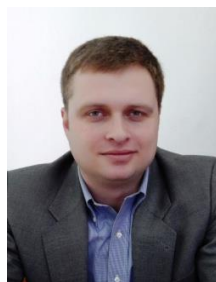
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Cieto sakausējumu struktūru veidošanās uz polikarbīda TiC-VC(NbC)-WC/nano WC bāzes

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Tika pētīts struktūru veidošanas process sakausējumos TiC-VC(NbC)-NiCr ar smalku vai nano WC sakausējuma papildinājumiem atkarībā no ķīmiskā sastāva un saķepināšanas temperatūras, izmantojot optisko mikroskopiju, SEM un XRD analīzi. Centru/aptvērumu struktūras sakausējumi tika konstatēti neatkarīgi no volframa karbīda piedevu daudzuma. Pētījums liecina, ka nano WC pievienošana samazina karbīda graudus, elementu pārdali centros un aptvērumos, kā arī notiek saķepināšanās temperatūras samazināšanās par 50–100° C.

Atslēgas vārdi – Sakausējums, centri, cietie sakausējumi, iekšējais aptvērums, mikrostruktūra, nano papildinājumi, ārējais aptvērums, titāna karbīds, volframa karbīds.