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On specifics of hardening mechanisms in metallic matrix composition*

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К вопросу об особенностях механизмов упрочнения в металлической матричной композиции***

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Introduction. Functional properties of diamond powders are determined by a large-scale structural factor since it affects the formation of structurally sensitive mechanical properties — stress limit and yield value. Considering the qualitative correlation between yield value and hardness, it is possible to predict an increase in hardness including highly rigid materials.

Materials and Methods. Physical characteristics of the basic types of fillers that make up the reinforcers are considered, systematized and tabulated. M2-01 tin bronze (20 wt. % tin, 80% copper) was used as a bond. Ultradisperse natural diamond (UDND, 0.5–4 wt. %) was added to it, as well as powders of natural diamond (3/2 µm fraction, 7/5 µm, –40 µm) obtained through processing diamonds at the enterprise of "Sakha Daimond" JSC. The above materials were made on the crushing and screening equipment and shaking tables. The stages of obtaining powders were recorded using the raster electron microscopy. Vibroscreens were applied for the grain-size classification of diamond powders. Physical and mechanical characteristics of the produced samples were tested by standard methods. VLTE-500 electronic fourth-class laboratory balance was used for weighing. Density was determined by MK 0–25 mm micrometer according to GOST 6507-78.

Research Results. Porosity was calculated through the actual and theoretical density. It was found that with a decrease in the filler size, an improvement in the physicomechanical properties of the binder modified with a diamond powder is observed. The best performance was observed in the samples with the UDND filler.

Discussion and Conclusions. As a result of the study, it was recorded that the calculated data differ from the experimental data since they show an increase in the material hardening pro rata to the amount of the diamond particles introduced into the volume. An assumption has been made that the considered hardening model (Orowan model) does not take into

Введение. Функциональные свойства алмазных порошков обусловлены масштабным структурным фактором, поскольку он влияет на формирование структурно-чувствительных механических свойств — пределов прочности и текучести. Учитывая качественную корреляцию между пределом текучести и твердостью, можно прогнозировать повышение твердости, в том числе высокотвердых материалов.

Материалы и методы. Рассмотрены, систематизированы и представлены в виде таблицы физические характеристики основных типов наполнителей, входящих в состав упрочнителей. В качестве связки использована оловянистая бронза М2-01 (20 мас. % олова, 80 % меди). В нее добавляли ультрадисперсный природный алмаз (УДПА, 0,5–4 мас. %), а также порошки природного алмаза (фракции 3/2 мкм, 7/5 мкм, –40 мкм), полученные при переработке алмазов на предприятии ОАО «Сахадаймонд». Названные материалы изготавливались на дробильно-классификационном оборудовании и вибростолах. Стадии получения порошков фиксировались с помощью растровой электронной микроскопии. Для классификации алмазных порошков по зернистости применяли вибросита. Физические и механические характеристики изготовленных образцов испытывали по стандартным методикам. Для взвешивания использовали лабораторные электронные весы четвертого класса ВЛТЭ-500. Плотность определяли микрометром МК 0–25 мм по ГОСТ 6507-78.

Результаты исследования. Через фактическую и теоретическую плотности рассчитана пористость. Выяснилось, что с уменьшением размера фракции наполнителя наблюдается улучшение физико-механических свойств связки, модифицированной алмазным порошком.

Наилучшие показатели отмечены у образцов с наполнителем из УДПА.

Обсуждение и заключения. В результате проведенного исследования отмечено, что расчетные данные отличаются от экспериментальных, т. к. показывают увеличение упрочнения материала пропорционально количеству вводимых в объем частиц алмаза. Выдвинуто предположение, что рассмотренная модель упрочнения (модель Оро-

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*** Работа выполнена в рамках инициативной НИР.

account the formation of carbon and the agglomeration of diamonds into larger objects in the matrix volume under an increase in the number of input diamonds. If the UDND particle volume reaches 3%, the carbon con
tent in the material increases. As a result, the filler particles are not fully oxidized, thus increasing the number of pores in the material.

вана) не учитывает образование углерода и агломерацию алмазов в более крупные объекты в объеме матрицы при повышении количества вводимых алмазов. Если объем частиц УДПА достигает 3 %, в материале растет содержание углерода. В результате частицы наполнителя полностью не окисляются, тем самым увеличивая количество пор в материале.

Keywords: bond, metal matrix, composite, hardener, ultrafine particles, hardening mechanisms.

Ключевые слова: связка, металлическая матрица, композит, упрочнитель, ультрадисперсные частицы, механизмы упрочнения.

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Introduction. It is known that the physicomechanical properties of diamond powders are determined by a larger specific surface area and grain dispersion. In particular, this is shown by the Hall – Petch equation which is performed over a wide range of grain sizes (up to 1 um). Functional properties of these materials are determined by the large-scale structure factor since it affects the formation of structure-sensitive mechanical properties – stress limit and yield value [1, 2]. Given the qualitative correlation between yield strength and hardness, it is possible to predict an increase in hardness including highly rigid materials: the finer the filler, the fewer defects it has and, accordingly, the higher the strength.

Materials and Methods. Strengthening mechanisms in highly rigid materials depend on the interaction pattern of the introduced particles or hardener fibers and the matrix material. A successful application of the dispersion strengthening effect is shown in [3–6, 7]. Under such strengthening, a structure that makes the dislocation motion harder is created in the materials. Discrete particles of the second phase characterized by high strength and melting point inhibit the dislocation motion especially strongly. Considering the two-phase structure and high hardness of the materials obtained, it should be expected that their wear resistance will also be higher than that of the nonhardenable matrix materials. Besides, the strength of the components interface is an important factor for the wear resistance of composites. A strong adhesive bond at the interface ensures a composite with high rigidity and higher static strength [3, 6–8].

According to the mechanism described by Orowan, ultrafine diamond particles distributed in the binder volume affect the strain hardening of the composite material. Particles of the particulate filler introduced into the matrix inhibit the dislocation motion in a metal increasing its strength at the standard and elevated temperatures. In addition, they represent a mechanical obstacle in the path of crack propagation that may appear in the matrix, and increase the fracture resistance of the composite material.

Another characteristic that determines the reinforcing filler – matrix relationship is the thermal linear expansion coefficient. For solids at constant pressure and temperature, the thermodynamic equilibrium criterion is Gibbs minimum potential (or energy). This value shows an energy change during a chemical reaction and demonstrates the possibility of chemical reactions between the material components [5]. Thus, a minimum change in Gibbs energy corresponds to a stable equilibrium between the components of the system (Table 1).

Table 1

Physical characteristics of the main types of fillers [9, 10, 11]

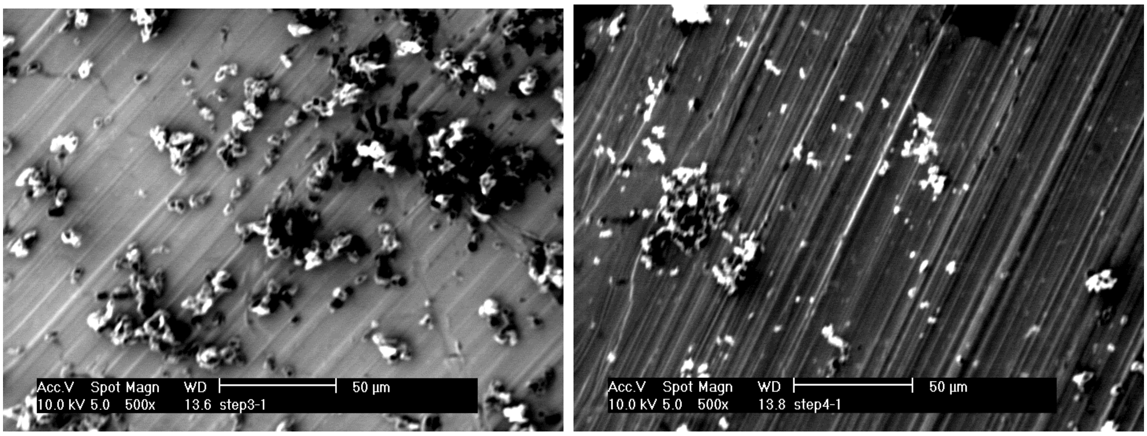
Substance and state	$\Delta G^{o}_{обр.}$, 298,15, kJ/mol Gibbs energy change	Microhardness, $\times 10^2$ Mpa	Temperature stability, °C
C (diamond)	2.377	1000	650–700
W	0	258	3300–3400
Al_2O_3	–1582.3	180–220	1500–1700
BN	–226.8	800–900	1100–1300
SiC	–60	300–320	1200–1300
BeO	–579.9	152	2500
Be_2C	–948	780	2150

The table shows that the optimal filler is diamond. It has a fairly low value of Gibbs energy change, the highest microhardness value, but the lowest temperature stability. Diamond has a high adsorption capacity [12] and is the least chemically active compared to other forms of carbon. These properties are important advantages when using diamond as a hardener.

The work objective is to study features of the mechanisms of forming the metal-matrix composition structure.

Objects of Study. We used M2-01 tin bronze (20 wt. % tin, 80% copper) as a basic binder. Ultradisperse natural diamond (UDND, 0.5–4 wt. %) was added to it, as well as powders of natural diamond (3/2 µm fraction, 7/5 µm, –40 µm).

Research Methodology. Natural diamond powders (NDP, 3/2 µm fractions, 7/5 µm, –40 µm) and the UNDN submicropowder were obtained during the processing of diamonds at the enterprise of “Sakha Diamond” JSC. The powders were made on the crushing and screening equipment and shaking tables under the optimum conditions. Fig. 1 shows the stages of obtaining the powders. The images were taken using the scanning electron microscopy (SEM).



a) *b*)

Fig. 1. SEM photographs of: fine-grained powder of 7 um or less (*a*); submicropowder (*b*)

Vibroscreens were applied for the grain-size classification of diamond powders. . Physical and mechanical characteristics of the produced samples were tested through standard methods. VLTE-500 electronic fourth-class laboratory balance was used for weighing. Density (ρ) was determined by MK 0–25 mm micrometer according to GOST 6507-78.

Research Results. Hardness was measured on Equotip 3 device, Proceq, according to the corresponding method of the GOST. The proportionality limit in compression and the elasticity modulus were determined according to GOST 25.503-97. The test results are shown in Table 2.

Table 2

NDP impact on physicomechanical properties of M2-01alloy

ND, %	Porosity, %				Hardness, HB				Proportionality limit in compression $\sigma_{пр}$, MPa				Actual density $\rho_{факт}$, kg/m3				Compressive modulus Ec, MPa
ND Dimensionality um	3/2	7/5	–40	UNDN	3/2	7/5	–40	UNDN	3/2	7/5	–40	UNDN	3/2	7/5	–40	UNDN	UNDN
0	41.0	41.0	41.0	41.0	41	41	41	41	9.7	9.7	9.7	9.7	7560	7560	7560	7560	5735.94
1	29.0	30.0	30.0	28.0	43	47	48	48	10.5	11.5	11.0	11.5	7630	7620	7610	7670	6771.03
2	27.0	28.0	28.0	26.0	43	43	51	53	10.5	11.5	12.0	12.5	7710	7700	7760	7750	6953.50
3	25.0	28.0	27.0	26.0	47	43	51	53	10.2	10.5	12.1	12.2	7730	7720	7770	7750	6580.27

To determine the elasticity modulus and proportionality limit, the samples were compressed on presses to a relative deformation of 15–16%, at a loading rate of 0.2 kN/s.

The porosity (P) was calculated through the actual and theoretical density using the formula:

$$П = (1 – \rho/\rho_т) \times 100\%, \quad (1)$$

where $\rho_т$ is the theoretical (calculated) density of nonporous material; ρ is the actual density of the sample.

The theoretical density was obtained by the formula:

$$\rho_т = 100/(C_1/\rho_1 + C_2/\rho_2 + C_3/\rho_3 + C_4/\rho_4), \quad (2)$$

where C_1, C_2, C_3 and C_4 are concentrations of copper, tin, NDP and UNDN in the powder mixtures according to their density ρ_1, ρ_2, ρ_3 and ρ_4.

The densities taken into account are:

- copper: 8.96 × 103 kg/m^3,
- tin: 7.28 × 103 kg/m^3,
- diamond: 3,5 × 103 kg/m^3,
- UDND: 3.1 × 103 kg/m^3.

The volume of samples was calculated by the formula:

$$V = (m_1 - m_2) / \rho_ж, \quad (3)$$

where V is pressing volume; m_1 is mass in air; m_2 is mass in water; $\rho_ж$ is liquid density.

In the course of the study, it turned out that with a decrease in the filler size, there was an improvement in the physicomechanical properties of the bond modified with diamond powder.

The elasticity modulus values were determined for the samples with the addition of the UDND and a pure binder. The best indicators are shown by the samples with the filler from UDND. At the same time, the physicomechanical properties under consideration deteriorate if the volume of the added UDND particles exceeds 2%.

The metallographic studies of the samples allowed us to establish how diamond particles affect the matrix structure. Fig. 2 shows the images of microstructures of the deformed samples.

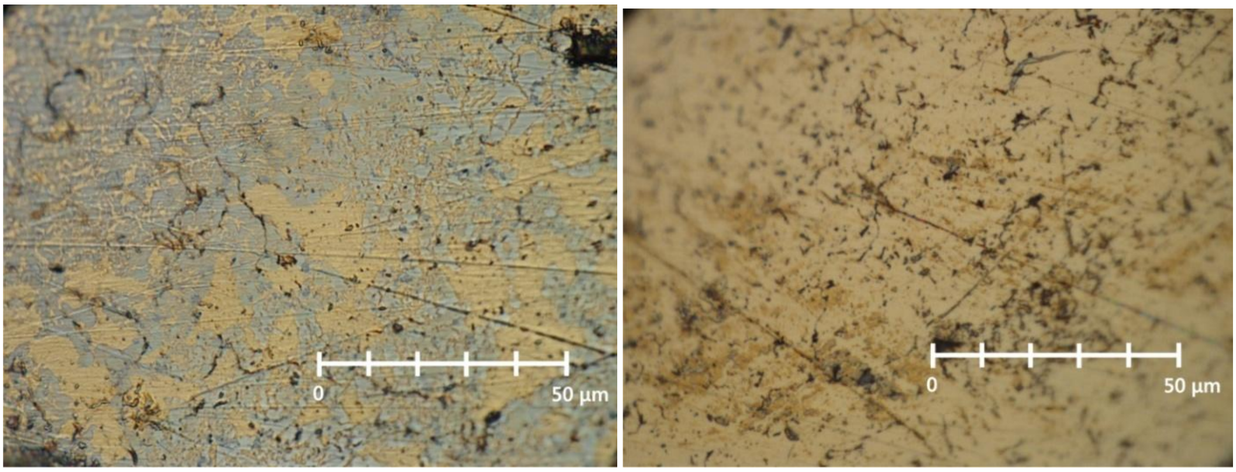


Fig. 2. Images of ground surface of deformed sample with addition of 2% of diamond powder particles under × 1000 magnification.

The pictures show clearly visible narrow and branched microstructure objects. Hypothetically, these are boundaries between the grains or microcracks formed under the deformation.

Inside the grains, there are also point microscopic objects that form a disperse substructure. Compared to the boundary-distributed point objects, their density is much less, but significantly more than in the original matrix which has no diamond fillers.

Based on the results of metallographic studies, it can be argued that the strengthening of the matrix material has two mechanisms – dispersion and grain-boundary ones.

If we are talking about a dispersion mechanism, the volume of NDP introduced into the matrix material can be calculated using Orowan equation [13]:

$$\zeta_N = \frac{Gb}{2\pi\lambda} k_0 \ln\frac{\lambda}{2b}, \quad (4)$$

where λ is the nearest distance between the particles; G is matrix shear modulus; b is Burgers vector; k_0 is coefficient characterizing the pattern of interacting atoms with dislocation.

The following values are chosen: $G = 0.367 \times 10^5$ MPa for bronze; $b = 2.564$ Å for copper; k_0 coefficient is equal to 0.85.

The nearest average distance between the particles, depending on the content and dispersion, is calculated by the formula proposed in [14]:

$$\lambda = \left[\left(\frac{200 + L_H}{1{,}91 L_H}\right)^{\frac{1}{3}} - 1\right] d, \quad (5)$$

where L_H is weight fraction of the filler; d is the diameter or thickness of the filler particles.

Table 3 shows the calculations of an average distance between filler particles depending on their volume and size.

Table 3

Nearest average distance between filler particles depending on their volume and size, and hardening according to Orowan equation under introduction of diamond particles

Particle size	7/5			3/2			–40			UDND		
Particle content, %	1	2	3	1	2	3	1	2	3	1	2	3
λ, um	125.3	98.19	85.02	52.19	40.91	35.42	417.56	327.30	283.40	6.26	4.91	4.25
ζ_N, MPa	0.13	0.16	0.18	0.28	0.35	0.40	0.04	0.05	0.06	1.91	2.38	2.70

The calculated data were substituted into Orowan equation, and thus the strengthening was determined through introducing the diamond powder particles into the matrix material.

According to the calculations, the greatest strengthening is provided through introducing the UDND into the matrix, which is generally validated by the experimental data.

When the grain geometry changes due to the agglomeration of filler particles at the interfaces in the material, it is advisable to calculate the material properties change according to the theory of grain-boundary strengthening [15, 16].

To determine the quantitative increase in the strength of the material through adding particles of diamond powders due to the grain-boundary strengthening, calculations were made using Hall – Petch empirical relationship [17]:

$$\Delta\sigma_{\text{T}} = k {d_з}^{-1/2}, \quad (6)$$

where k is Hall – Petch coefficient for this material; $d_з$ is grain size.

For calculations, we used the samples showing the greatest increase in strength according to Orowan theory. The calculations were performed according to the data obtained from the processing of the surface microstructure images through the technique proposed in [18].

The Hall – Petch coefficient is applied to copper. According to [19], it is a variable value; it depends on the average grain size and varies in the range of 0.01–0.24 MPa × m$^{1/2}$. The calculations show that the greatest strengthening is provided by the introduction of ultrafine NDP into the matrix material. In general, this is confirmed by the experimental data.

The average grain size is calculated according to the metallographic studies of the sample surface:

$$d_з = \sqrt{\frac{4\left(\frac{S_{общ}}{N_{общ}}\right)}{\pi}}, \quad (7)$$

where $S_{общ}$ is total area of objects; $N_{общ}$ is total number of objects.

With an average grain size of about 10^{-1} μm, the Hall – Petch coefficient is about 0.01 MPa × m$^{1/2}$.

The calculations based on Hall – Petch ratio indicate an increase in the yield strength of the material with the addition of particles of NDP. The yield strength reaches the maximum design value when the content of fillers is 1% (Fig. 3).

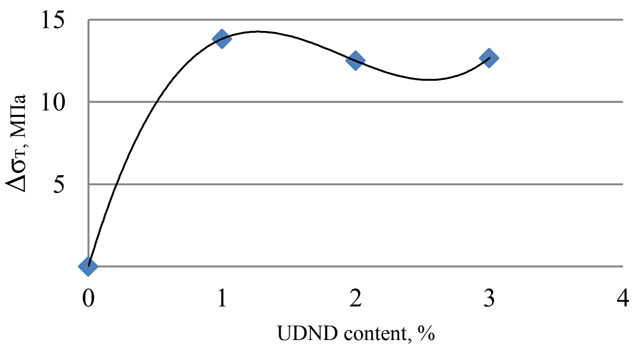


Fig. 3. Yield strength – UDND content dependence

Discussion and Conclusions. The calculations show that the samples with the addition of NDP have a smaller grain size compared to the initial ones. This fact can be explained as follows. The diamond particles, settling at the grain boundaries of the material, help to reduce their average size. As a result, the geometry of the boundaries between the grains changes; barriers to dislocations are formed; and thus, the potential capability of the material to resist plastic deformation is enhanced.

The yield strength increases by about 12–13 MPa which correlates with the calculated data obtained using Orowan theory for dispersion strengthening. If we are talking about polycrystalline material, then, in principle, the yield strength increases with decreasing the grain size. Diamond particles added to the matrix volume increase the yield strength since they change the geometry of grains reducing their average area and size.

The calculated data differ from the experimental results since they show an increase in the material strengthening pro rata to the number of diamond particles introduced into the volume. It can be assumed that the Orowan strengthening model does not consider the formation of carbon and the agglomeration of diamonds into larger objects in the volume of the matrix when increasing the number of diamonds introduced.

The decrease in the number of pores when adding the UDND particles in the amount of 1–2% can be explained by the high sorption properties of the filler. During sintering of compacts obtained through the powder metallurgy, the UDND particles absorb oxygen contained in the powder mixture with the formation of CO and CO_2 reducing gases. These gases destroy the oxide film covering the powder mixture particles and prevent oxidation during sintering, thereby reducing the total volume of gases in the powder mixture. At the same time, reducing gases accelerate the sintering process of the material. The combination of these factors ultimately reduces the residual porosity in the material which is validated by the calculated data. If the UDND particle volume reaches 3%, an increase in the carbon content in the material occurs. As a result, the filler particles are not fully oxidized, thereby increasing the number of pores in the material.

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