A New the Chnology for Producing Carbide Alloys With Gradient Structure

T N Oskolkova
Russia, Novokuznetsk, ul. Kirova,42, tel. (3843)74-87-63

E-mail: oskolkova@kuz.ru

Abstract. A carbide alloy with gradient structure consisting of viscous core of WC10KS alloy and more wear-resistant surface of alloy WC6-OM has been obtained by means of electrodischarge hardening by alloying. The core of this alloy can bear considerable shock loads, and its surface serves as wear-resistant cutting tools.

Introduction
WC–Co alloys are the strongest of available sintered carbide alloys but they do not always meet service durability standards. In the bulk of depreciated tools wearing and failures of carbide parts make up 80%. In this regard one of the promising trends in the development of carbide alloys is inventing technologies which provide higher wear resistance without reducing viscosity. Possible ways of development in this sphere are modifying carbide alloy surface with carbides, borides and the like, as well as treatment of the surface with concentrated energy flows [1-6]. In Russia WC–Co carbide alloy plates with TiC and TiN ion-plasma coating are produced. There are some other ways to increase durability of carbide alloy tools alongside with coatings. A method of producing carbide alloy plates by means of sintering with gradient strength is among them.

Results and discussion
The Institute of Ultra-Hard Materials of the National Academy of Sciences of Ukraine worked out a method of producing an alloy with variable content of cobalt heightwise a plate by means of impregnation of a sintered carbide alloy. This alloy is to be employed in mining machines. The possibility of obtaining gradient strength through a carbide alloy from viscous core to wear resistant surface is theoretically grounded. Thereby it is possible to alter the content of tungsten and cobalt in the alloy 8cm heightwise from 80% and 20% (WC20) to 98% and 2% (WC2) correspondently. As a result, wear resistance of the working part of the plates is as high as that of WC2 and the core can bear considerable bending stress.

Similar research took place in Russia. There is a method of obtaining carbide alloy with variable content of bonding, in which the content of tungsten and cobalt is changed from the surface to the core in the process of pressing plates: WC3 – WC6 – WC10 – WC15. As a technical solution, it was necessary to find the way of producing laminated gradient plates with viscous core and harder surface in order to provide their wear resistance to different materials. The solution is the following: compression of refractory powders and cobalt, preliminary sintering, surface alloying, final sintering. The preliminary sintering is carried out at the temperature of 830 - 900°C. For surface alloying, carbide alloy powder with low cobalt content is impregnated in the mixture of spirit and glycerin in the ratio 2:1 in
ultrasonic field during 4 – 8 minutes. Ultrasonic field allows balancing particles in the suspension, making them movable, introducing disperse component into carbide alloy pores.

Thus, the gradient plate consists of a viscous core, which serves as a damper and buffers shock loads, but it can lack wear resistance. It is the transition section (plate surface – coating) that provides the properties which correspond to a certain application of a plate. The transition section must possess the most efficient ratio of wear resistance, hardness and viscosity, its thickness being not less than 300 mkm, because the effective wearing of the transition section takes place in this range. Manufacturing a gradient plate of carbide alloy can serve as an example. A plate of WC20 alloy was previously sintered at 850°C and then it was impregnated in the mixture of spirit and glycerin in the ratio 2:1 which contained particles of carbide alloy WC3M (with concentration 40%). The impregnation was carried out in an ultrasonic bath during 5 minutes. After that, the plate was sintered again at the temperature of 1380 °C in hydrogen medium. Then its surface was covered with multilayer coating of gas-vapour phase. As a result, we obtained a gradient plate which had a core made of WC20, a transition section not less than 250 mkm thick composed of a mixture of large grains of WC20 and grains WC3M and an even layer of finely-grained alloy WC3M 150 mkm thick. Cobalt concentration was variable across the layer and changed from 6% at the surface to 20% at the core of the plate.

But this method has some drawbacks: the technology of manufacturing a multilayer carbide alloy with gradient structure is rather complicated, long, energy consuming and requires advanced equipment. A multilayer carbide alloy can be obtained only on a flat surface. Filling a press mould by several feeders is difficult to proportion, which in practice prevents obtaining a plate with optimal combination of useful properties.

Nevertheless, there is a theoretical possibility to obtain gradient strength of carbide plates from viscous core to wear resistant surface by means of electrodischarge hardening by alloying. Until now depending on the alloying electrode material coating by means of electrodischarge hardening by alloying has been applied to increase several-fold resistance to wearing of metal-cutting, bench-work, medical tools, cold metal treatment dies, as well as to improve anti-frictional properties of wear surfaces, increase heat and corrosion resistance of metal parts, change conducting characteristics of contact elements. In other words, working characteristics of parts made of the most widely spread structural and tool steels were improved by means of covering the surface with a thin layer of coating with the help of electrodischarge hardening by alloying.

It is useful to study ways of electrodischarge hardening by alloying of carbide alloy WC10KS surfaces in order to reinforce and restore them after use. Such application has not been described before.

Depending on technological purpose different coatings can be applied onto a surface:

a) blanket coating, b) mixed coating consisting of different materials, c) discrete coatings consisting of micro sections.

Within this research, a low-cobalt coating on the surface of high-cobalt carbide alloy WC10KS was formed by means of electrodischarge hardening by alloying. Carbide alloy WC6-OM was used as an alloying element. As a result, less strong core of the part can bear considerable shock loads and bending stresses and the harder surface has high wear resistance, which provides great durability of carbide alloy WC10KS.

Advantages of electrodischarge hardening by alloying consist in
1) availability of complex micrometallurgical processes;
2) extremely strong adherence of the applied coating layer with the surface;
3) simplicity of the process;
4) eliminating of contraction of the part being treated;
5) small size and low energy consumption of the equipment.

The essence of electrodischarge hardening by alloying is as the following: a spark discharge causes anode (electrode) erosion and the products of the erosion are transferred to the cathode (the part). In this process, the part is being covered with a layer with transformed composition and structure which depend on an electrode material the electrical mode of the equipment. High discharge temperature (5000 – 10000 °C), short action (10^{-4}…10^{-3} seconds), instant cooling of the heated areas bring us to
the conclusion that ultrafast temperrering takes place after electrodischarge hardening by alloying. Alongside with this process there is a contact or drop transfer of alloying elements from the hardening electrode onto the treated surface when they osculate and further diffusion spreading of these elements through the coating.

The work principle of the device for application of coatings is based on alternating discharges of charge-storage capacitors when a vibrating electrode touches the surface of the treated part during its reciprocating motion. Spark discharge of charge-storage capacitors cause electrode erosion, transfer diffusion of the electrode material into the surface layer of the treated part.

Surface hardening of carbide alloy WC10KS by means of electrodischarge hardening by alloying was performed with the help of portable device UR – 121 produced by Open stock company “Kontsern Podolsk”. Treatment of the carbide alloy by an alloying electrode WC6-OM was carried out in two modes:

Mode 1 – 2 minutes per 1 cm$^2$ with electrode vibration frequency 100Hz, + 1 minute per 1cm$^2$ with electrode vibration frequency, set automatically by a magnetic system in the range from 140 to 500Hz;

Mode 2 – 1 minute per 1cm$^2$ with electrode vibration frequency, set automatically by a magnetic system in the range from 140 to 500Hz.

Alloy WC6-OM which consists of 91.9 WC + 6 % Co + 2 % TaC + 0.1 % VC has constant strength, doping agents VC and TaC help to obtaining small-grain structure by preventing growth of WC-phase grains. At the same time WC6-OM alloy wear resistance is as high as that of the most wear resistant alloy of WC–Co (B 253) group, but its strength is higher.

The technique of obtaining coating on a carbide alloy surface is the following: the surface of a carbide plate is treated with spirit to remove thoroughly all traces of oil and grease before electrodischarge hardening by alloying. After that, a graphite layer is applied onto the deoiled surface in order to prevent decarbonisation and as a consequence embrittling $\eta_1$- phase of double tungsten and cobalt carbide which is inadmissible for carbide alloy structure.

To study special characteristics of the alloy structure after the treatment and to determine the depth of the hardened surface zone optical microscope OLIMPUS – GX 50 and scanning electronic microscope «Philips SEM 515» were used.

Fig 1 shows microstructure of WC10KS alloy with hardened layers of WC6-OM after electrodischarge treatment at different modes. Badly etching layers of different thickness (5 … 25 mkm) can be seen on the surface.

Scanning electronic microscopy proves gradient structure on WC10KS alloy: increased content of tungsten and reduced content of cobalt in the surface layer (Fig. 2).
Figure 1. Microstructure of WC10KS alloy with WC6-OM coating applied at different modes, x 1000

X-ray research showed that treatment of carbide alloy surface by means of electrode discharge hardening by alloying causes changes in its phase composition (Fig. 3).

Alongside with tungsten monocarbide WC and cobalt bonding which are found in the original carbide alloy, ditungsten monocarbide W₂C and carbide WC₁₋ₓ are formed in the surface layers of the parts treated at two modes. It is known that ditungsten monocarbide W₂C has greater hardness than that of WC (Fig. 3).

Figure 2. Microstructure of WC10KS alloy with WC6-OM coating at X-rays: cobalt (a); tungsten (b) x 1000
Changes in phase composition of the surface layer of the carbide alloy influenced nanohardness indices. Nanoindentation of the carbide alloy results in increasing nanohardness up to 22000 MPa (Fig. 4).

Wear resistance tests were carried out on «PC-Operated High Temperature Tribometer» at the room temperature. A degree of wearing was determined by means of measuring the depth and the area of the track made by an unmoving diamond indenter on a rotating sample under the load of 3H, with rotating speed 4000, linear speed 2.5 cm/s. For comparison similar tests were carried out with original parts.
Wearing of samples with WC6-OM coating after electrodischarge treatment showed that the track depth on the coated sample is 10.8 mkm while the original sample had the track of 58 mkm. Track section area of wear out samples is 941 mkm$^2$ and 12921 mkm$^2$ correspondently. Friction coefficient ($\mu$) of WC10KS alloy with WC6-OM coating applied by electrodischarge treatment is 0.23 which differs from the original sample for which $\mu = 0.41$.

As far as electrodischarge hardening by alloying always leads to increasing roughness of a surface it is important to study microgeometry of the surface after hardening of WC10KS. The results of the study are shown in the table in Fig. 6. In this research the microgeometry if the carbide alloy surface after treatment was determined by profilometry method at «Micro Measure 3D station». Hardening of the carbide alloy surface increases roughness of the surface but it remains within technical specifications with allowed surface finish characteristics $R_a = 2.5$ mkm.

| Treatment                  | Roughness $R_a$, mkm |
|----------------------------|-----------------------|
| Original sample            | 1.32                  |
| After surface hardening    | 2.15                  |

Electrodischarge hardening by alloying for application of coating on carbide alloy surface by proper electrodes allows producing carbide plates with gradient structure, e.g. WK3 – WK6 – WK8 – WK10 – WK15 – WK20. It is also possible to restore surfaces of different carbide alloys after use. It will increase service life of tools consisting of such alloys and save expensive materials (tungsten, cobalt). Thus developing tungsten carbide alloys with gradient structure can be considered as a new stage in carbide alloy production.
Conclusion
A carbide alloy with gradient structure consisting of viscous core made of WC10KS alloy and more wear resistant surface made of WC6-OM alloy is produced by means of electrodischarge hardening by alloying. Increasing wear resistance is caused by ditungsten monocarbide W₂C, which improves working characteristics of inserts made of carbide alloy based on tungsten monocarbide WC.

This research was carried out within a state order by Ministry of Education and Science of the Russian Federation № 11.153.2014/K

References
[1] Nozdrin I V Particle size of vanadium and chromium borides and carbides in a plasma flux / I V Nozdrin G V Galevskii L S Shiryaeva M A Terenteva Steel in Translation 2011 T 41 № 10 p 799-804
[2] Nozdrin I V Reactor for plasmometallurgical production of refractory borides and carbides / I V Nozdrin L S Shiryaeva G V Galevskii V V Rudneva Steel in Translation 2011 T 41 № 8 p 644-648
[3] Nozdrin I V Plasma synthesis and physicochemical certification of chromium nanocarbide / I V Nozdrin V V Rudneva Steel in Translation Vol 53 № 12 2012 p 797-801
[4] Oskolkova T N Pulse plasma treatment of the surface of alloy VK10KS / T N Oskolkova E A Budovskikh Metal Science and Heat Treatment 2012 vol 53 № 11–12 p 608 – 610
[5] Oskolkova T N Electric explosion alloying of the surface of hard alloy VK10KS with titanium and silicon carbide / T N Oskolkova E A Budovskikh Metal Science and Heat Treatment 2013 vol 55 № 1 p 96 – 99
[6] Oskolkova T N Features of structure formation of the surface layer in the course of electroexplosive alloying tungsten carbide hard alloy / T N Oskolkova E A Budovskikh V F Goryushkin Non-Ferrous Metals 2014 vol 55 № 2 p 196 – 200