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# Doping of WC-Co Hard metal with Vanadium Carbide

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## ABSTRACT

*The urgent problem of the JSC Almalyk MMC is the need to increase the wear resistance of products made from hard alloys, which is caused by low wear resistance of tools made from them. The analysis of the causes revealed the probable causes of this lag: - the structure of the alloy or its components; - undesirable impurities in the alloy or components; - possible alloying of imported analogues. It is shown that when doping a hard alloy with vanadium, an increased wear resistance of the alloy is achieved. From the series of diffractograms and images on an electron microscope, it follows that the addition of vanadium carbide - 1% by mass, reduces and stabilizes the grain size of the alloy: nanostructuring is observed. The wear resistance and hardness of samples of WC-Co and WC-VC-Co systems were measured. Images of electron microscopy of their surfaces are made, X-ray diffraction data of these samples are studied.*

**Keywords:** *Hardmetals, Vanadium Carbide, Tungsten Carbide, Cobalt, Wear Resistance, Hardness.*

## INTRODUCTION

One of the points of application of tungsten metallurgy is the production of hard metals (HM). As a matrix for retaining grains of tungsten carbide, a "bundle" of cobalt (it does not form carbides and does not destroy them), nickel, Ni-Mo alloy [1] is used in the composite material. Sintered HM is produced by the powder metallurgy method, the products are amenable to processing.

Molded HM are designed for surfacing the tool [2]. Powder HMs is distinguished by the metals of carbides. Plates of them have high hardness and wear resistance.

The actual problem of the main non-ferrous metals manufacturer in the republic - NPO Almalyk GMK JSC, was the need to increase the wear resistance of products from the combine, in particular, the VK-6 alloy. The fact is that tools from it, including those installed in drilling equipment, have recently shown a relative "lag" in quality from imported analogs.

Analysis of the reasons revealed possible versions of this situation:

- Non-optimized structure of the alloy or its components [3];
- Undesirable impurities in the raw material for the formation of alloy components;
- Possible additional alloying of imported analogues.

Proceeding from the foregoing, the goal of the research was to find ways to increase the wear resistance of the hard alloy of the WC-Co system. Proceeding from the goal, the objectives of the study were: the selection of the ligature, which increases the wear of the HM VK-6, the manufacture of the wear test; the hardness of alloyed samples; their physical-chemical research.

With the same content of cobalt, the physico-mechanical and cutting properties are largely determined by the grain size of the tungsten carbide phase. Technological methods allow obtaining alloys with an average grain size of carbides - from a fraction of μm to 15 μm. Attempts are known for alloying hard metals. One of the goals is to regulate the grain size that affects its wear resistance.

And the grain size depends on the presence of "grain growth inhibitors". These include carbides of tantalum, chromium and vanadium. Of particular interest are publications on the evaluation of the efficiency of alloying WC-Co alloys with vanadium carbide. The approach is not new. Initially, the use of VC was justified by preventing the growth of grains. VC is used as a substitute for WC. This is the approach in creating a new type of hard metals.

**Table1.** *Nomenclature of a number of sintered hard VK alloys*

| Trade mark | WC % | Co, % | Bending strength, MPa | Hardness, HRA | Density, g / cm$^3$ | Thermal Conductivity, W / (m□°C) | Young's modulus, Gpa |
|---|---|---|---|---|---|---|---|
| VK4 | 96 | 4 | 1500 | 89.5 | 14.9-15.2 | 50.3 | 637.5 |
| VK6 | 94 | 6 | 1550 | 88.5 | 15 | 62.8 | 633 |
| VK8 | 92 | 8 | 1700 | 87.5 | 14.8 | 50.2 | 598 |

**Table2.** *Wear resistance test for WC-Co and WC-VC-Co samples (No. 1 - without V, No. 2-with V) - 2 kg load, abrasive contact time 90 min*

| Indicator of samples | Ex. Mass | After the test | Weight loss, g |
|---|---|---|---|
| **Small samples** | | | |
| No. 1 - without V | 21.6930 | 21.5211 | 0.1719 |
| No. 2 – with V | 19.2564 | 19.1133 | 0.1431 |
| The difference in mass loss, g | | | 0.0288 |
| Difference in wear, % | (0.0288/0.1719)·100 | | 16.75% |
| **Large samples** | | | |
| No. 1 - without V | 41.0316 | 40.9484 | 0.0883 |
| No. 2 – with V | 34.5264 | 34.4642 | 0.0622 |
| The difference in mass loss, g | | | 0.0261 |
| Difference in wear, % | (0.0261/0.0883)·100 | | 29.56% |

The technology of grinding has been optimized and evaluated for the new WC- "WC-12 wt. % Co" type with 10 VC-Co alloy. Reduced grain size (W, V, Co) C in the sintered material to a critical value inhibits the initiation of grain growth. The influence of alloying of solid alloys of the % of the mass of VC obtained by plasma-spark sintering (SPS) on sliding friction and wear was compared with the alloy without 10% vanadium carbide at 1100- 1130 ° C. A significant improvement in the wear resistance of the alloy WC-12 wt.% Co-10 wt.% VC was found, compared to the alloy 12 wt.% Co [4]. It is shown that dense SPS samples obtained at a temperature of 1200 $^{o}$C (5 min, 40 MPa) with VC additive reduce the growth of WC grains in SPS. In addition, the WC grain size decreased from 540 to 380 nm, hardness increased from 1828 to 1902 HV [5].

Alloys WC-VC-Co, starting with $V_8C_7$, WC, and Co powders, have been developed. After sintering, the alloys consist of WC, (W, V) C and Co phases, with an average carbide grain size of 1-2 nm. They exhibit hardness equal to or higher than that of WC-Co hard alloys, with equal cobalt content [6]. The sinterability of W-V-C-Co alloys was better, and the hardness was higher than the hardness of WC-Co alloys with equal cobalt content. The strength of W is found to be higher than that of WC-Co alloys of the same hardness [7]. It is shown that WC-Co-VC coatings obtained from optimized powders have a higher abrasion resistance than WC-Co coatings [8]. It was found that the mechanical properties of composites strongly depend on the uniformity of the phase distribution of the tungsten matrix and the reinforcing nano-granular component [9]. The nanocomposite WC-10Co powder is obtained. Its properties, such as nanohardness, are studied. Vickers hardness was found to be 28.3-78.3 GPa, which is higher than for pure WC-10 Co alloy [10].

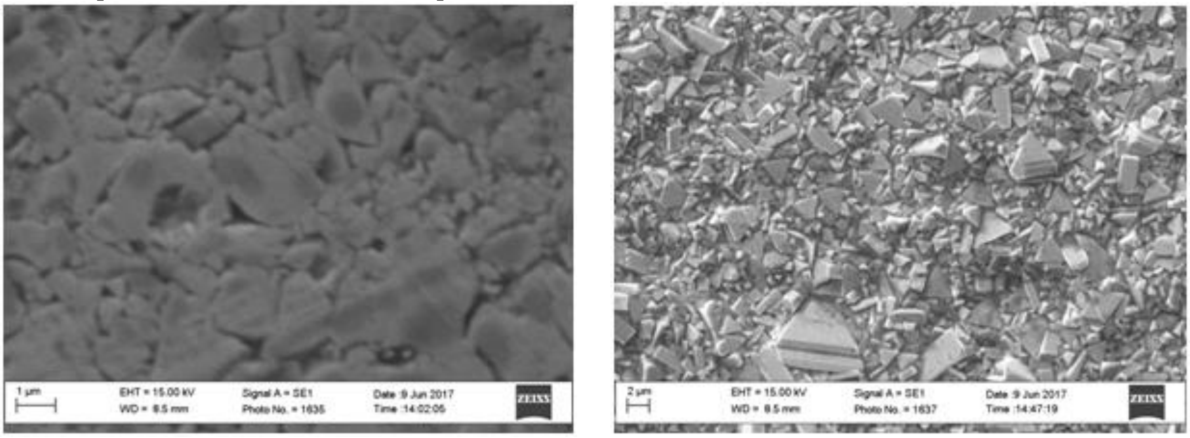

**Fig1.** *Electron microscopy of samples No. 1 - without V (left) and No. 2 - with V (right).*

**Table3.** *Probe element analysis of sample No. 2*

| Element | Line's type | concentration | Relative k | Wt.% | Sigma Wt.% | Etalon name | Etalon preinstalled |
|---|---|---|---|---|---|---|---|
| C | K series | 0.05 | 0.00047 | 9.85 | 0.33 | C Vit | Yes |
| O | K series | 0.11 | 0.00037 | 6.67 | 0.23 | SiO2 | Yes |
| Al | K series | 0.05 | 0.00034 | 2.10 | 0.07 | Al2O3 | Yes |
| V | K series | 0.00 | 0.00003 | 0.18 | 0.11 | V | Yes |
| Co | K series | 0.15 | 0.00145 | 7.83 | 0.28 | Co | Yes |
| W | M series | 1.09 | 0.01091 | 73.37 | 0.42 | W | Yes |
| **Total** | | | | 100.00 | | | |

## Materials and Methods

The object of research is a WC-Co system of alloy, components and raw materials for its production, as well as vanadium dope. Almalyk GMK JSC produces a number of hard alloys of the tungsten group (Table 1). Scheme of the process is the following 1) obtaining powders of carbides and Co by reduction from oxides; 2) grinding powders of carbides and cobalt (made on ball mills for 2-3 days) to 1-2 microns; 3) screening and re-grinding if necessary; 4) preparation of the mixture (the powders are mixed in amounts corresponding to the chemical composition of the alloy produced); 5) cold pressing (organic glue is added to the mixture for temporary preservation of the mold); 6) sintering under load (hot pressing) at 1400 ° C (at 800-850 ° C the glue burns without residue); at 1400 ° C, Co melts and wets the carbide powders, upon subsequent cooling Co crystallizes, connecting carbide particles.

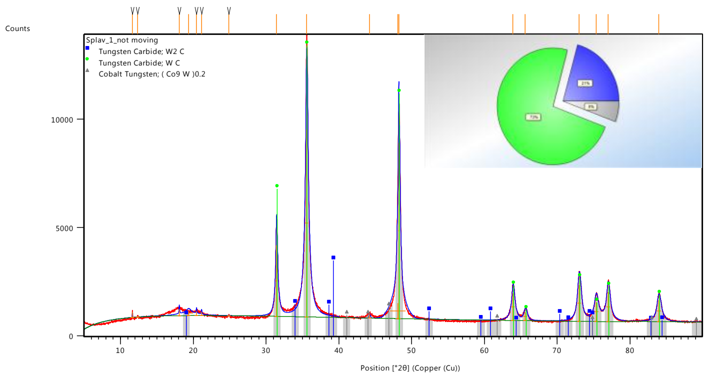


**Fig2.** *Diffractogram of sample No. 1 (without vanadium)*

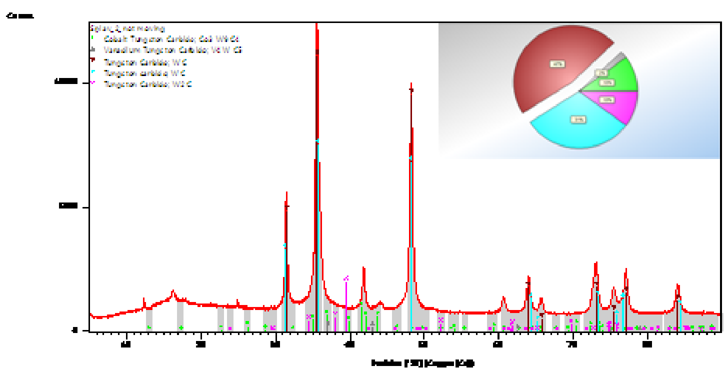

**Fig3.** *Diffractogram sample No. 2 (ligature - 1% of mass VC).*

The hardness and wear resistance of WC-Co and WC-VC-Co materials was evaluated. Testing of the samples for wear resistance was carried out on the installation made in the Academy of sciences of Uzbekistan. Measurements of their hardness by Rockwell HRA method were performed in the workshop of NPO Almalyk MMC; X-ray phase control - on an X-ray diffractometer EMPYREAN XDR with measurements "on the lumen" and with an element analysis probe by X-ray fluorescence.

## Results and Discussion

Vanadium carbide is used as a partial substitute for tungsten carbide in VK-6 alloy of Almalyk Mining and Metallurgy Company, where preparatory operations were performed: - 4 samples were produced: 2 - serial, 2 - serial doped with 1% VC; - a test rig for the wear resistance of samples was made; - comparative testing of the samples for wear on this installation was carried out. As a result, it has been found out that doping with 1% vanadium carbide (VC) of the existing VK-6 alloy increases the wear resistance in the first cycle by 16.75%; in the second - by 29.56% (Table 2).

The hardness tests of samples of VK-6 hard alloys (not doped and doped with V) on Rockwell have been performed. It was found that for unalloyed samples, HRA = 88.5; vanadium alloyed samples - HRA = 88.7, that is, the introduction of 1% VC slightly increases the hardness of the alloy. From the series of diffractograms and surface images of VK-6 alloy samples (not alloyed with vanadium) (No. 1) and doped with vanadium (No. 2), it follows that the addition of vanadium carbide - 1% by weight. Reduces and stabilizes the grain size of the alloy - nano-structuring of samples No. 2 is observed, which leads to an increase in wear resistance and hardness. They were slightly higher than the usual micro-sized (approximately 500 μm) WC-Co alloy with the same cobalt content. It is characteristic that the density of the WC-VC-Co formed material is somewhat lower than the WC-Co material with the same cobalt content. The density of VC, WC 5.57 and 15.6·$cm^{-3}$, the microhardness of the $V_8C_7$ and WC phases is 2900 and 2000 HV (Vickers), respectively. The density of new grades (W, V) C of alloys: 11-12 g·$cm^{-3}$. This gives a significant reduction in wear in application. Viscosity (Pulquist strength) of fine WC-VC-Co alloys is equal to or higher than the same index for WC-Co alloys with an equal Co fraction and higher than the viscosity of the ultra-fine WC-Co grades of equal hardness. WC-VC-Co alloys from standard WC and $V_8C_7$ powders up to 1 μm in size can reach the hardness level typical for WC-Co alloys with an equal Co content, but formed from expensive ultrafine powders [11]. Vanadium is predominantly in the form of $V_8C_7$ [12].

## CONCLUSIONS

Common methods for modifying hard metals are the structuring of components and micro alloying. In particular, alloys with a smaller carbide phase are more wear-resistant. Of the alloying additives, vanadium carbide is the most common: from 1 to 12% of the mass of the alloy. A study was performed to inhibit the growth of grain VK-6 1% vanadium carbide. It is shown that an increased wear resistance and a stable high hardness of the alloy are achieved. From the series of diffract grams and images on an electron microscope, it follows that the addition of vanadium carbide - 1% by mass, reduces and stabilizes the grain size of the alloy: nanostructuring is observed. It is proposed to continue the investigation by expanding the range of hard alloy concentrations with vanadium.

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