PROSPECTS OF COMPUTER MODELLING FOR A LEVEL OF WEAR RESISTANCE OF PM HARD MATERIALS ON THE BASIS WC-Fe-Ni

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Abstract

Work results are submitted, and opportunities for non-traditional application for powder metallurgy of quantum-mechanical methods of theoretical modelling of wear resistance level of hard materials are shown. Physical model of wear resistance of solutions is used at their abrasive wear process during cutting, establishing communication between the size of relative wear resistance and the changes in electronic structure of material. Settlement estimations of mechanical properties, energy of bonding and wear resistance for the solution «WC_{1-x} $(Fe\ Ni)_x$ (x = 0; 0.1; 0.2; 0.3; 0.4; 0.5; 1.0)» are submitted. Opportunity of "designing" for structure of a solution is discussed, using the factor of compatibility of refractory basis and matrix size thermo-e.m.s.

Keywords: computer modelling, wear resistance, hard materials, electron structure

INTRODUCTION

The level of properties of hard materials over the last 70 - 80 years in their wide application has increased rather little: the hardness and conductivity of hard materials have not practically changed, and the strength has increased its total in 1.2 - 1.4 time. The specified circumstance can be explained, first of all, by the fact that the chemical structure of the basic marks of hard materials has not changed significantly, and the increase of their durability has been achieved as a result of the perfection of technological processes of the manufacture of hard materials. In the last decade, the opportunities have repeatedly increased due to the successes of information technologies and adjacent areas of mechanical engineering. To the present time, there has been a sharp contradiction between opportunities in metal cutting technologies, on the one hand, and properties of tool materials – on the other, which constrains development. The problem of creating of new tool materials on a qualitatively other level, namely on the basis of the theory of the structure of electronic spectra and with that of phases, making the base of hard materials. Such a choice of a problem, to our mind, is justified by the rather modest results of a huge quantity of research carried out, directed to the creation of hard materials with high properties, and were received at a traditional microstructural level.

At the moment the researchers study a nature of the phenomenon, connected to increase of wear resistance at reduction of the size of thermo-e.m.s. of the cutting tool [1, 2], at least, for two reasons: first, with occurrence of work, the developing model of Mott on hard materials [1, 2], and secondly, with the development of methods of accounting electronic structure [3, 4]. There was the opportunity by settlement method to investigate a cutting material of known structure, or to simulate new structure. The last circumstance is

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especially tempting, as the rates of modern tool manufacture require the creation to be cheaper and effective with an increased wear resistance and productivity. The perfection of the structure of a material at a microlevel defines the contents of one of the directions of decrease of a relatively new level and is directly connected with the tempting by phenomena registered in a material.

In the present work, the attempt of structure "designing" of a hard materials is undertaken, using the factor of compatibility carbide tungsten and a matrix from refractory metals, size registered thermo-e.m.s. The results on wear resistance, mechanical and physical properties of system WC-Fe-Ni are submitted, in which the concentration Fe-Ni in a matrix of hard materials changed in a wide interval.

METHOD AND DETAILS OF CALCULATION

The electronic characteristics of refractory connections, i.e. the electron density-of-states (DOS) function, which determines the electronic properties of a substance, was theoretically calculated using the so-called local coherent-potential method of multiple scattering, which has received wide application for the study of hard materials [3-5].

The cubic tungsten carbide with structure as NaCl, has a rather wide area of non-stoichiometric on carbon, and has a high temperature of melting, hardness and durability, and also the propensity to form double carbide with transitive 3d-metals. The data about peculiarities of the chemical bonding, and changes in the then electronic structure of the cubic tungsten carbide at a partial replacement of tungsten atoms by iron (nickel) atoms, has not enough for understanding of laws of formation in the published literature, for example, wear resistance of system «tungsten carbide - iron - nickel».

For all different atoms of the system, the clusters are considered to be centred at the atoms. For instance, the cluster centred at the tungsten atom is shown in Fig.1. On the circuit, the iron atom and nickel atom occupy statistical positions in underlattice of tungsten atoms.

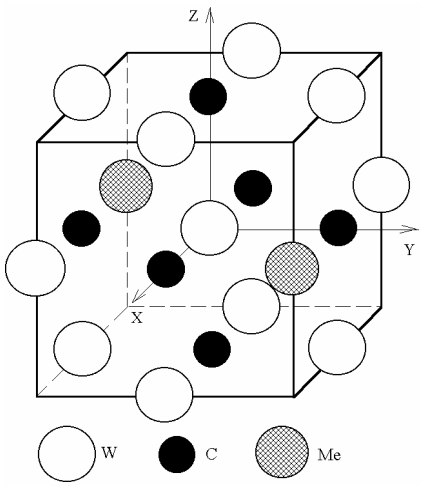

Fig.1. The unit cell of the system $W_{1-x}Me_xC$ (x = 0.17).

Crystal potential in MT-approach was under construction for the known circuit. The effective potential of the whole crystal was calculated according to the standard scheme described in detail in [3], determined as a sum of the contributions of the Coulomb

potential, Madelung potential, and exchange potentials. For four types of atoms of a system, considered was a cluster from 93 atoms. The parameter of a crystal lattice in the given account was determined on a Vegard rule. The local electron DOS of C, Fe, Ni, and W in the system $W_{1-x}(Fe,Ni)_xC$ have been calculated following the method described earlier [5]

$$n_l^A(E) = -\frac{\sqrt{E}}{\pi} \int_0^{r_{ws}} (r R_l^A(E,r))^2 dr \frac{\mathrm{Im}}{\mathrm{Im}\, t_l^A(E)} \frac{Tr}{T_{lm,l'm'}^{00,A}(E)} \qquad (1)$$

where *A* denotes the type of the clusters (C, Fe, Ni or W), *l* is the orbital quantum number, $R_l^A(E,r)$ are the radial wave functions, T is a matrix element of the scattering operator, and index 0 shows the centre at which the atom of A type is situated. The total electron DOS per unit cell for one spin projection *N (E)* was found as the sum of local electron DOS:

$$N(E) = (1-x)\cdot \sum_{l=0}^{2} n_l^W(E) + x\cdot \sum_{l=0}^{2} n_l^{Fe(Ni)}(E) + \sum_{l=0}^{1} n_l^C(E) \qquad (2)$$

In the analysis of the electronic structure of complex multicomponent materials, as a first approach it is possible, instead of formula (2) to use a ratio of

$$N(E) = (1-C)\, N^{WC}(E) + C\, N^{FeNi}(E) \qquad (3)$$

where C - concentration of an alloy iron - nickel, $N^{WC}(E)$, $N^{FeNi}(E)$ total electronic density of states (TDOS), hard solutions tungsten carbide, and iron - nickel accordingly.

For understanding of the nature of physical processes determining the tribology properties of the material of a cutting tool, it is necessary to consider the interaction of atoms among themselves in a crystal carried out by valence electrons, and described by the equation of Shredinger. Size thermo-e.m.s. are defined by the character of distribution DOS in a vicinity of a level Fermi. Less size thermo-e.m.s. is experimentally established than the above wear resistance of a material. Thus, absolute meaning thermo-e.m.s. can act as the important indicator in search of structure for new cutting tool materials, acting in a role «bridge» between their electronic structure and the wear resistance.

One of the main tasks of a science concerning friction and deterioration, is the development of analytical dependencies for a settlement estimation of the size of deterioration (or intensity of wear process) with an account of the probability of a greater number of influencing factors. Let's consider the most investigated kind of wear process - abrasive, which agrees with the data by Vierrege G. [6], and is shown with uniform intensity in all range of speeds (temperatures) cutting.

In the first approach, the interrelation between the electronic characteristics of a material and relative wear resistance at an abrasive wear process, can be investigated within the framework of model advanced in a cycle of work [1, 2, 7]. In the given model, the analytical ratio, the wear resistance with parameters of electronic structure (density of electronic condition, energy Fermi, number of filling electron s, p, d-levels, energy of connection of atoms) and absolute thermo-e.m.s., a tool material is defined as follows

$$I_{rel} = b\cdot\left\{\left(\int_{E_b}^{E_F-\Delta} E\, N(E)\, dE + \Delta\cdot E_F\, e^{\frac{\varepsilon E}{K_\varepsilon T}} + K_C + K_{H1}\right)^2 + K_{H2}\right\} \qquad (4)$$

The received expressions allow a data account complete and local partial of the density of electronic condition and experimental values thermo-e.m.s., to receive estimations of wear resistance of a material of a product at an abrasive wear process.

At the first stage of theoretical modelling of wear resistance of hard material, the electronic structure of a matrix, consisting of an alloy Fe-Ni (50:50), paid off. According to

the above described, a circuit electronic structure of system Fe-Ni with a structure of lattice NaCl was designed. It was supposed, that the alloy Fe_xNi_{1-x} keeps the system structure, that corresponds to known representations [8]. The question of choosing as a lattice is especially important as to theoretical consideration, as it is known, that the structure NaCl in pure iron exists only at high temperatures, and is both stabilised by the various additives and makes a basis of a crystal lattice of many alloys. In system Fe-Ni we shall believe that the Ni can be considered as the additive, stabilising a crystal lattice of iron (as NaCl). For instance, the cluster centred at the iron atom is shown in Fig.2. Accounting for the following electronic configurations: iron $Fe3d^64s^2$ and nickel $Ni3d^84s^2$ complete and local density of electronic condition are calculated for each atom in an alloy. Comparison of the local electronic condition designed in the present work of atoms of iron and Ni, with accounts of other authors [9-11] specifies them as atom. The parameter of a lattice of alloy Fe-Ni varied in a wide interval and was accepted equal and = 9.40 a.u., which was in agreement with published data on the valence top of a strip of iron and nickel. For transition to an account of physical properties and parameters of wear resistance, the estimation of parameters of electronic structure came true, it is similar to work [1, 2, 7].

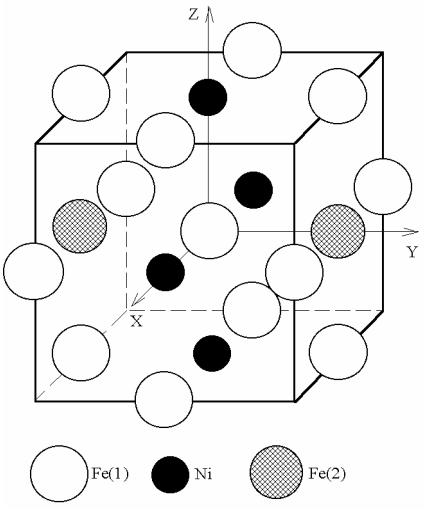

Fig.2. The unit cell of the system Fe-Ni.

The calculation of wear resistance of a material with the use of a ratio (4) assumes presence of data about the size of thermo-e.m.s. characteristic for researched material. Within the framework of the model advanced in work [12], temperature factor of thermo-e.m.s. of a material of structure Fe-Ni is designated: $(\varepsilon/T)_{FeNi} = -3.003 \cdot 10^{-9}$ V/K. For investigated temperature of cutting (t = 600°C) the size of thermo-e.m.s. has been made size $\varepsilon_{FeNi} = -2.619 \cdot 10^{-6}$ V. For a comparison of settlement meaning of thermo-e.m.s. to experimental data, received from thermo-e.m.s., we shall use the dependence $\varepsilon_X = \varepsilon_{FeNi} - \varepsilon_{WC}$, (where $\varepsilon_{WC} = -23.0 \cdot 10^{-6}$ V/K) [13]. Then the relative size of thermo-e.m.s. of the alloy Fe-Ni will make the size $\varepsilon_X = 20.381 \cdot 10^{-6}$ V/K, on the order there is more experimental meaning ($-5.0 \cdot 10^{-6}$ V/K).

EXPERIMENTAL PROCEDURE

As is shown in work [12] for tool materials, the tendency is an increase in wear resistance (is observed at cutting metals) with reduction of size absolute thermo-e.m.s. Therefore, the first stage of work experimentally studied, changes thermo-e.m.s. In alloys of refractory metals (making a matrix in hard materials) preferably the carbide tungsten (the grains of which make a refractory skeleton) depending on temperature. In Tab.1, there are the results of an experimental study of the influence of structure based on change in thermo-e.m.s. in systems WC-MeM (where Me and M - refractory metals) resulted, for which criteria accepted at work it is necessary to expect the most accomplished structure, determined by small thermo-e.m.s. in hard material.

Tab.1. Experimental meanings of thermo-e.m.s. of systems Fe-Ni and Fe-Cr-Ni mainly carbide tungsten.

T [°C]	Meanings thermo-e.m.s. $\varepsilon \cdot 10^6$, V			
	Fe-Ni (50:50)	Fe-Cr-Ni (70:20:10)	Fe-Ni (90:10)	Fe-Ni (75:25)
100	-2.0	0.9	-	-1.3
150	-4.2	1.0	-0.6	-2.4
200	-5.1	1.4	0.2	-2.9
250	-5.0	0.9	-1.6	-1.8
300	-	-	-1.6	-3.7
350	-5.6	0.2	-1.0	-1.6
400	-4.8	1.7	-3.3	-2.2
500	-4.1	1.4	-2.1	-2.1
600	-5.0	4.0	-5.0	-5.5

Tab.2. Experimental meanings thermo-e.m.s. of refractory metals mainly carbide tungsten.

T [°C]	Meanings thermo-e.m.s. $\varepsilon \cdot 10^6$, V							
	Ti	Cr	Mn	Fe	Co	Ni	Cu	Mo
100	0.5	0.9	-0.05	1.96	-0.4	0.5	1.39	1.52
150	0.8	1.3	0.1	2.8	-2.1	-0.5	2.05	2.27
200	0.3	1.1	-0.6	3.4	-1.7	-1.2	2.5	2.46
250	0.4	1.3	-0.5	4.0	-2.9	-1.9	2.9	3.2
300	1.2	-	-	-	-	-	-	-
350	2.2	2.3	-0.8	5.5	-4.6	-1.3	4.1	3.8
400	0.7	2.0	0.1	5.7	-7.8	-3.5	5.6	6.0
500	-0.8	0.9	0.7	3.1	-5.1	-2.1	6.8	2.9
600	7.0	4.0	7.2	10.5	-5.0	-4.5	9.0	8.6

In Table 2 there are the data about the thermo-e.m.s. of refractory metals, from which investigated alloys were made.

The analysis of experimental data, generalised in the tables, testify that the system Fe-Ni can be considered as an initial base for searching for optimum structure of a matrix of hard alloy on the basis of carbide tungsten. The analysis of the given system can indirectly prove to be true by its use in the system of high-strength alloys [14]. We shall

study, on a sample from system Fe-Ni, an opportunity for perfection of the structure of tool materials.

The theory developed here can explain the known fact of increase in wear resistance of hard alloys based on the carbide tungsten at an increase of titanium concentration. For example, analysis Tab.2. (in particular column-2) testifies that titanium has the minimum thermo-e.m.s. (mainly carbide tungsten) from the investigated refractory metals. Therefore, it is necessary to expect that hard solutions "carbide tungsten-titanium" will have heightened wear resistance that confirms the results of work [1, 12].

RESULTS AND DISCUSSION

The electron structure of the systems WC, FeNi, $W_{1-x}(Fe,Ni)_xC$ ($x = 0 \div 0.9$) has been investigated. Within the framework of one approach, a comparison of the electronic structure of the considered solutions in comparison to binary analogues is done. Calculation of meaning of partial charges in a hard solution Fe-Ni has allowed us to calculate the meaning of factor Kc (5.95011 Ry). Integrating total DOS of a valence band of an alloy Fe-Ni has allowed one to determine a rule at a level Fermi (0.76 Ry).

Using the formula (4), we shall offer an estimation of wear resistance for alloy Fe-Ni. The size of an interval is equal 0.10 Ry. It is accepted, that the varied parameters accept meanings: $K_{H1} = 4.5$ and $K_{H2} = 0.001$. According to formula (4), using an experimental meaning of thermo-e.m.s. (submitted in Tab.1) for a wide temperature interval (100°C - 600°C), we shall receive values of relative wear resistance. Received meaning of relative wear resistance (23.5) correlates with an experimental estimation for iron (19.0) and nickel (17.5) [15]. Estimations carried out on the energy of chemical bonding (in the approach of Fridel) and hardness, is similar to work [12], and show that the values of hardness (1.679 GPa), energy bonding (3.2 Ry/unit cell) do not vary in the considered temperature interval at the given values of thermo-e.m.s. This fact corresponds to known representations about the character temperature (high-speed) dependence of abrasive wear [16].

We shall proceed to modelling hard metals, consisting of carbide tungsten and a matrix from refractory alloy, and containing iron and nickel. In the given material WC-FeNi, the concentration of a matrix changed at an interval (0,1...0.5). For forecasting physical and tribology properties of the given material, a certain technique is used, the basis of which is incorporated in work [17]. The estimation of the parameters of electronic structure of the given material was made on the basis of the approximation (4). In Fig.3., complete density of the electronic condition of hard solutions «carbide tungsten-iron-nickel» is submitted. The analysis of the electronic structure of hard solutions $WC_{1-x}(FeNi)_x$ has allowed us to estimate some structural - sensitive properties, in particular, temperature factors of electroresistance and thermo-e.m.s., which are submitted in Tab.3.

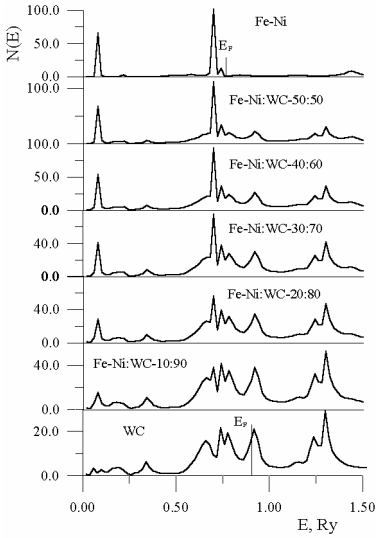

Fig.3. The total density of electron states [(in 1/(Ry · unit cell)] of the systems FeNi, WC and $WC_{1-x}(Fe\ Ni)_x$.

Tab.3. Settlement values of some parameters of alloy WC_{1-x} (FeNi)x (for a level Fermi EF = 0.90 Ry)

Concentration Fe-Ni in alloy [%]	Level Fermi $N(E_F)$, Ry	Quantity valence electrons	Thermo-e.m.s., μV/K	Temperature factors of electroresistance, μOh /K^2
0 (WC)	14.56	9.98	$2.10 \cdot 10^{-3}$	-0.326
10	26.49	9.94	$1.67 \cdot 10^{-3}$	-0.632
20	23.85	9.90	$1.23 \cdot 10^{-3}$	-0.599
30	21.22	9.86	$7.91 \cdot 10^{-4}$	-0.555
40	18.59	9.82	$3.42 \cdot 10^{-4}$	-0.499
50	15.96	9.78	$-1.12 \cdot 10^{-4}$	-0.431
100 (FeNi)	1.40	9.58	$-2.48 \cdot 10^{-3}$	0.546

In research of a nature of temperature conductivity in alloys, the iron-nickel [2] has appeared an especially fruitful comparison of several characteristics of investigated alloys to the dependence of density of the electronic condition at a Fermi level from concentration. As friction and wear are thermodynamic processes, in this case, the special interest represents the construction of similar dependencies for alloys $WC_{1-x}(FeNi)_x$, which are submitted in Fig.4.

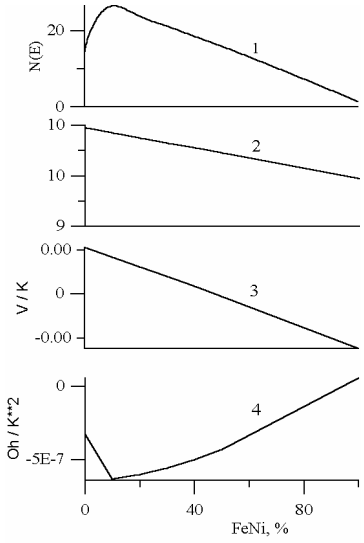

Fig.4. The dependence of density of electronic condition at a level Fermi (1), quantity valence electrons (2), thermo-e.m.s. (3) and temperature factors of electroresistance (4) from concentration in systems $WC_{1-x}(FeNi)_x$ (x = 0; 0.1; 0.2; 0.3; 0.4; 0.5; 1.0).

The preliminary analysis of dependencies submitted in Fig.4. with use as a criterion "of a minimum size of thermo-e.m.s.", allows to assume, that structure of a hard material with the contents "iron-nickel" of about 45%, can have optimum tribology properties. However, as marked R. Kiffer and P. Shvarzhkopf [17], the application of iron and nickel as a binding means for a hard material on a WC basis, gave alloys the durability of only (40 ÷ 60)% of the durability of a firm alloy on a WC-Co basis. The reason of such a decrease of properties of hard materials with iron and nickel can consist of the heightened ability of WC to be dissolved in a firm phase in these binding materials, and also in its propensity to form a fragile double carbide as $Ni_xW_xC_y$ or $Fe_xW_xC_y$ [17]. Study of the influence of Co, of Ni and Fe as of an alloy binding at reception on the basis of WC has shown [18], that the favourable influence of Co in comparison with Ni consists of an opportunity of reception of finer particles Co (compared to Ni), which will form superficial layers on WC grains, slowing their growth. The partial replacement of Co (up to 30%), provides the reception of firmer and fragile alloys in case of an application of iron and slightly softer hard alloys at replacement of Ni [17]. In both cases, a decrease of durability was observed. The partial replacement Co (or Ni) refractory metals Cr, Mo or W, corresponds to a decrease in the contents of a viscous binding material of a matrix, and brings in complete linkage of free carbon on the work data [17].

An estimation of wear resistance of solutions $WC_{1-x}(FeNi)_x$ used the following representations: the values of wear resistance of hard materials made of two solutions, can be proportional to their mass factors according to the formula:

$$I_{rel} = k_a \cdot I_{WC} + k_b \cdot I_{FeNi} \qquad (5)$$

where I_{rel} , I_{WC} , I_{FeNi} - accordingly resulting, and components of wear resistance k_a, k_b - mass factors. For solutions $WC_{1-x}(FeNi)_x$ in Tab.4., results of an estimation of wear resistance are brought, forth.

Tab.4. Settlement values of wear resistance of solutions $WC_{1-x}(FeNi)_x$ (factors ν_{WC} and ν_{FeNi} define the contents of a component in a solution).

ν_{WC}	ν_{FeNi}	k_{WC}	k_{FeNi}	I_{rel}
1	0	1	0	330.450
0.9	0.1	0.9390	0.0610	311.723
0.8	0.2	0.8724	0.1276	291.300
0.7	0.3	0.7996	0.2004	268.940
0.6	0.4	0.7195	0.2805	244.354
0.5	0.5	0.6310	0.3690	217.192
0	1	0	1	23.540

The data analysis of Tab.4. testifies, that at a considered interval of concentration, the size of wear resistance calculated in formula (5), decreases on (6...34)%, mainly the carbide tungsten. These results on wear resistance are possible to consider as a tentative estimation.

For an estimation of wear resistance based on changes in the electronic structure of solutions $WC_{1-x}(FeNi)_x$, use the formula (4). The size of an interval was equal to 0.10 Ry. The varied parameters accept meanings: $K_{H1} = -9.35$ and $K_{H2} = 0.001$. As to size of thermo-e.m.s., an estimation of this type is used

$$\varepsilon = k_a \cdot \varepsilon_{WC} + k_b \cdot \varepsilon_{FeNi} \qquad (6)$$

where ε_{WC}, ε_{FeNi} - experimental thermo-e.m.s. values. The meanings of relative wear resistance, received within the framework of the model advanced above, (for temperature of contact T = 873 K), are submitted in Tab.5.

Tab.5. Settlement values of wear resistance of hard materials $WC_{1-x}(FeNi)_x$.

Concentration Fe-Ni in alloy, %	Thermo-e.m.s., μV/K	Hardness H , GPa	Wear resistance I_{rel}
0 (WC)	-23.00	23.57	330.45
10	-26.05	20.38	285.73
20	-29.38	18.98	266.13
30	-33.02	17.64	247.24
40	-37.03	17.34	229.04
50	-41.45	15.09	211.54
100 (FeNi)	-73.00	1.68	23.54

An analysis of the last two tables shows that the distinction in estimations of wear resistance with the use of the formulas (4) and (5) makes only 9%, that allows itself in some cases, to be limited by a qualitative estimation (5).

It is necessary to note, that in the given work, an adiabatic approach is used. In particular, by consideration of the electronic structure of tool materials, a superposition of electronic structures are used of two solutions WC and Fe-Ni, in case of the absence of mutual solubility of the considered elements.

Thus, despite essential differences of the structure of solutions WC, FeNi, $WC_{1-x}(FeNi)_x$, for them a character of correlative communication between wear resistance and absolute force is held.

CONCLUSIONS

By the accounts of size of wear resistance for different structures of tool cutting material, it is shown that the alloy with a smaller thermo-e.m.s. has a large wear resistance. These results of theoretical accounts confirm the given numerous experiments in friction and cutting carried out for hard materials, ceramics, and cutting steels.

In work on a particular example, opportunities of the application for powder metallurgy in quantum-mechanical methods of theoretical modelling at a level of wear resistance for tool and hard materials are illustrated.

The developed model of interrelation of physical properties and parameters of durability (wear resistance) of tool cutting materials, based on changes of their electronic condition can be advanced on other structural types of materials.

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