



VANADIUM CARBIDE COATINGS: DEPOSITION PROCESS AND PROPERTIES

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Summary

Vanadium carbide coatings on carbon and alloyed steels were produced by the method of diffusion saturation from the borax melt. Thickness of the vanadium carbide layer was 5-15 μm , depending upon the steel grade and diffusion saturation parameters. Microhardness was 20000-28000 MPa and wear resistance of the coatings under conditions of end face friction without lubrication against a mating body of WC-2Co was 15-20 times as high as that of boride coatings. Vanadium carbide coatings can operate in air at a temperature of up to 400 °C. They improve fatigue strength of carbon steels and decrease the rate of corrosion in sea and fresh water and in acid solutions. The use of vanadium carbide coatings for hardening of various types of tools, including cutting tools, allows their service life to be extended by a factor of 3 to 30.

Key words:

Vanadium carbide, coatings, borax melt, wear resistance, cutting and forming tools

1. Introduction

Formation of carbide coatings on surfaces of carbon-containing steel parts by the no-electrolysis method from the salt melts is a promising technology for thermochemical treatment. Carbide coatings of this type are characterized by high wear, corrosion and erosion resistance. The technology is environmentally clean. Its basic operations, such as immersing workpieces into the borax melt containing a carbide-forming element, holding at preset temperatures and during a preset time, cooling and washing off the remaining borax in hot water, are simple to perform. Advantages of the technology are that the materials and thermal equipment used are inexpensive and readily available, as well as

that it is possible to combine oxidation-free heating of workpieces for quenching with the process of formation of carbide coatings and subsequent heat treatment (quenching) of the coated parts.

The method for production of carbide coatings from the salt melts, termed the TD –process, was developed as far back as 1971 by the Toyota Central Research Laboratory (Japan) [1]. Now it is widely accepted far beyond Japan (European countries, USA, Australia). The E.O.Paton Electric Welding Institute has been involved into the work on production of carbide coatings from the borax melt since 1985, while since 1996 this work has been performed in collaboration with the "Chromin" Company (The Netherlands). This paper gives results of the collaborative work of the E.O.Paton Electric Welding Institute and Chromin on production, investigation and practical application of vanadium carbide coatings on tool carbon and alloyed steels.

As compared with other metal carbides, vanadium carbide is characterized by a combination of high hardness and sufficient ductility. For example, microhardness of vanadium carbide amounts to 29000 MPa and elasticity modulus is 280-430 GPa, while the corresponding values of titanium carbide are 29000 MPa and 460-600 GPa and those of tungsten carbide are 21000 MPa and 510-720 MPa, respectively. This makes vanadium carbide a promising material for hardening of machine parts and tools, including cutting tools.

II. Experimental

Investigation of the mechanism of vanadium carbide coating and optimization of the technology for deposition of the vanadium carbide coatings were done on carbon steels (carbon content – from 0.2 to 0.8 wt. %) in a temperature range of 800-1050 °C and at a holding time of 1-5 h. Structure and phase composition of the coatings were studied by metallography, microhardometry, X-ray phase analysis and X-ray microanalysis. The atomic C/V ratio was determined on the basis of results of evaluation of the lattice constant of vanadium carbide and data on its dependence upon the composition in the homogeneity range [2].

Oxidation resistance of vanadium carbide coatings was determined by the gravimetric method in air (derivatograph Q-1500 D, heating rate – 10 °C/min) and corrosion resistance – by the potentiostatic method in sea

and fresh water, in 5 and 10 % solutions of hydrochloric acid, and in alkaline medium of potassium hydroxide.

Tribological properties of the coatings were studied by the following methods:

1. Abrasive wear was studied by friction of the test and reference samples on a surface with abrasive particles fixed to it (abrasive paper) under static loading and at no heating. In addition, this included comparative tests of vanadium carbide coatings with a number of other coatings.
2. Gas-abrasive wear was studied by simultaneously affecting the test and reference samples by a flow of hard particles formed by a centrifugal accelerator under fixed testing conditions.
3. Wear under conditions of end face friction without lubrication on a mating body was studied depending upon the displacement speed and loading.
4. Cavitation wear was studied in a flow of fluid under a pressure at the inlet equal to 20 MPa and a pressure gradient of 0.83.

III. Results and discussion

Sequence of the process of formation of the carbide layer on steel was established on the basis of results of kinetic investigations, structural and phase analysis and thermodynamic calculations.

According to the thermodynamic calculations, interaction of borax with ferrovanadium at temperatures of 1000-1500 K is a multi-stage process. Intermediate products of the process are vanadium oxide, boron oxide and sodium hyperoxide. Formation of atomic vanadium is most probable to occur as a result of reaction between vanadium oxide and potassium hyperoxide. It should be noted that the thermodynamic probability of such as reaction depends but slightly upon the temperature.

Results of our investigations suggest that the process of formation of a carbide layer on the surface of carbon steel consists of the following stages:

1. Adsorption of atomic vanadium on the surface of steel;
2. Diffusion of vanadium in the bulk and, at a higher rate, along the grain boundaries of a steel sample to form solid solution of the Fe-V-C system;

3. Counter-diffusion of carbon mostly along the grain boundaries to the surface of the steel sample and formation of vanadium carbide as a result of interaction of carbon with an adsorbed layer of atomic vanadium (thermodynamically allowed reaction over the entire temperature range);
4. Growth of regions of the carbide phase until they coalesce to form a continuous carbide layer.

After that the process stops abruptly, as diffusion of carbon to the outside boundary through a carbide layer acts as a bounding link, which limits the ultimate thickness of the layer for the investigated temperature-time range of the process to a value of 5-15 μm .

Vanadium carbide is known [3] to have a rather wide range of homogeneity: from $\text{VC}_{0.75}$ (15.1 wt. % or 43 at. % C) to $\text{VC}_{0.96}$ (18.5 wt. % or 49 at. % C). Atomic nodes in the carbon sub-lattice of non-stoichiometric VC_{1-x} remain vacant. Building up of the VC layer at the final stage of its formation occurs primarily on the outside of the steel sample. Adsorption of atomic vanadium on the sample surface owing to the presence of convective flows in the borax melt is rather intensive, this making diffusion of carbon from the base through the carbide layer a bounding stage of the process. The suggested mechanism of formation

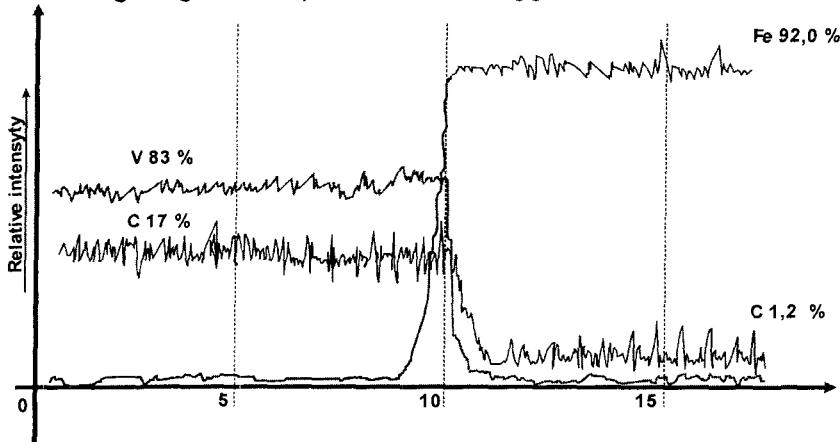


Fig. 1. Distribution of vanadium (a) and carbon (b) through thickness of the carbide layer on carbon steel

of the carbide layer is proved by results of investigation into distribution of elements through thickness of the layer (Fig. 1), which is indicative of the absence of the vanadium concentration gradient and an increase in the carbon concentration in a direction to the external boundary of the layer.

The maximum permissible thickness of the carbide layer and its microhardness at preset temperatures and time of the process depend upon the carbon content and nature of alloying elements in steel (Table 1).

Thus, an increase in the carbon content of steel itself and on its surface layer (which can be achieved by preliminary carburizing) allows thickness of the carbide layer (Fig. 2) and its microhardness to be substantially increased. In this case the composition of VC_{1-x} approaches the upper boundary of homogeneity (Table 1).

Alloying elements can either increase or decrease diffusive mobility of carbon in austenite, thus affecting the rate of its delivery to the interface with the carbide layer. Such elements as Cr, Mn and Mo, which form more stable carbides than Fe_3C , decrease the relative coefficient of thermodynamic activity of carbon in austenite, whereas elements which do not form stable carbide but just disturb perfection of the crystalline lattice (e.g. nickel) act in the opposite direction.

Therefore, while the vanadium carbide layer formed on carbon steel 1045 with a carbon content of 0.54 % at a process temperature of 980 °C and holding for 6 hours has thickness of $11 \pm 0.5 \mu m$, on steel 1.7225 alloyed with chromium to 1.2 % and molybdenum to 0.3 %, having the same carbon content (up to 0.45 %) its thickness is no more than $8 \pm 0.5 \mu m$ (Figs. 2 b and 3 a). Preliminary carburizing of steel 1.7225 allows thickness of the layer to be increased to $13 \pm 1 \mu m$ under the same conditions of VC deposition (Fig. 3 b). On steel 1.4122 with a higher chromium content (17 % Cr) without preliminary carburizing the continuous carbide layer is not formed at all (Table 1).

The positive point of the technology of vanadium carbide coating in the borax melt is the absence of a carbon-free zone under the carbide layer. This is attributable to a higher diffusive mobility of carbon in metal, as compared with the carbide phase, as diffusion of carbon in metals occurs by a pure interstitial mechanism [4].

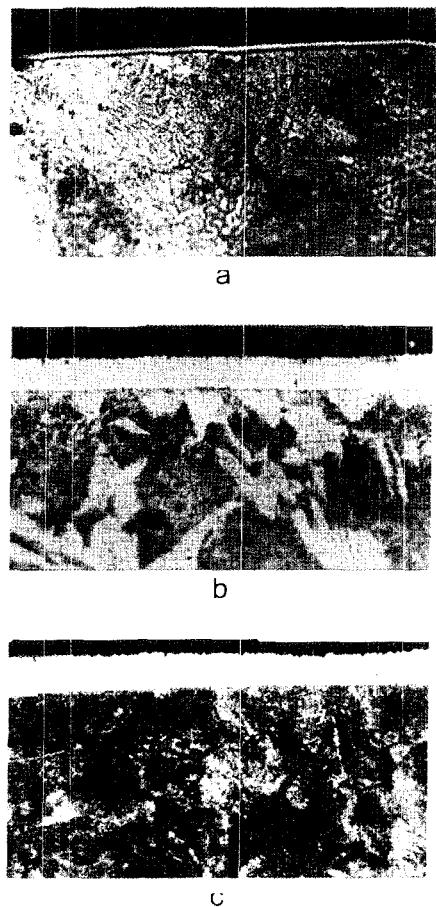


Fig. 2. Microstructure of vanadium carbide coatings on carbon steels deposited at a temperature of 980 °C and holding for 6 h (a – St. 0.20 % C, b – St. 0.45 % C, c – St. 0.8 % C), $\times 500$

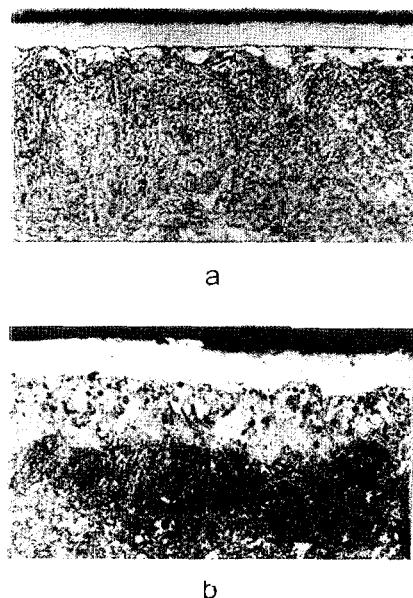


Fig. 3. Microstructure of vanadium carbide coatings on alloyed steels deposited at a temperature of 980 °C and holding for 6 h (a – steel 1.7225, b – carburized steel 1.7225), $\times 500$

Table 1. Characteristics of VC coatings on steels (deposition conditions: 980 °C, 6 h)

Steel grade	Content of carbon and main alloying elements, wt. %	Properties of coatings			Notes
		Thickness, μm	Microhardness, MPa *)	Phase composition	
St. 1020**)	C – 0,20	1,5 ± 0,5	-	-	Formation of a thin carbide layer
St. 1045***)	C – 0,54	9 ± 0,5	19000 - 20000	VC _{0,85}	Carbide layer is dense, homogeneous
St. 1078***)	C – 0,8	13 ± 0,5	12000 - 25000	VC _{0,87}	Carbide layer is dense, homogeneous
St. 1078***) cemented	C – 1,2 **)	13 ± 1,0	26000 - 28000	VC _{0,87}	Same, but cracks are formed in some regions in measurement of microhardness
1.1730	C – 0,45 Mn – 0,7	11 ± 0,5	19500 - 20100	VC _{0,83}	The zone of alloyed ferrite adjoins the coating
1.1730 cemented	C – 0,8 **) Mn – 0,7	13 ± 0,5	19500 - 21000	VC _{0,84}	Cracks are revealed in some regions of the coating in measurement of microhardness

1.0601	C – 0,6; Mn - 0,8 Cr≤0,4; Ni≤0,4	$8 \pm 0,5$	18540 - 19500	VC _{0,84}	The zone of ferrite grains adjoins the sense carbide layer
1.0601 cemented	C – 0,7; Mn - 0,8 Cr≤0,4; Ni≤0,4	$13 \pm 1,0$	18540 - 20100	VC _{0,84}	Carbide layer is dense, homogeneous
1.7225	C – 0,42; Mn - 0,7 Cr - 1,1; Mo - 0,2	$8,5 \pm 1,0$	16000 - 19500	VC _{0,85}	Grains of alloyed ferrite are revealed under the carbide layer
1.7225 cemented	C – 0,77**); Mn - 0,7 Cr - 1,1; Mo - 0,2	$12,5 \pm 0,5$	18500 - 22900	VC _{0,86}	Insignificant porosity is detected in the ferrite-carbide sub-layer adjoining the carbide layer
1.4122	C – 0,35; Cr - 17 Mo - 1,0; Ni≤1,0	-	-	VC _{0,75} α - Fe, Cr ₇ C ₃	Coating is discontinuous and has the form of individual grains on the surface of steel
1.4122 cemented	C – 4,14**); Cr - 17 Mo - 1,0; Ni≤1,0	$7 \pm 0,5$	10500	VC _{0,77}	Carbide layer is porous

1.2379 (D2) ^{***})	C - 1,55; Cr - 11,5 Mo - 0,75; V - 1,0	$5,5 \pm 0,5$	-	$VC_{0,85}$	There is no transition zone under the VC layer
1.4112	C - 0,9; Cr - 18,0 Mo - 1,2; V - 0,1	$5,5 \pm 0,5$	-	$VC_{0,81}$	There is a transition layer with a small number of carbide inclusions under the VC layer
1.4571 cemented	C - **); Mn - 2,0; Cr - 17; Mo - 2,0; Ni - 12,0	$8,0 \pm 0,5$	15400-16040	$VC_{0,77}$	Structure under the VC layer is more fine-grained than that of the base

*) Microhardness was not measured at coating thickness of $\leq 6\mu m$

**) Carbon content of the surface layer of cemented steel

***) AISI-SAE system

The investigation of the process of oxidation of vanadium carbide coatings on steel shows that at temperatures of above 550 °C the process is dramatically accelerated (Fig. 4) to form porous and multi-phase scale (basic phases V_2O_3 and Fe_2O_3). Diffusion porosity is formed at the interface, leading to separation of the layer (Fig. 5). However, at temperatures below 400 °C the VC coatings have a sufficiently high heat resistance. This circumstance should be allowed for in heat treatment of parts after coating.

Because of high hardness of the carbide layer and high residual compressive stresses present in it (according to [5] the vanadium carbide coated steel with 1.6 % C has $\sigma_{res} = 24000$ MPa), the vanadium carbide coated steel is characterized by high wear resistance.

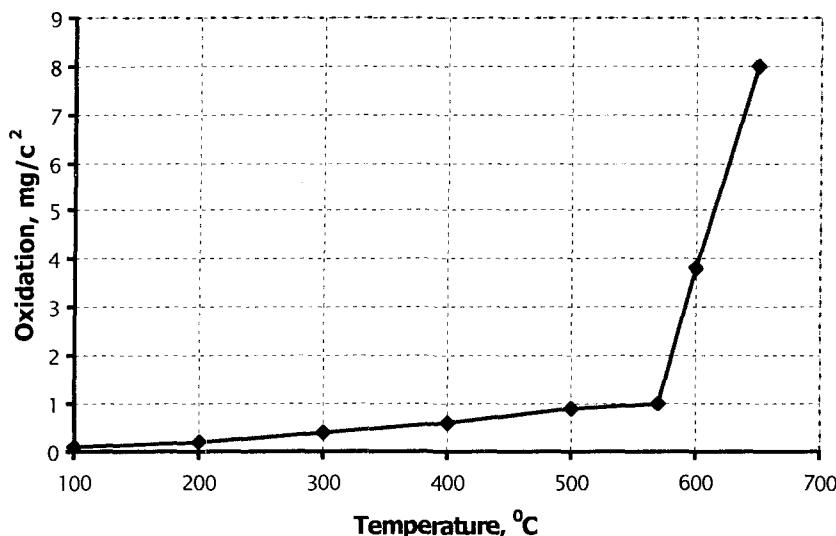


Fig. 4. Dependence of an increase in weight of the vanadium carbide coating upon the temperature in oxidation in air (heating rate – 10 °C/min)

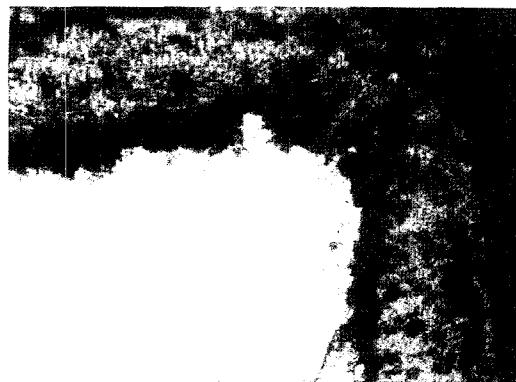


Fig. 5. Microstructure of the oxidized vanadium carbide coating on steel, X 200 (initial thickness of the VC layer – 12 μm)

Investigations of wear resistance of the vanadium carbide coatings under conditions of abrasive wear on the abrasive paper show that relative wear resistance decreases with an increase in the wear path. For example, while at a path of 10 m it is equal to 30 relative to the reference sample (quenched steel CrWMn containing 0.85-0.95 % C, 0.5-0.8 % Cr, 0.5-0.8 % W, 0.9-1.2 % Mn and 0.15-0.35 % Si), at a path of 30 m it decreases to 4.3. Therefore, life of the vanadium carbide coatings under the abrasive wear conditions depends upon their thickness.

Wear resistance of the vanadium carbide coated steel under gas abrasive wear conditions, depending upon the abrasive attack angle, is 3-25 times as high as that of alloyed steel with 0.3 % C (30CrMnSi) (Fig. 6). Wear of the vanadium carbide coatings on steel U8 under conditions of end face sliding friction without lubrication on the mating body of alloy WC-2Co (displacement speed – 0.5 m/s, pressure on the samples – 3 MPa) is 1-2 $\mu\text{m}/\text{km}$ at a friction coefficient of 0.4-0.5. To compare, wear of boride coatings on steels under the same conditions is 20-25 $\mu\text{m}/\text{km}$, i.e. it is 15-20 as high as that of the vanadium carbide coatings. Comparative wear resistance of vanadium carbide coatings relative to some others coatings is shown on Fig.7 (conditions of rubber wheel abrasion tests).

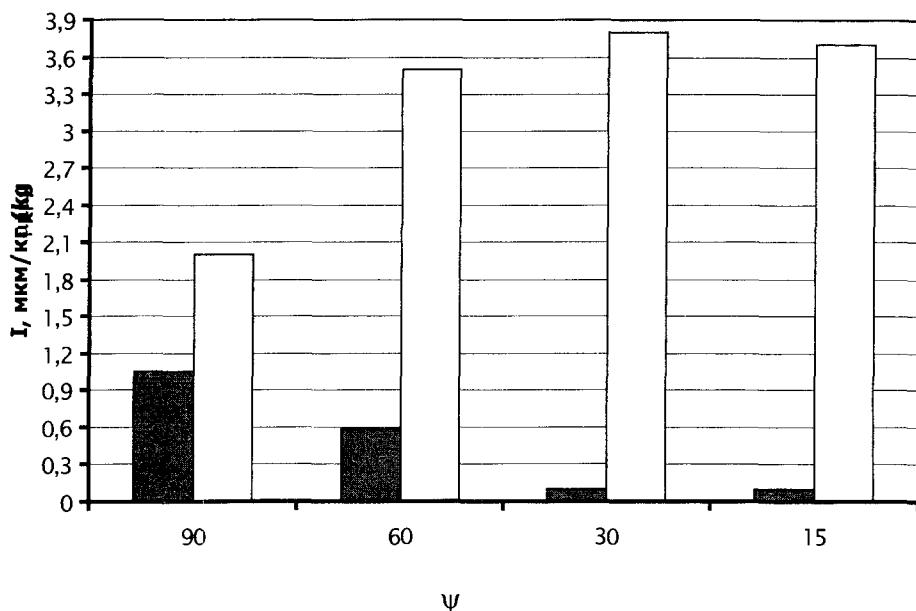


Fig. 6. Linear wear (J) of the vanadium carbide coating at preset abrasive attack angles (~ - wear of the coating; ~ - wear of the reference sample of alloyed steel 30KhGSA, centrifugal accelerator rotation speed – 100 rps, abrasive – SiO_2 with particle sizes of up to 1 mm)

Testing the vanadium carbide coatings to cavitation resistance at a working fluid pressure gradient of 0.83 and a test time of 12 h showed an increase of 25-30 times in the cavitation resistance of the coated steel, as compared with the uncoated one. As shown by the investigations, a shock wave generated at collapse of the cavitation bubbles leads just to deformation of the carbide grains, causing no cracking or fracture of the coating. The result obtained is in agreement with the investigations [1], where impact tests using a steel ball caused no cracking and no separation of the vanadium carbide layer even after 200,000 impacts. To compare, the electrolytic chromium layer separates after 50,000 impacts, the depth of the impact trace being identical in both cases.

Owing to the presence of high residual compressive stresses the vanadium carbide coatings increase fatigue fracture resistance of steels. The low-cycle fatigue tests using the electrohydraulic testing machine

UE-20 showed that samples of high-carbon steel containing 0.8-0.9 wt. % C with the vanadium carbide coatings withstood the largest number of cycles to fracture (18000 cycles under a maximum load in a cycle equal to 900 MPa). The same steel without a coating fractures in the working portion of a sample during the process of single loading to 890 MPa, and steel with 0.45 % C under a load of 795 MPa withstands 2520 cycles. Deposition of the vanadium carbide coatings on steel with 0.45 % C allows fatigue fracture resistance to be increased approximately 2 times.

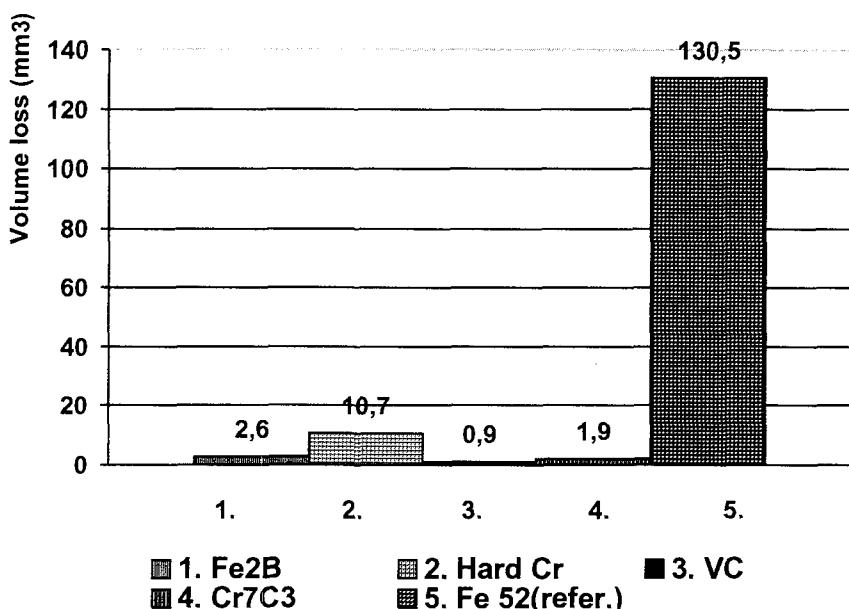


Fig. 7. Comparative wear resistance of different coatings

Investigation into corrosion resistance of the vanadium carbide coatings in sea and fresh water, in 5 and 10 % solutions of hydrochloric and sulphuric acids and in alkaline medium of potassium hydroxide (5 and 10 % KOH solution) was conducted using the potentiostatic method. Analysis of the anode polarization curves shows that in the field of active dissolution there is a linear relationship between the potential and logarithm of the current density. Further increase in the potential is accompanied by a gradual inhibition of the dissolution process and achievement of the saturation current. The corrosion potential of the vanadium carbide coatings in all media, except alkaline solution, shifts to

the range of positive values, as compared with that of steel. Corrosion rate of the coatings, expressed in terms of current, in sea and fresh water is 10-20 times, and in acid solutions – 70-400 times as low as that of steel with 0.2 % C in such media. In alkaline solutions the rates of corrosion of the VC coating and steel are almost identical.

High hardness, strength of adhesion to the substrate and wear resistance of the vanadium carbide coatings, as well as small thickness of the layer, which hardly changes sizes of the parts and does not disturb sharpness of the cutting edges (Fig. 8), maintaining of initial surface finish (surface roughness from $R_a \geq 0.5 \mu\text{m}$ is not deteriorated after deposition of the diffusion layer) make the vanadium carbide coatings rather promising for commercial application.



Fig. 8. Sectional view of an edge with vanadium carbide coating

At present the vanadium carbide coatings are applied to different machine parts and tools used in machine building, metal- and wood-working and meat-processing industries.

Figure 9 shows some parts with the vanadium carbide coatings. Results of practical tests are indicative of an extension of life of the parts and tools with the vanadium carbide coatings from 3-4 to 30 times, as compared with the mass-produced parts (Table 2). The "Chromin" Company has arranged a shop for deposition of the vanadium carbide coatings.

Table 2. Practical application of carbide coatings

Part	Extension of service life, times
Die for deep drawing of metal	30
Punch for cold pressing of powders, as compared with borated one	4...6
Textile machine thread-guides	8...10
Tools for calibration of holes (core) in stainless steel parts	30
Wood working tools	4...6
Paper drills	5...6
Knives for cutting of ceramics	4...6
Calibration punches	3...6
Rubber processing tools	3
Output cone for cigarette formation	20...25
Blocks of wrenches and threading dies of wedge suspensions of spiders for drilling equipment	10...15

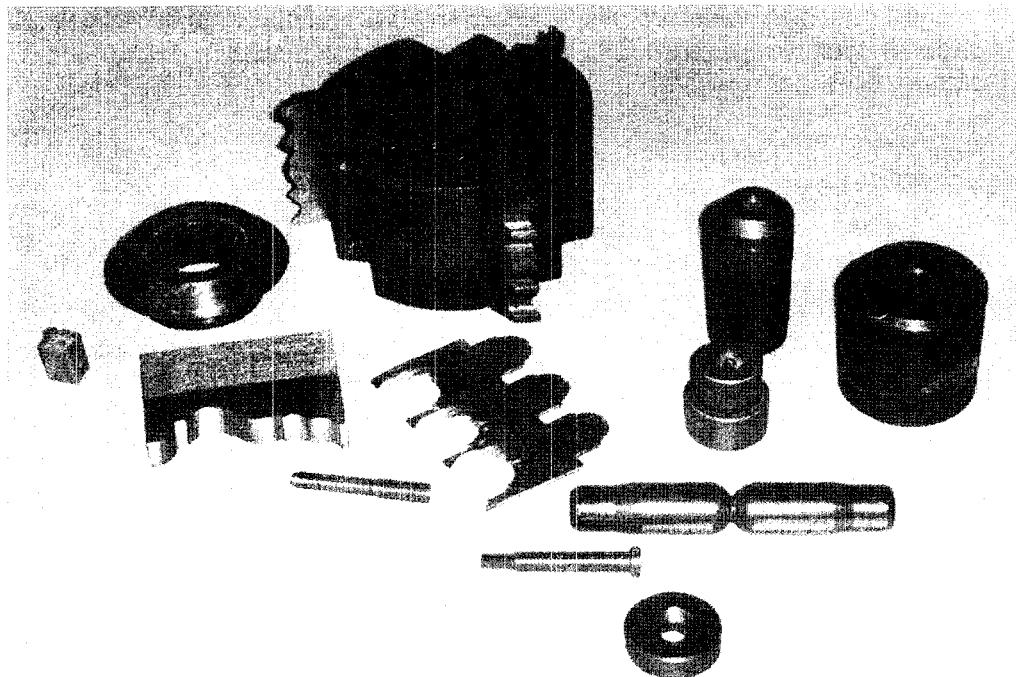


Fig. 9. Parts with vanadium carbide coatings

IV. Conclusions

Formation of vanadium carbide coatings on surfaces of parts is an efficient and promising area of thermochemical treatment. The no-electrolysis method of producing of diffusion coatings from the borax melt containing a carbide-forming element is characterized by simplicity and cheapness, as compared with other methods. Thickness of the continuous carbide layer formed at a preset temperature and time of the process depends upon the carbon content of steel and upon the nature and amount of alloying elements contained in it.

Diffusion coatings of vanadium carbide on steels are characterized by high wear resistance under conditions of sliding friction in air without lubrication and under wear and cavitation conditions. Also, they feature high corrosion resistance in different environments. The use of vanadium

carbide coatings holds promise for hardening of machine parts operating under friction and wear conditions, including impact loading, as well as cutting, drawing, extrusion and press-forming tools.

Results of practical application indicate that life of the parts extends from 3 to 30 times.

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