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Effective Mineral Coatings for Hardening the Surface of Metallic Materials

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Abstract—The structural changes that occur in the surface and surface layers of steel 20Kh13 and titanium alloy PT-3V (Russian designation) samples after each stage of hardening due to a formed mineral surface layer are studied by optical microscopy, transmission electron microscopy, and scanning electron microscopy. Electric spark alloying, pressing, and ultrasonic processing are used to reach the effect of volume compression of the base metal and the mineral in the plastic deformation zone. As a result, applied mineral particles concentrate in preliminarily created microvoids in a thin surface layer. The surface layer thus modified acquires a high hardness and wear resistance. Durometry shows that the hardness of the processed sample surfaces increases more than twofold. Therefore, the developed technology of creating a mineral coating can be used to increase the tribological properties of the surfaces of the parts, units, and mechanisms of turbine, pump, and mining equipment, which undergo intense wear during operation.

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INTRODUCTION

The commercial application of natural minerals for the hardening of the surface layers of structural materials is finding a niche due to the effects that result in an increase in the wear resistance and antifriction and other specific properties of friction pairs. This is also promoted by the development of technological procedures of formation of such layers. Nevertheless, it is necessary to comprehensively understand the physical processes that occur on the surface of structural materials (steels, alloys) covered by mineral coatings in order to predict their behavior in the friction pairs of various parts, units, and mechanisms and to improve a technological process.

The natural "sliding mirrors" of rock beds served as a prototype of the coatings formed on the surfaces of the working friction pairs. Historically, serpentinites were the first to be widely used to decrease the wear of machine elements [1]. Serpentinites represent the group of minerals of the subclass of layered silicates, which include a number of $Mg_3[Si_2O_5](OH)_4$ structural modifications and polytypes. Serpentinite usually contains Fe^{2+}, Fe^{3+}, Al, and Ni impurities and sometimes Ti, Mn, and Ca [2]. Serpentinites are the most widespread minerals but their characteristics are not most efficient for creating high-strength coatings on metallic products [3]. Serpentinites, i.e., the rock that mainly consists of serpentinite minerals and various impurities, are used in industry [3].

Certain types of mineral materials, which can sharply decrease the mechanical losses in friction pairs and ensure corrosion resistance and good flows around surfaces, are now used. The types of materials are determined according to the quantity and composition of impurities, the structure–phase state of the components, and some other signs [1, 3, 4].

The following parts of turbine and pump equipment are thought to be covered by mineral coatings: blades, shaft parts, and bearings operating under extreme conditions. The erosion wear of the blades of the last stages of heat and power stations is a well-known known and unsolved problem of power and machine building [5].

The long-term experience of operation of the last stages of high-power condensation and thermal steam turbines indicates that the erosion wear of the inlet and outlet edges of blades is one of the main causes that determine the reliability of their operation [5]. The degree of erosion wear of blades increases at the periphery. According to the results of studying the operation of 25 T-100-130 thermal turbines and 15 T-250/300-240 turbines [6, 7], the average resource of the blades of the last stages was 50 ths h, and damages appeared in the inlet and outlet edges of blades in the form of cracks induced by stress concentration because of drop impact erosion. The wear of the inlet and outlet edges of blades because of the erosion influence of a vapor flow up to the allowed value and because of the presence of unallowable defects in the blades (cracks, point and linear through blowouts) led to the necessity of changing the blades, i.e., to additional costs. Therefore, the problem of increasing the reliability and resource of the blades of the last stages of heat and power stations is challenging.

Taking into account the possibility of increasing the wear resistance and the anticorrosion properties of the metallic parts operating under extreme conditions (aggressive air atmosphere, water, oil, high temperatures) by creating a mineral surface layer [1, 3, 4, 8], we studied worn parts before and after the deposition of mineral layers. The purpose of this work is to study the structural changes in the surface and near-surface layers of steel and a titanium alloy covered with a mineral surface layer according to the technology developed in NPO Geoenergetika.

EXPERIMENTAL

Various modified mineral layers created according to the technology of NPO Geoenergetika were deposited onto the surfaces of metallic samples in the form of rings and disks 20Kh13 (Russian designation) steel (State Standard GOST 8560–78) and a PT-3V titanium alloy (State Standard GOST 19807–91).

The process of creating mineral layers consists in the introduction of nanocomposite mineral powder particles into microvoids in the metal surface to be hardened using an ultrasonic device and ball and roll knurling. As a result, a surface layer having high antifriction, wear-resistant, and extreme pressure properties is formed [4, 8].

A wear-resistant mineral layer was deposited onto the surface of the part with a special technological setup [9]. This setup can be used to perform electric spark alloying, ultrasonic processing, and the formation of surface layers with given tribotechnical properties [4]. The basic technology serves as the basis for further development of technologies to obtain the required characteristics of surface layers.

The total procedure of processing the surfaces of parts subjected to friction during operation includes the following two stages:

(i) electric spark processing and surface texturing,

(ii) alloying of preliminarily processed surfaces by mineral particles using the ultrasonic setup.

Depending on the method of pressing and minerals, we prepared coatings of six types. The mineral layer thickness was varied from 20 to 100 nm. In experiments, we analyzed the state of surface after each procedure by optical microscopy, transmission electron microscopy (TEM), and scanning electron microscopy (SEM).

When taking TEM micrographs, we used a system combining TEM and ion column FIB, which allowed us to cut electron-transparent sample segments using SEM [10, 11].

Micrographs of the surface structure of samples were taken with a Supra 40 scanning electron microscope equipped with an X-Flash energy dispersive X-ray spectrometer and a Quantax 4000 software package.

The microhardness was measured using a Fischersope H100 nanohardness tester.

RESULTS AND DISCUSSION

Depending on a technological problem, the second stage of surface treatment was performed either after the first stage or without conducting the first stage.

As the deposition of a mineral coating, electric spark processing increases the surface roughness, and surface smoothening is achieved using ball and roll knurling [4].

Figure 1 shows six types of surface structure in samples with various mineral coatings.

As follows from [3, 4, 8], quartz and serpentinite can be used to form the optimal composition of mineral materials for coatings on friction pairs and the parts of steam turbines in order to obtain satisfactory tribological parameters of the coatings.

In this work, we used a wide spectrum of mixtures based on quartz and serpentinite-group minerals with an optimized composition.

The average mineralogical (substance) composition of quartz SiO_2 is as follows:

Structure-phase composition of the base substance	α-Quartz + coesite + stishovite (90%)* and feldspar (10%)
Purpose	Material for antifriction and anticorrosion coatings
Grain hardness	*HV* 1400–2000
Material constitution of rock, %:	
SiO_2	90
carbonates (calcite) $CaCO_3$	9
impurities	1
Impurity composition	Leucoxene $CaTiSiO_5$, pyrite FeS_2, ilmenite $FeTiO_3$, arsenopyrite FeAsS, ilmenorutile $FeTi_2O_5$, magnetite Fe_3O_4, and iron chips Fe
Granule size distribution of minerals	SiO_2 (99%) < 50 μm, $CaCO_3$ < 1 μm, impurities < 15 μm
Type of milling	Fine
Average granulometric composition, wt %:	
0–5 μm	25
5–10 μm	35
10–15 μm	31
15–20 μm	7
>20 μm	2

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* Content of three modifications of silica SiO_2.

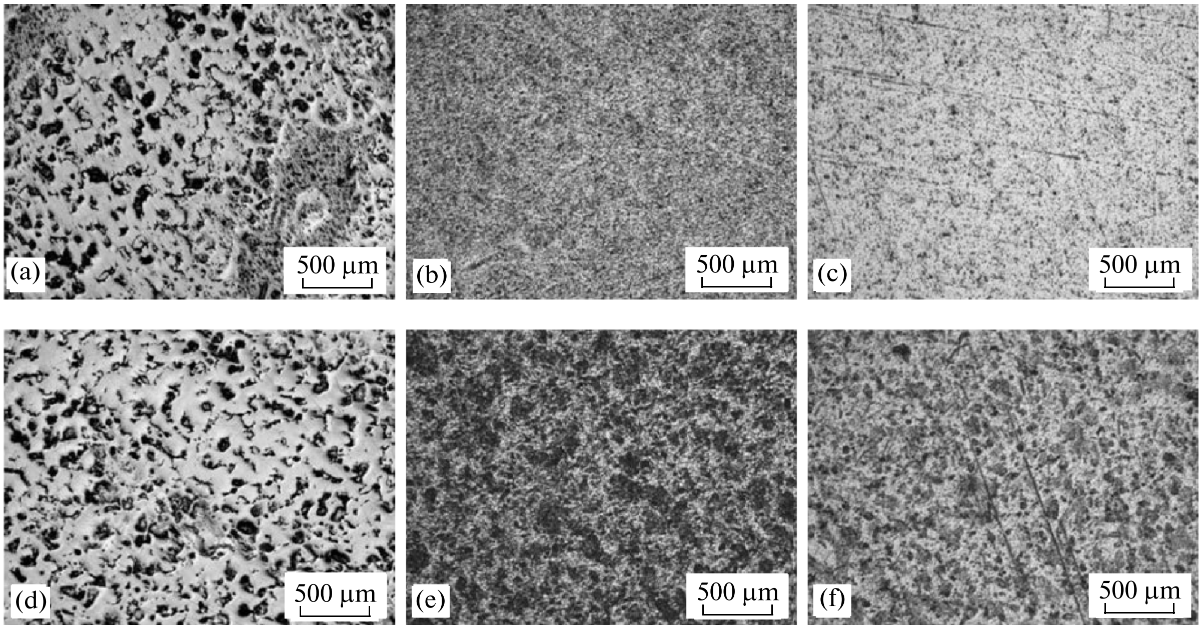

Fig. 1. Optical micrographs of mineral coatings applied onto steel 12Kh13-Sh samples.

The average mineralogical (substance) composition of the serpentines is as follows (base mineral formula is $Mg_6[Si_4O_{10}](OH)_8$):

Purpose	Material for antifriction coatings on machine parts
Average rock density, g/cm^3	2.67
Average material constitution of rock, wt %:	
serpentinite	65
olivines* and pyroxenes**	≤10
magnetite (unbound)	≤15
mica and chlorite	≤5
carbonates	5
other impurities	≤1
Total grain hardness	HV_{50} 350–470 HV_{20} 400–840
Hardness of unbound magnetite	HV_{20} 1100–1370
Average granulometric composition, wt %:	
0–10 μm	55
10–20 μm	35
20–30 μm	5
30–40 μm	3.5
>40 μm	1.5

The composition of the mineral materials for the working parts of steam turbines and steel and titanium rods (base mineral formula is $Mg_6[Si_4O_{10}](OH)_8$ + quartz SiO_2) is as follows:

Purpose	Composition for mineral coatings of steel and titanium rods
Material constitution, wt %:	
serpentinite	7.5
quartz	17.5
industrial oil I20	75

State of Surface after Electric Spark Processing

Steel 12Kh13-Sh (Russian designation) samples were subjected to electric spark processing and knurling (Fig. 2 shows the cross section of a steel sample after processing). Depending on the processing parameters, the zone of structural changes extended up to 4 μm.

Microstructural investigations showed the presence of a surface layer with a granular structure, which differs clearly from the volume structure. Note that the technological process results in a change in the surface of a metallic part rather than coating formation.

The study of the physical properties showed that the average hardness of the unprocessed surface of 12Kh13-Sh (Russian designation) steel, which was determined from indentation made with a Fischersope H100 nanohardness tester, is 2530 ± 80 MPa, and the

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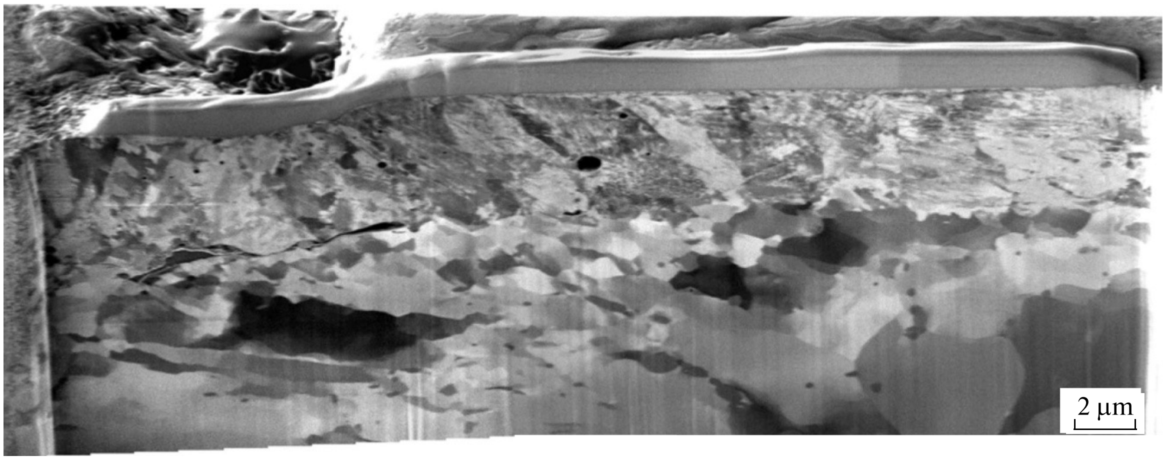
* Magnesia–iron silicate $(Mg,Fe)_2[SiO_4]$.

** Chain silicates.



Beam 300 kV	Magnification 20.0 kX	Tilt 43.8°	Scan H45.26 s	pA 11.0	HFW 15.2 μm

Fig. 2. TEM micrograph of the cross section of a processed steel 12Kh13-Sh sample (cross section was obtained with a focused ion beam).

hardness of the processed surface increases to 6300 ± 1000 MPa (Fig. 2). Similar results were obtained for a PT-3V (Russian designation) titanium alloy, in particular, the surface hardness increased by a factor of 2.2–2.5.

Thus, the proposed simple technological process is shown to be efficient: the use of electric spark alloying and ball and roll knurling leads to a significant increase in the surface hardness of a metallic part.

An advantage of the developed technology consists in the fact that the process is localized and the entire part is not heated; that is, the part sizes are retained. Using this technology, we can process only the regions that undergo friction. This finding widens the spectrum of metallic materials to be used in tribological processes, since the well-known surface processing technologies such as nitriding and carbonization are excluded [12].

State of Surface after Alloying with Serpentinites

Compositions based on serpentinites and/or quartz can be deposited both after the first stage of processing and independently, i.e., without the first stage. To provide a uniform distribution of submicrocrystalline particles on the surface, they are applied in the form of an oil suspension, and mixtures are used for creating a mineral layer and cannot be used for, e.g., a lubricant in an oil system with a pump. The surface of the part to be processes is submerged in a suspension or is wetted with it. Indentations (pits) are then created with the indenter of the ultrasonic device and filled with mineral particles with oil. Serpentinite and/or quartz particles are concentrated in these pits, which creates the following double effect that influences the tribological parameters: first, hardening is achieved around pits due to cold plastic deformation; second, the rate of formation of a liquid film increases (Fig. 3). The latter finding is very important, since it is known that microvoids of various shapes, diameters, and depths favor the formation of a hydrodynamic film at start–stop of, e.g., the bearings of a shaft neck and hinder the wear due to the fact that they significantly decrease the surface area of a mixed and boundary lubricant. According to [3, 4], the second stage of technology results in modified surfaces that ensure the minimum mechanical friction losses and have high wear resistance due to the solid "cushion" formed at the first stage [8]. Therefore, this technology [13] can be recommended to increase the tribological properties of the surfaces of the parts, units, and mechanisms of turbine, pump, and mining equipment, which undergo intense wear under various operating conditions.

SEM micrographs revealed a flaky morphology in the submicron range.

Figure 3 shows SEM images of a sample surface with the scheme of finding mineral composition elements. These elements are silicon, magnesium, and oxygen, which enter into the composition of serpentinites and are absent in the 12Kh13-Sh steel composition. The predominant location of these elements in indentations points to the fact that the surface of the 12Kh13-Sh (Russian designation) steel sample is alloyed by serpentinites with the indenter. It is also seen that the indentations containing serpentinites also have silicon and aluminum. These micrographs were taken during the identification of only one element.

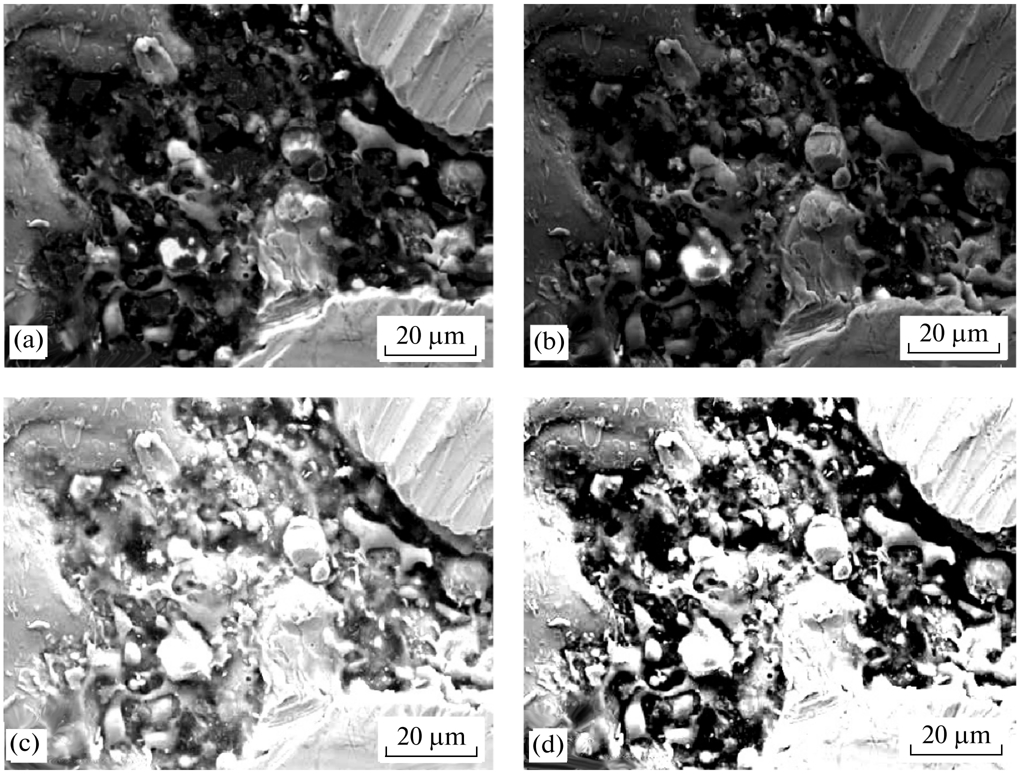


Fig. 3. SEM micrographs demonstrating the microrelief (indentations) of a steel 12Kh13-Sh sample alloyed with serpentinite with the scheme of finding its elements : (a) oxygen (black), (b) aluminum (white), (c) silicon (dark gray), and (d) magnesium (black).

Figure 4 shows the state of surface after only the second stage of technology. SEM micrographs demonstrate a network of voids and indentations or pits filled with alloying elements, namely, oxygen, silicon, and magnesium.

Micrographs taken at a higher magnification clearly demonstrate microvoids arbitrarily arranged over the entire working sample surface (Figs. 4a–4c). The arrangement of microvoids is chaotic. However, they occupy significant area. Therefore, it is the microvoids that hold a lubricant, which improves the working characteristics of friction pairs under extreme operating conditions (when the supply of a lubricant decreases) [8].

CONCLUSIONS

(1) We determined changes in the surface layer of steel 20Kh13 and titanium alloy PT-3V samples (Russian designation) after each stage of creating a mineral layer according to a proposed technology. Using a simple technological process, we increased the surface hardness of the samples more than twofold.

(2) Microstructural investigations showed that the surface layer has a structure that differs clearly from the volume granular structure. The developed technological process changes the surface of a metallic part. Depending on the processing parameters, the transformed modified layer extended up to 4 μm from the surface.

(3) One of the advantages of the developed technology consists in the fact that the process is localized and the entire part is not heated; that is, the part sizes are retained. Using this technology, we can process only the regions that undergo friction in friction pairs.

(4) Using electric spark alloying, pressing, and ultrasonic processing, we were able to reach the effect of volume compression of the base metal and mineral nanoparticles in the plastic deformation zone. As a result, the surface layer of the parts was hardened. This "cold" processing creates a thin surface layer, which contains mineral particles concentrating in preliminarily formed microvoids. Thus, a modified layer having a high hardness and wear resistance forms in the surface layers of steel or titanium alloy samples.

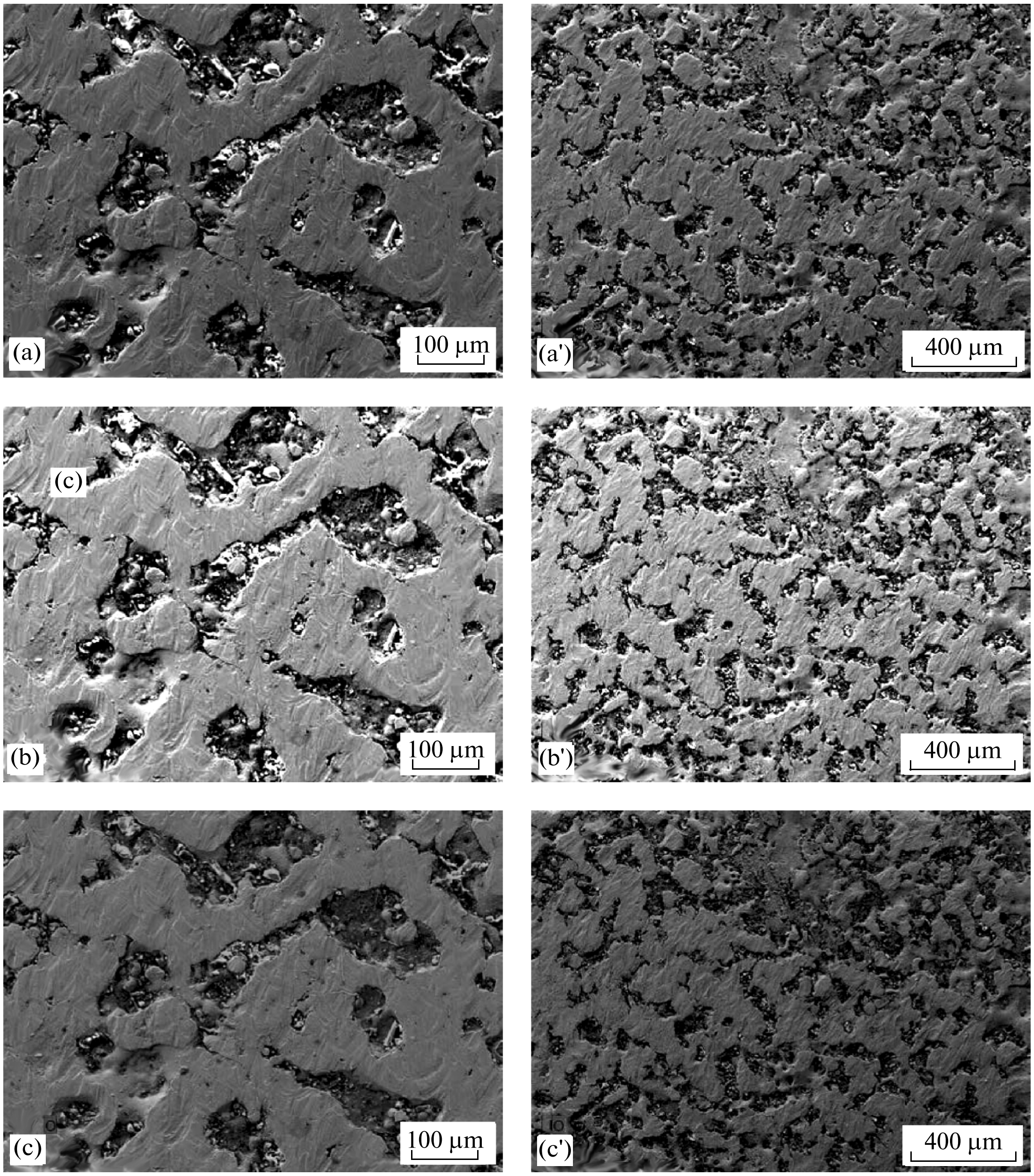


Fig. 4. SEM micrographs ((a–c) ×1000, (a'–c') ×500) of a steel 12Kh13-Sh sample alloyed with serpentinite with the scheme of finding its elements : (a, a') silicon (white); (b, b') magnesium (black); and (c, c') oxygen (black).

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