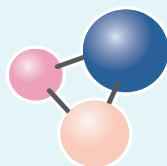


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4 bld. 1 Leninskiy Pros., Moscow 119049, Russian Federation

Phone: +7 (495) 638-45-35. E-mail: izv.vuz@misis.ru

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Research article

Научная статья



Evolution of the structural-phase state of steel swarf during its processing into a powdered product

E. N. Korosteleva^{1, 2}, I. O. Nikolaev¹¹ Institute of Strength Physics and Materials Science, Siberian Branch of the Russian Academy of Sciences

2/4 Akademicheskii Pros., 634055 Tomsk, Russia

² National Research Tomsk Polytechnic University

30 Lenina Pros., Tomsk 634050, Russia

 elenak@ispm.su

Abstract. Industrial waste recycling is not only linked to significant environmental challenges but also to the recovery of material resources. Typically, these recovered materials are reused within the same technological niche where the waste was generated, often through remelting or adding them to the charge. This study presents an alternative approach that enables the production of a functional powder product from steel swarf during the recycling process, which can subsequently be utilized in the creation of powder metal matrix composites. The initial structure of the swarf, following the turning of a steel billet, was examined using scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis after a processing complex involving additional oxidation and grinding. This analysis aimed to assess the degree of transformation in the structural-phase state of the steel swarf during its processing. It was observed that the swarf post-turning exhibited a complex morphological structure with an uneven distribution of oxygen and carbon. The oxygen present in the initial state of the swarf was insufficient to form a noticeable volume of oxides detectable by X-ray diffraction. However, SEM revealed individual oxide inclusions, each no more than 5 μm in size, located sporadically. Additional oxidation followed by grinding in a vibrating mill altered the structure of the steel swarf, increasing the volume fraction of oxide phases. The study's findings indicate that the resulting powder from recycled steel swarf is essentially a metal matrix composite with oxide inclusions based on an iron matrix, which holds potential for various future powder technologies.

Keywords: steel swarf, grinding, oxidation, structure, iron oxides, composite powders, sintering

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Эволюция структурно-фазового состояния стальной стружки в процессе ее переработки в порошкообразный продукт

Е. Н. Коростелева^{1, 2}, И. О. Николаев¹

¹ Институт физики прочности и материаловедения Сибирского отделения РАН
Россия, 634055, г. Томск, пр-т Академический, 2/4

² Национальный исследовательский Томский политехнический университет
Россия, 634050, г. Томск, пр-т Ленина, 30

✉ elenak@ispms.ru

Аннотация. Утилизация отходов промышленного производства связана не только с решением экологических проблем, но и с повторным использованием материальных ресурсов. Чаще всего возвращаемые в производство материальные ресурсы стараются применить в той же технологической нише, где формировались сами отходы, через их переплавку или добавление в шихту. В данной работе предлагается альтернативный подход, позволяющий при утилизации стальной стружки получать функциональный порошковый продукт, который можно в дальнейшем использовать при создании порошковых металломатричных композитов. С помощью растровой электронной микроскопии и рентгенофазового анализа была исследована структура стружки в исходном состоянии (после токарной обработки заготовки из стали 45) и после дополнительного комплекса обработки (окисления и измельчения) с целью оценки степени трансформации ее структурно-фазового состояния в процессе переработки. Показано, что стружка после токарной обработки имеет сложный морфологический вид с неоднородным распределением кислорода и углерода. Растровая электронная микроскопия исходного состояния стружки позволила выявить отдельные включения оксидов размерами не более 5 мкм в удаленных друг от друга локальных местах. Однако небольшой совокупный объем и индивидуальный размер оксидных включений затруднили идентификацию этих фаз с помощью рентгенодифракционного метода. Дополнительное окисление с последующим измельчением в вибромельнице трансформирует структуру стальной стружки, повышая объемную долю оксидных фаз. Результаты проведенных исследований показали, что полученный порошок из переработанной таким образом стальной стружки представляет собой фактически металломатричный композитный материал с оксидными включениями на основе железной матрицы, который можно использовать в дальнейшем в разных порошковых технологиях.

Ключевые слова: стальная стружка, измельчение, окисление, структура, оксиды железа, композиционные порошки, спекание

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Introduction

In the framework of resource efficiency and waste utilization strategies, powder metallurgy technologies are highly preferable. This is particularly evident in the recycling of metallic waste within the engineering sector [1–3]. Metal processing on various machines contributes significantly to the total volume of manufacturing waste. Regardless of the processing type and tools used, metal swarf is always produced when manufacturing any part and is often recycled as metal scrap in metallurgical processes [2; 3; 5–7].

Traditionally, metalworking waste is reused either in remelting processes or as a charge for bulk powder blanks and coatings [1; 2; 4–13]. The range of materials studied is broad, encompassing traditional steels, cast irons [5; 6], non-ferrous metals, and alloys [13–15]. Typically, the first stage of recycling metalworking

waste involves cleaning it of impurities and contaminants [16–19]. These primarily include organic contaminants from various lubricating-cooling fluids (LCF) and excess oxygen from oxidation processes during machine processing and waste storage [16]. However, these “harmful” impurities and contaminants can be sources of additional elements for forming a functional multicomponent structure in the recycled waste, ultimately transforming it into a powder form.

Several factors motivate this task. First, the swarf structure differs from the original metal billet due to the defect structure formed during cutting [20]. Second, processing modes and environments, including coolant use and oxidation processes, significantly influence it. Third, the swarf is a sufficiently activated material that can undergo additional processing, including oxidation and crushing, to convert it into a powder form [19; 21; 22].

Considering waste from processing steel billets, the resulting swarf can serve as a convenient raw material for preparing powder compositions with a specific combination of components. For example, excess oxygen and oxidation products in the waste from processing steel billets can form oxide inclusions in the steel matrix. The proposed combination of components ($\text{Fe} + \text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4 + \text{FeO}$) can act as a precursor for further use in other multicomponent powder compositions [21–23]. The oxide phases formed after processing steel swarf, along with the iron itself, can actively interact with titanium, aluminum, or other elements [24; 25], creating prospects for developing new metal-matrix composites. Converting steel swarf fragments into powder with a specific phase composition, morphology, and particle dispersion for further use in powder mixtures is essential.

Various methods can grind steel swarf, including electro-physical [8] or simple mechanical methods [19]. Depending on the intended application of the powder blanks, the technological parameters of crushing are determined to obtain powder particles of the required sizes from the recycled waste. Mechanical grinding using crushers or vibratory mills with steel balls is most common [19; 21]. The swarf structure transforms at each processing stage.

Unfortunately, there are currently few studies in this area, making it challenging to predict the possible evolution of the structural-phase state of metalworking waste for further use. If the products of processing steel swarf are considered potential components in powder mixtures, it is interesting to study the evolution of the structure of steel swarf from the initial turning process to converting it into powder form using additional oxidation and grinding. Such analysis is significant in developing new composite materials with oxide inclusions, which was the aim of this study.

Materials and methods

Steel billets made from carbon steel 45, the most common alloy in engineering production, were used as the research material. Its chemical composition according to GOST 1050-2013 is as follows (wt. %):

C	0.42–0.50
Si	0.17–0.37
Cu	≤ 0.25
As	≤ 0.08
Mn	0.50–0.80
Ni	≤ 0.25
P	≤ 0.035
Cr	≤ 0.25
S	≤ 0.04

Steel swarf was obtained at a machine-building enterprise after the facing operation without using lubricating-cooling fluids (LCF). Its general appearance in the initial state, microstructure of its fragments after etching with a 4 % aqueous solution of nitric acid, phase composition, and surface morphology after machining are shown in Fig. 1. It is worth noting that the results of X-ray phase analysis of swarf from steel 45 did not reveal lines of oxide phases, showing a practically standard set of phases characteristic of this grade of steel (Fig. 1, *d*), consistent with previous results [26]. The size of swarf fragments after machining the steel billet was 3–7 mm in width and 10–30 mm in length, necessitating grinding using a vibratory mill designed by ISPMS SB RAS (Russia). Grinding was carried out in an air environment for 10 hours with steel balls of 15 mm diameter at a swarf-to-balls mass ratio of 1:30.

Despite the machining conditions and associated processes of temperature fluctuations, oxygen saturation, and work hardening, the swarf remained ductile, complicating the grinding process. Therefore, additional oxidation of the swarf fragments was employed, increasing their brittleness and enabling the production of powder with a wide range of particle dispersity – from 50 to 350 μm . To assess the compressibility and sinterability of the resulting powder, cylindrical samples 10–13 mm high and 10 mm in diameter were pressed and sintered in a vacuum furnace at temperatures ranging

$$\theta = \left(1 - \frac{\rho_{\text{smp}}}{\rho_{\text{theor}}} \right) \cdot 100 \%,$$

where ρ_{smp} is the actual density of the sample (g/cm^3), and ρ_{theor} is the theoretical density calculated by the additive method for powder particles from the recycled steel swarf, assuming at least 30 vol. % oxide phase and the remainder as a solid solution based on iron corresponding to steel 45.

Since the quantitative values of the oxide fraction are averaged, determining the exact theoretical density is challenging. Therefore, to assess the pore content, the quantitative metallography method was additionally used. The structural-phase changes in the steel swarf were investigated by comparing the results of structural and elemental analyses and the morphology of its fragments in the initial state after turning the steel billet and a set of subsequent actions – oxidation, grinding, pressing, and vacuum sintering.

The studies were conducted using optical metallography, X-ray phase analysis (XRD), and scanning electron microscopy (SEM) with energy-dispersive

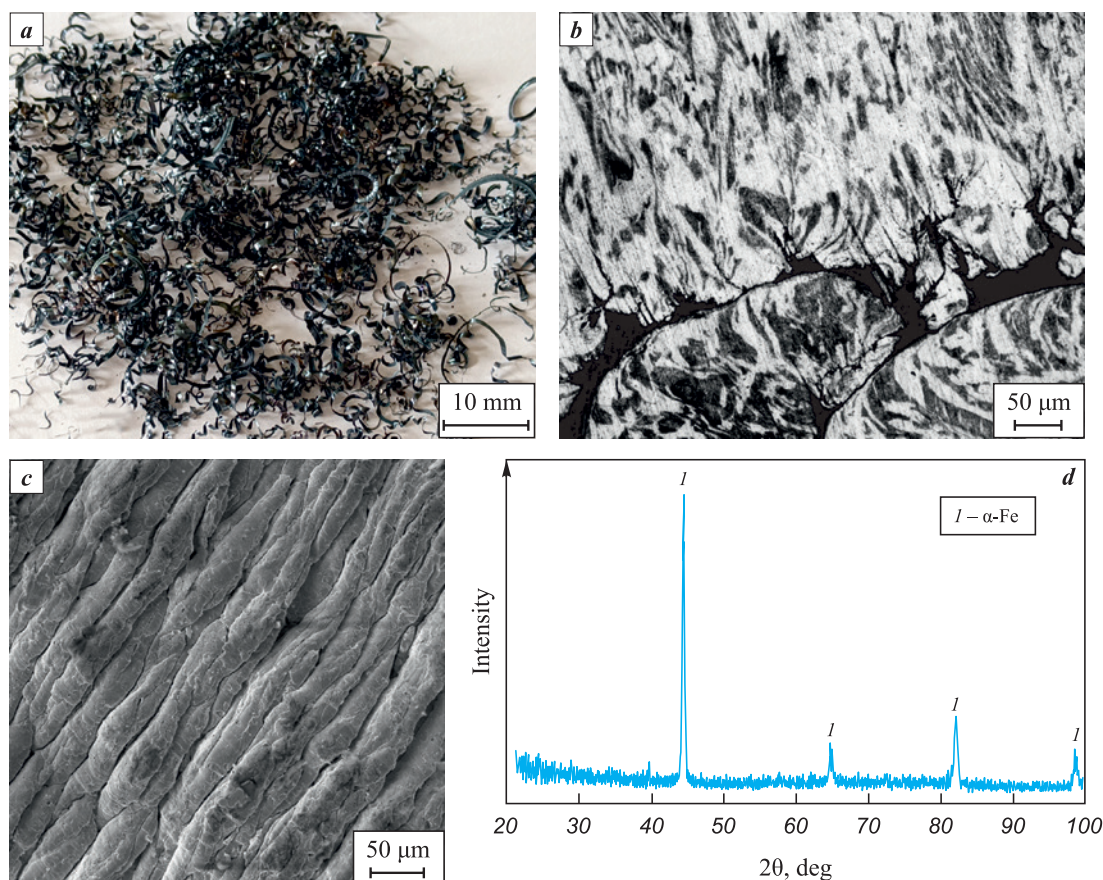


Fig. 1. General appearance of steel swarf (*a*), microstructure of its fragments (*b*), SEM image of one of the surface areas (*c*), and their phase composition (*d*) after machining

Рис. 1. Общий вид стружки из стали 45 (*a*), микроструктура ее фрагментов (*b*), РЭМ-изображение одного из участков поверхности (*c*) и фазовый состав после металлообработки (*d*)

microanalysis. These analyses were performed using the equipment of the Tomsk Regional Shared-Use Center of NR TSU and the Shared-Use Center of ISPMs SB RAS. The specific equipment used included: optical microscope AXIOVERT-200MAT (Carl Zeiss, Germany), X-ray diffractometers XRD (Shimadzu 6000, Japan) and DRON-8 (NPP Burevestnik, Russia), and scanning electron microscope MIRA 3LMU (TESCAN, Japan).

Results and discussion

The preliminary analysis of the steel swarf showed that after machining without using lubricating-cooling fluids (LCF), a highly defective structure formed on its surface (Fig. 2). Elemental analysis revealed an uneven distribution of carbon and oxygen (Fig. 2, *c*, *d*). The noticeable presence of oxygen on the swarf surface suggests the formation of a certain volume of iron oxides. However, the XRD analysis did not detect oxide phases (Fig. 1, *d*) in sufficient quantity for identification.

It can be assumed that the oxidation processes during initial machining primarily contribute to the formation of amorphous oxide films, which are not visible to XRD, preventing the formation of iron oxide crystallites in significant quantities. Scanning electron microscopy at high magnification revealed individual inclusions that can be attributed to iron oxides based on the elemental distribution map in the local area of the swarf surface (Fig. 3). However, their size and quantity fall below the sensitivity threshold of the X-ray diffractometer.

Since the steel swarf remained ductile after turning, and the oxide phase content was minimal, it was decided to further oxidize the swarf fragments. This aimed not only to increase the iron oxide content but also to enhance the swarf's brittleness. Thus, the oxidation process would achieve two goals: effective swarf grinding and increased iron oxide content. The simplest methods for this were used: heating in air or soaking in water followed by drying.

Despite the straightforward task of oxidizing carbon steel swarf, the specifics of iron oxidation must be

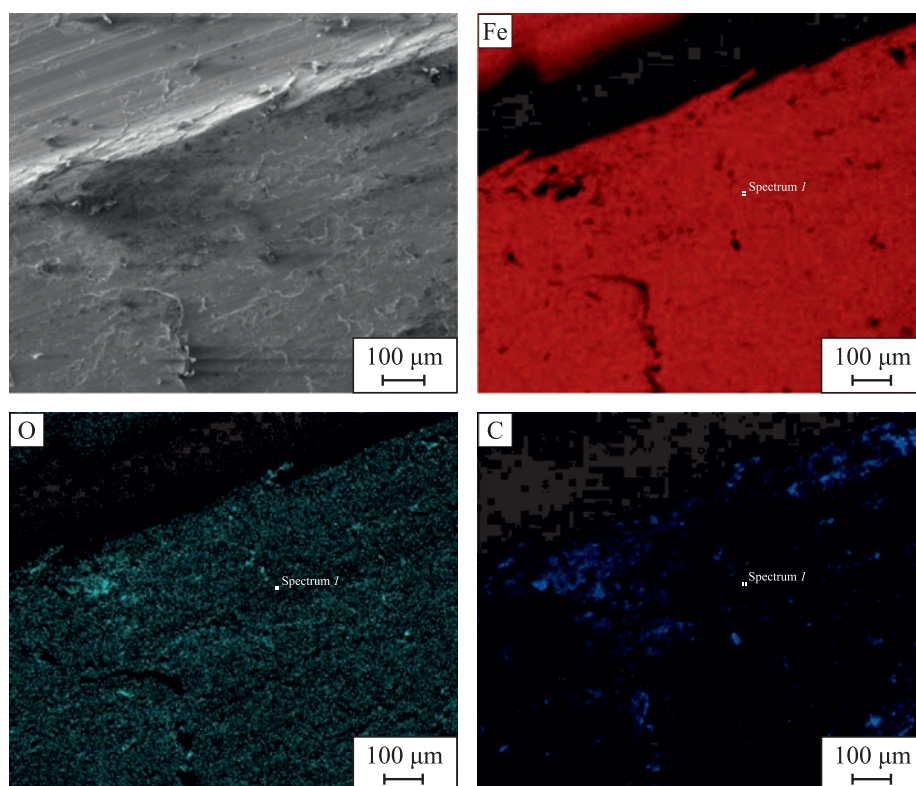


Fig. 2. SEM image of the cut surface and elemental distribution maps of iron, oxygen, and carbon in the steel swarf after processing the steel 45 billet

Рис. 2. РЭМ-изображение поверхности среза и карты распределения железа, кислорода и углерода в стальной стружке после обработки заготовки из стали 45

considered. Iron forms several oxides: FeO , Fe_2O_3 and Fe_3O_4 . The oxidation process also goes through several stages, where one oxide can transform into another under certain conditions or act as a barrier to its formation. There are also specific temperature regimes

that predetermine the formation of a particular group of oxides [27].

When heating steel swarf in a muffle furnace in air up to 400°C , XRD results showed that such thermal treatment not only removed the work hardening from

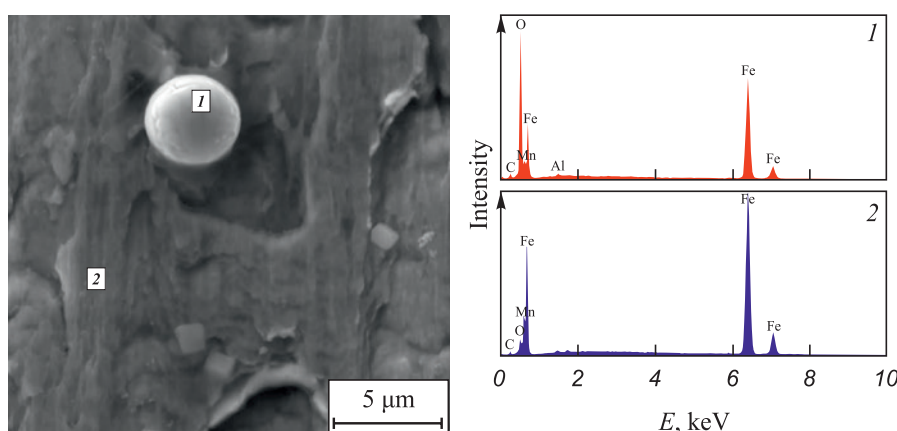


Fig. 3. SEM image ($\times 10,000$) and EDX spectral analysis results of local points on the surface of the steel swarf
1 – area corresponding to the iron oxide spectrum; 2 – area of the base material

Рис. 3. РЭМ-изображение ($\times 10\,000$) и результаты спектрального анализа (ЭДС) локальных точек на поверхности стальной стружки

1 – область, соответствующая спектру оксида железа; 2 – область основного материала

machining, which hindered grinding in the vibratory mill but also formed carbide-containing phases based on Fe_2C , FeC , FeCO_3 or $\text{Fe}(\text{CO})_5$ (Fig. 4, *a*). Since the lines of these phases were few and their intensity very weak, correctly identifying these phases is challenging and requires separate investigation. It is assumed that a mixture of carbide or oxycarbide phases primarily formed on the surface of the swarf fragments may be present.

The main goal of the experiment was to test different methods to increase the iron oxide content in the steel swarf. Therefore, *X*-ray phase analysis focused on identifying those oxides not detected by XRD after thermal treatment.

Another oxidation method involved soaking the swarf in water for at least 48 h. Wetting with water followed by air drying at room temperature allowed XRD to detect up to 30–40 vol. % iron oxides within 48 h (Fig. 4, *c*). There remains a challenge

in distinguishing the phases of magnetite Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ by *X*-ray diffraction, requiring further study. Additionally, an option was explored to obtain powdered fragments from swarf waste by precipitating the suspension of ground steel 45 swarf products from water after evaporation (Fig. 4, *b*).

After drying the aqueous solution, a fine powder was obtained. Phase analysis revealed a complex configuration of iron dihydroxycarbonate $\text{Fe}_2(\text{OH})_2\text{CO}_3$ in the presence of iron oxides. Since this powder product had a very complex composition (requiring separate study) and the productivity of this method was significantly lower than that of the conventional method of soaking in water, drying, and subsequent grinding, further research focused on the sifted powder from the ground swarf after soaking in water.

Structural-phase and elemental analyses of the pre-oxidized and ground swarf showed that during

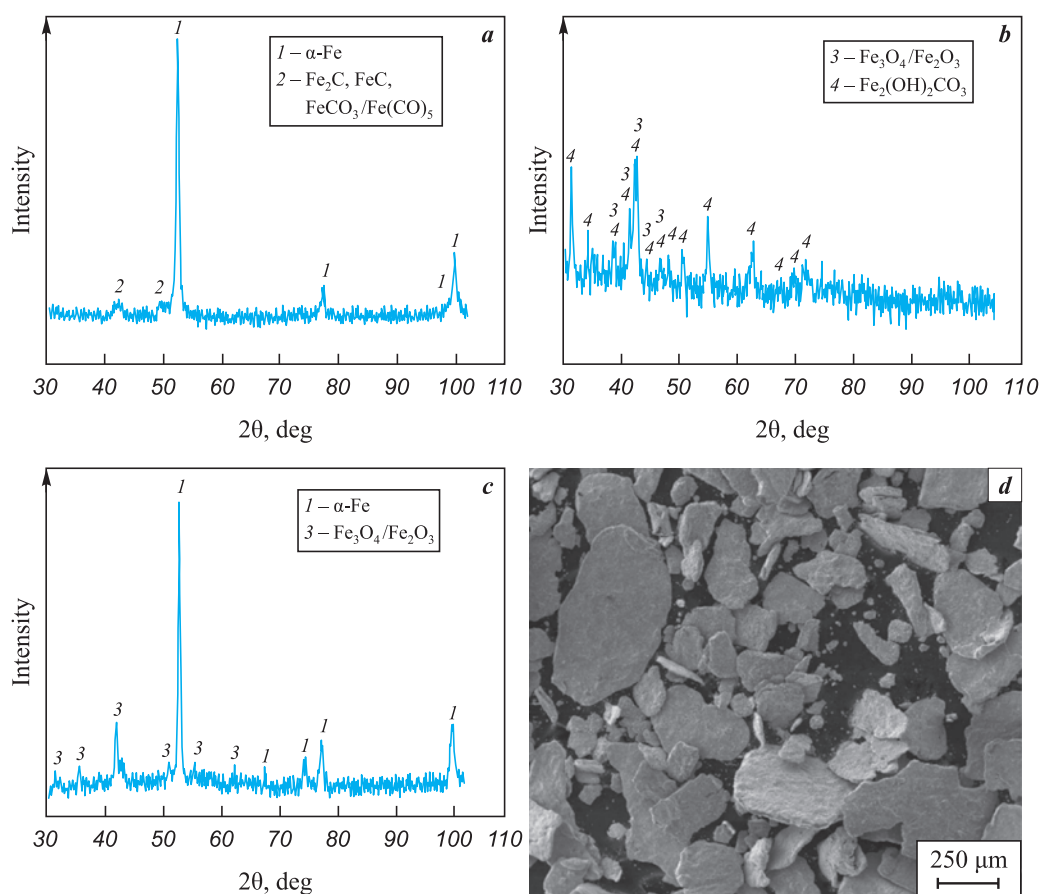


Fig. 4. Phase composition (*a–c*) and general appearance (*d*) of metal ground steel 45 swarf

- a* – swarf after annealing in air in a muffle furnace at 400 °C;
- b* – precipitated suspension after evaporation from an aqueous solution with steel swarf;
- c* and *d* – swarf after soaking in water for 48 h and drying at room temperature

Рис. 4. Фазовый состав (*a–c*) и общий вид (*d*) измельченной металлической стружки из стали 45

- a* – стружки после отжига на воздухе в муфельной печи при $t = 400$ °C;
- b* – осажженной взвеси после испарения из водного раствора со стальной стружкой;
- c* и *d* – стружки после выдержки в воде в течение 48 ч и сушки при комнатной температуре

the selected comprehensive treatment with oxidation in water and intensive mechanical crushing, the fragments of steel 45 swarf transform into a composite metal matrix powder material (Fig. 5). The particles consist of an α -Fe matrix, with iron oxides Fe_2O_3 or Fe_3O_4 as inclusions. It is noteworthy that the oxide phases primarily form on the surface of the ground oxidized swarf fragments (Fig. 5, *a*), while the original structure is preserved inside the particles.

The swarf fragmented into particles of a wide size range – from large fragments (300–350 μm) to small ones (20–50 μm). The presence of a significant amount of oxides (at least 30 vol. %) could pose challenges for compacting the obtained powder. Therefore, samples were pressed at a low pressure (350–400 MPa) without adding any plasticizers to test this.

Despite the presence of oxides, the powder was well-compacted, and under the selected pressing load, the residual porosity of the samples was about 40 %. Subsequent vacuum sintering of the pressed samples led to a reduction in porosity due to shrinkage, the intensity of which increased with the sintering temperature (see the Table).

Relative change in volume and porosity of compacts from recycled steel swarf after vacuum sintering

Относительное изменение объема и пористости прессовок из переработанной стальной стружки после вакуумного спекания

Sintering temperature, °C	$\Delta V/V_0$, %	$\Delta\theta/\theta_0$, %
1000	5.9	4.2
1200	25.0	10.5

Despite the presence of oxides, the powder was well-compacted, and under the selected pressing load, the residual porosity of the samples was about 40 %. Subsequent vacuum sintering of the pressed samples led to a reduction in porosity due to shrinkage, the intensity of which increased with the sintering temperature (see the Table). The structural-phase state of the powder compact sintered at 1000 °C is shown in Fig. 6. XRD results of the obtained compacts indicated that the formed group of iron oxides $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$ transitions to monoxide FeO, with α -Fe being the primary phase (Fig. 6, *a*). The interparticle contact zones

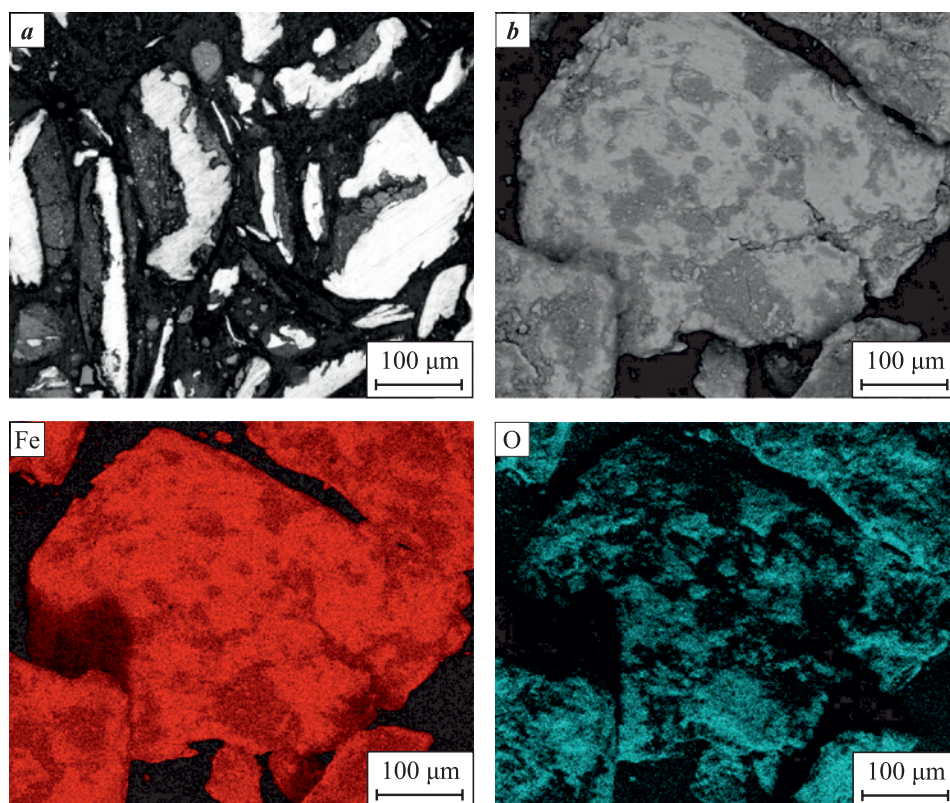


Fig. 5. Metallographic (*a*) and SEM (*b*) image of crushed particles of treated steel swarf with elemental distribution maps of iron and oxygen

Рис. 5. Металлографическое (*a*) и РЭМ (*b*) изображения дробленых частиц обработанной стальной стружки с картами распределения железа и кислорода

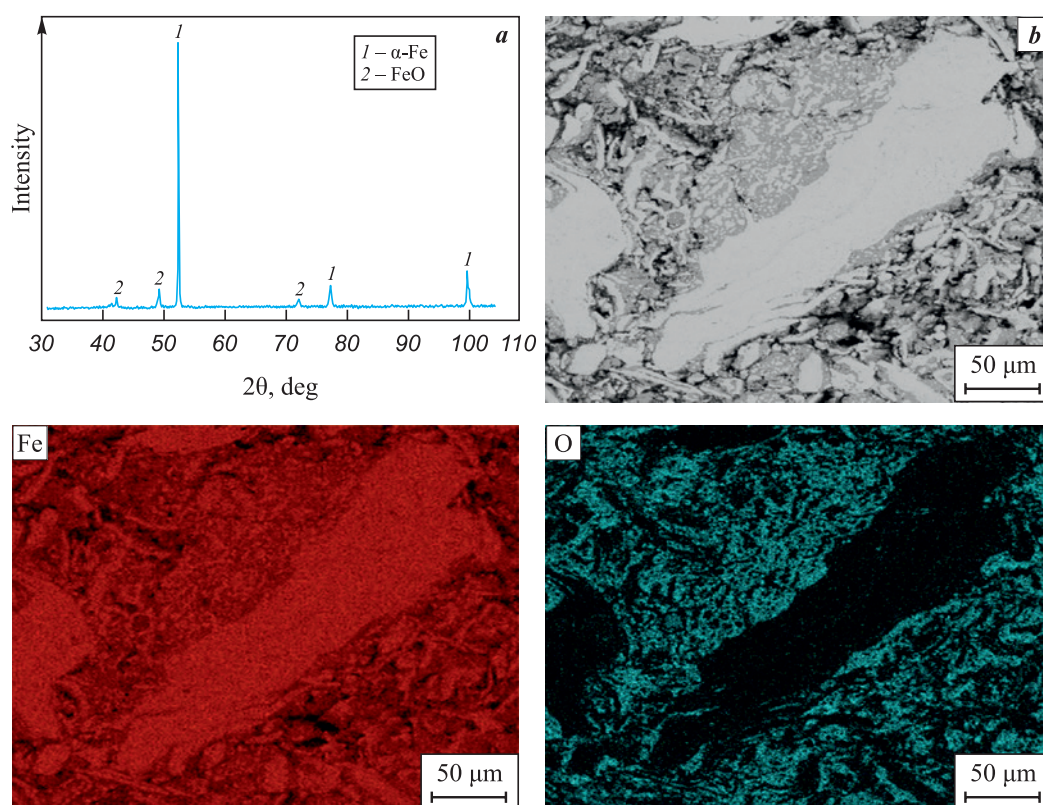


Fig. 6. Phase composition (a), microstructure (b) and elemental distribution maps of iron and oxygen in the compact sintered at 1000 °C from recycled steel swarf powder

Рис. 6. Фазовый состав (a), микроструктура (b) и карты распределения железа и кислорода в спеченной при $t = 1000$ °C прессовке из порошка переработанной стальной стружки

are predominantly filled with oxide components, while the main particle area is almost free of oxygen (Fig. 6). This structural configuration hinders the sintering of fragmented steel swarf particles due to the oxide-containing periphery acting as a barrier. The oxygen-rich extended regions in the recycled swarf powder particles can potentially play an active role in contact interactions with other powder components, such as aluminum or titanium [24], and participate in accompanying reduction reactions or intermetallic synthesis, which is a separate research topic. It is worth noting that the structural-phase state formed in the recycled steel swarf powder could be of interest for other prospective uses [28; 29], especially where the presence of iron oxides is relevant.

Conclusions

1. Steel swarf after turning operations on steel 45 billets exhibits specific structural features due to the deformation and physicochemical processes associated with machining. In its initial state, it demonstrates a structure with an uneven distribution of carbon and oxygen, localized in certain areas as fine inclusions within the steel matrix.

2. The XRD analysis of the swarf in its initial state revealed a phase composition identical to that of the steel 45 billet, with the swarf fragments remaining ductile. Additional oxidation of the metalworking waste in water promotes the growth of the oxide phase and facilitates the grinding process of the swarf in a vibratory mill, yielding particles sized 50–350 μm.

3. The analysis of the resulting powders from the oxidized and ground steel 45 swarf in the vibratory mill showed that the powder particles are a metal matrix product with oxide inclusions predominantly in the surface layers. Despite the presence of at least 30 vol. % iron oxides, the powder is well-pressed and sintered, demonstrating volumetric shrinkage and reduced porosity.

4. The elongated regions of oxide phases formed in the ground swarf fragments are active structural inclusions that can interact with additional powder components containing other elements, such as aluminum or titanium. This allows the investigated powder from steel swarf to be considered a potential precursor or oxide-containing component for producing multicomponent metal matrix composites with an oxide phase, utilizing waste from the machine-building industry.

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Information about the Authors

Elena N. Korosteleva – Cand. Sci. (Eng.), Associate Professor at the Department of Mechanical Engineering, School of Advanced Engineering Technologies, National Research Tomsk Polytechnic University; Senior Researcher at the Laboratory of Physics of Powder Material Consolidation, Institute of Strength Physics and Materials Science of the Siberian Branch of the Russian Academy of Sciences (ISPMS SB RAS)

 **ORCID:** 0000-0002-4363-3604

 **E-mail:** elenak@ispms.ru

Ivan O. Nikolaev – Research Assistant at the Laboratory of Physics of Powder Material Consolidation, ISPMS SB RAS

 **ORCID:** 0000-0003-4529-6477

 **E-mail:** rmkast97@gmail.com

Сведения об авторах

Елена Николаевна Коростелева – к.т.н., доцент отделения машиностроения Инженерной школы новых передовых технологий, Национальный исследовательский Томский политехнический университет (НИ ТПУ); ст. науч. сотрудник лаборатории физики консолидации порошковых материалов, Институт физики прочности и материаловедения Сибирского отделения Российской академии наук (ИФПМ СО РАН)

 **ORCID:** 0000-0002-4363-3604

 **E-mail:** elenak@ispms.ru

Иван Олегович Николаев – лаборант-исследователь лаборатории физики консолидации порошковых материалов, ИФПМ СО РАН

 **ORCID:** 0000-0003-4529-6477

 **E-mail:** rmkast97@gmail.com

Contribution of the Authors**Вклад авторов**

E. N. Korosteleva – determined the research objective, formulated the research task, planned the experiments, analyzed and summarized the results, and wrote and edited the manuscript.

I. O. Nikolaev – prepared the experimental material and samples, conducted structural studies, participated in the discussion of the results, and prepared the illustrations.

Е. Н. Коростелева – определение цели работы, постановка задачи исследований, планирование экспериментов, проведение анализа и обобщение полученных результатов, написание и редактирование текста статьи.

О. И. Николаев – подготовка экспериментального материала и образцов, проведение структурных исследований, участие в обсуждении результатов, оформление иллюстраций.

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Research article

Научная статья



Experimental study of the feasibility of producing materials based on the metastable phase Ti_2Fe through explosive compaction and heat treatment

A. V. Krokhalev, V. O. Kharlamov[✉], D. R. Chernikov,
S. V. Kuzmin, V. I. Lysak

Volgograd State Technical University
28 Lenin Prosp., Volgograd 400005, Russia

✉ harlamov_vo@mail.ru

Abstract. The primary regularities in the formation of the structure and phase composition of Fe–Ti system materials, which are promising for hydrogen storage under explosive compaction of titanium and iron powder mixtures, are considered. It has been established that under a loading regime ensuring shock-wave compression pressure $P = 11.5$ GPa and heating in the falling shock wave to 777°C , the powder mixture is compacted to an almost non-porous state due to the uniform plastic flow of particles in a direction perpendicular to the direction of shock compression. Under more severe loading conditions ($P = 12.5$ GPa and $t = 831^\circ\text{C}$), a monolithic state is also achieved, but the deformation character of the powder mixture component particles changes fundamentally: plastic deformation of the particles is localised in their surface layers and has a pronounced jet character with the formation of specific “vortices”. The influence of the plastic deformation mechanism of powder particles on the formation process of the metastable intermetallic phase Ti_2Fe with increased hydrogen capacity has been discovered. It has been established that solid layers of Ti_2Fe up to $20\ \mu\text{m}$ thick are formed at the contact boundaries of iron and titanium particles only in the case of jet flows of surface layers of particles. It has been shown that the cause of this effect is the local heating of the contact areas to a temperature above 1085°C , which according to the phase diagram of the Ti–Fe system, is the minimum temperature for the existence of a liquid phase in it. It has been demonstrated that an effective method for producing materials based on Ti_2Fe is the combination of explosive compaction of Fe and Ti powder mixtures and subsequent heat treatment with heating to 1100°C (reactive sintering in the presence of a liquid phase).

Keywords: explosive powder compaction, metastable intermetallic Ti_2Fe , hydrogen capacity, heat treatment, reactive sintering in the presence of a liquid phase

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Экспериментальное исследование возможности получения материалов на основе метастабильной фазы Ti_2Fe с помощью взрывного прессования и термической обработки

А. В. Крохалев, В. О. Харламов[✉], Д. Р. Черников,
С. В. Кузьмин, В. И. Лысак

Волгоградский государственный технический университет
Россия, 400005, г. Волгоград, пр-т им. Ленина, 28

✉ harlamov_vo@mail.ru

Аннотация. Рассмотрены основные закономерности формирования структуры и фазового состава материалов системы Fe–Ti, перспективных для хранения водорода, при уплотнении взрывом порошковых смесей титана и железа. Установлено, что при использовании режима нагружения, обеспечивающего давление ударно-волнового сжатия $P = 11,5$ ГПа и разогрев в падающей ударной волне до 777 °C, происходит уплотнение порошковой смеси до практически беспористого состояния за счет равномерного пластического растекания частиц в направлении, перпендикулярном направлению ударного сжатия. При более жестком нагружении ($P = 12,5$ ГПа и $t = 831$ °C) также достигается монолитное состояние, но характер деформации частиц компонентов порошковой смеси принципиально изменяется: пластическая деформация частиц локализуется в их поверхностных слоях и имеет ярко выраженный струйный характер с образованием специфических «завихрений». Обнаружено влияние механизма пластического деформирования частиц порошка на процесс образования метастабильной интерметаллидной фазы Ti_2Fe с повышенной водородной емкостью. Установлено, что сплошные прослойки Ti_2Fe толщиной до 20 мкм формируются на границах контактирования частиц железа и титана лишь в случае реализации струйных течений поверхностных слоев частиц. Показано, что причиной подобного эффекта является локальный разогрев приконтактных областей до температуры выше 1085 °C, являющейся, в соответствии с диаграммой состояния системы Ti–Fe, минимальной для существования в ней жидкой фазы. Показано, что эффективным методом получения материалов на основе Ti_2Fe является совмещение взрывного прессования смеси порошков Fe и Ti и последующей термической обработки с нагревом до 1100 °C (реакционное спекание в присутствии жидкой фазы).

Ключевые слова: прессование порошков взрывом, метастабильный интерметаллид Ti_2Fe , водородная емкость, термическая обработка, реакционное спекание в присутствии жидкой фазы

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Introduction

The development of hydrogen energy imposes ever-increasing demands on hydrogen storage systems [1]. One of the most promising and safe methods for hydrogen storage is the use of hydride-forming intermetallics [2]. For example, the volumetric density of hydrogen in hydrides based on intermetallics ranges from approximately 60 to 100 kg/m³, whereas in the gaseous state, even at a pressure of 400 bar, it is only about 20 kg/m³ [3]. Such high values of hydrogen capacity enable the creation of anode materials for metal hydride batteries with a discharge capacity reaching 400 mA·h/g [1].

In addition to the currently most widespread intermetallic $LaNi_5$, one of the most attractive materials for

hydrogen storage is the intermetallic $TiFe$, which is characterized by low cost and the ability to operate at low pressures and ambient temperatures [1].

Currently, many researchers [4–11] are focused on studying the possibility of solving the “activation” problem of this material [12–15]. The issue is that $TiFe$ is very sensitive to air and forms a passivating layer that prevents hydrogen absorption. The classical activation method involves heat treatment, which consists of cyclic exposure to elevated and room temperatures at high hydrogen pressure [16]. However, other methods are now considered more promising, such as mechanical treatment (ball milling, cold rolling, high-pressure torsion) [8; 17–20], the use of increased (compared to stoichiometric) Ti content [5; 9], and

the addition of alloying elements such as Mn, Cr, Zr, Y, etc. [6; 10; 21–23].

When using an excess of Ti and alloying, it was found [5; 6; 9; 10; 21–23] that in addition to TiFe, a solid solution based on β -Ti (referred to in some works as the BCC phase or Ti_4Fe phase) and the intermetallic Ti_2Fe appear in the structure of the material, which act as a kind of “gate” for hydrogen [6–8]. Several studies [4; 5; 9–11] also note a general increase in the hydrogen capacity of materials during primary hydriding, indicating hydrogen absorption not only by the main TiFe phase but also by the secondary β -Ti and Ti_2Fe phases. Statistical analysis of data obtained by various authors for three-phase materials based on TiFe, which do not require activation and contain excess amounts of Ti and/or Mn and Zr, showed that their hydrogen capacity during primary hydriding follows the law of additivity and can be described by the equation [24; 25]

$$H = 0.01537[\text{TiFe}] + 0.03213[\text{Ti}_2\text{Fe}] + \\ + 0.03847[\text{Ti}_4\text{Fe}],$$

where H is the hydrogen capacity of the material, wt. %; $[\text{TiFe}]$, $[\text{Ti}_2\text{Fe}]$, and $[\text{Ti}_4\text{Fe}]$ – are the contents of the respective phases, wt. %.

As follows from the given equation, the hydrogen capacity of the TiFe phase in the multiphase TiFe– Ti_2Fe – Ti_4Fe material is about 1.54 wt. % H (which is quite close to the experimental value of 1.70–1.85 wt. % H for the TiFeH hydride given in [10]), the capacity of the BCC solid solution Ti_4Fe is 3.85 wt. % H (slightly exceeding the known capacity of 3.7 wt. % H for the Ti_4FeH_8 hydride [9]), and the capacity of Ti_2Fe is about 3.21 wt. % H (also slightly higher than the theoretical estimate of 3.09 wt. % H for the $\text{Ti}_2\text{FeH}_{4.75}$ hydride given in [9]). It is interesting to note that in the presence of secondary β -Ti and Ti_2Fe phases, the main TiFe phase apparently does not form the TiFeH_2 hydride with the maximum possible capacity of 1.8–1.98 wt. % H [10], which is more than compensated by the contribution of β -Ti and Ti_2Fe .

Another important fact from the statistical analysis [24; 25] and consistent with the conclusions of [9] is that increasing the content of β -Ti in Ti and Fe-based materials reduces their reversible hydrogen capacity, indicating that the saturation of this phase with hydrogen is irreversible. The ability of the intermetallic Ti_2Fe to release stored hydrogen depends on the content of alloying elements: in their absence or with a small amount of Mn, hydrogen saturation is reversible [25], but with Zr alloying, ensuring maximum Ti_2Fe content in the material's structure, it is irreversible [9; 25]. This

leads to the conclusion that the most promising way to improve Ti–Fe system materials, capable of doubling their reversible hydrogen capacity, is to increase the Ti_2Fe content in their structure without using alloying. However, known attempts to solve this problem, based on melting the components followed by annealing [16; 26; 27], have failed [5].

This work explores the possibility of using explosive compaction of iron and titanium powder mixtures for this purpose. The starting point for choosing this method was the well-known fact of frequent intermetallic formation during explosion welding of steels and titanium alloys [28; 29], as well as the fact that during explosive compaction of powders and explosion welding, the area of intense plastic deformation on the surface of the joined components forms similarly [30; 31]. Using powder significantly increases the surface area in the material volume and reduces the effective diffusion paths of elements during interfacial interactions.

Materials and methods

To produce the materials, titanium powder grade PTM-1 and PZhV powder with particle sizes up to 200 μm from a commercial supplier in as-received condition were used. The Ti powder particles had a spongy shape, while the Fe particles were rounded with a pronounced polycrystalline structure (Fig. 1, *a*). The component content in the powder mixture was 36 wt. % Fe and 64 wt. % Ti, which is nearly stoichiometric for Ti_2Fe (see Fig. 1, *b*) and ensures equal volumetric content of Fe and Ti in the mixture.

Explosive compaction was performed by placing the initial powder mixture on the surface of a steel substrate and loading it with a flat, normally incident detonation wave through an intermediate layer separating the detonation products from the powder (Fig. 2). The calculation of the physical compression parameters implemented in the experiments was performed using the (P, U) -diagram method [33]. The calculation results are presented in the Table.

The phase composition, structure, and chemical composition of the phases of the obtained samples were investigated by X-ray phase analysis using a D8 Advance X-ray diffractometer (Bruker Optik GmbH, Germany) and scanning electron microscopy using a Versa 3D microscope (FEI, Czech Republic) with an integrated Apollo-X energy-dispersive X-ray microanalysis system (EDAX, USA).

Experimental results

The study of the materials obtained through explosive compaction showed that using this method,

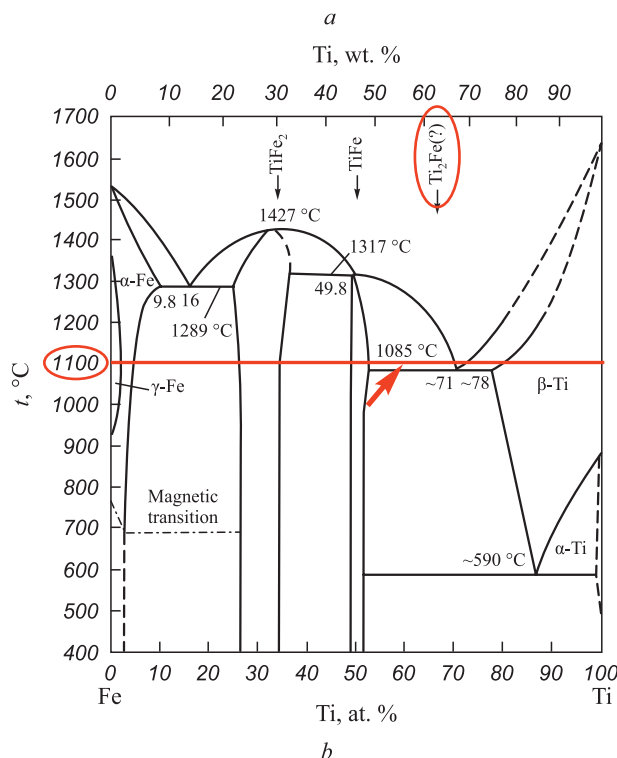
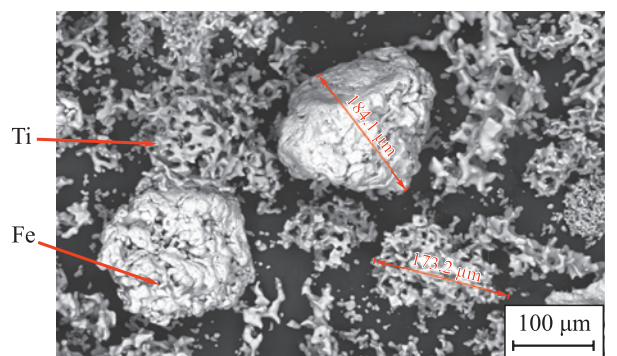


Fig. 1. View of Fe and Ti particles in the initial powder mixture (a) and phase equilibrium diagram (b) in the Fe–Ti system [32]

Рис. 1. Вид частиц Fe и Ti в исходной порошковой смеси (a) и диаграмма (b) стабильного фазового равновесия в системе Fe–Ti [32]

which ensures a shock-wave compression pressure of $P = 11.5$ GPa and a heating temperature up to 777 °C, the powder mixture is compacted into an almost monolithic material (Fig. 3, a). In this process, the deformation of the particles occurs due to uni-

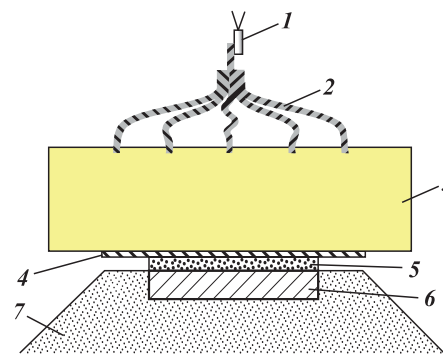


Fig. 2. Scheme of explosive loading [33]

1 – electric detonator; 2 – detonating cord; 3 – explosive charge; 4 – intermediate gasket; 5 – powder; 6 – substrate; 7 – sand pad

Рис. 2. Схема взрывного нагружения [33]

1 – электродетонатор; 2 – детонирующий шнур; 3 – заряд взрывчатого вещества; 4 – промежуточная прокладка; 5 – порошок; 6 – подложка; 7 – песчаная подушка

form plastic flow, resulting in noticeable flattening in the direction of shock compression and spreading in the transverse direction. No traces of changes in the initial phase composition were detected (Fig. 3, c). Even in the immediate vicinity of the interfacial boundaries, the chemical composition of the phases remained practically unchanged (Fig. 3, b).

Under more severe shock-wave compression conditions ($P = 12.5$ GPa and $t = 831$ °C) the deformation character of the component particles of the powder mixture changes fundamentally. Plastic deformation localizes in their surface layers and exhibits a pronounced jet character with the formation of specific “vortices,” as described in detail in [33; 35].

At the interfacial surfaces, solid layers up to 20 μm thick of an intermetallic compound (Fig. 4, b) are formed, which, based on its chemical composition (Fig. 4, c) and crystalline structure (Fig. 4, d), can be identified as the metastable phase Ti_2Fe .

Detailed examination of the microstructure in the interaction zone of the original powder mixture components indicates its chemical heterogeneity, expressed as periodic (with a period of 1.5 – 2.0 μm) composition oscillations of the intermetallic compound (Fig. 4, d). The deviation from the average stoichiometric ratio of components reaches up to 7 %.

Parameters of shock-wave compression of powder mixture

Параметры ударно-волнового сжатия порошковой смеси

Charge height, mm	Powder layer height, mm	Gasket thickness, mm	Detonation velocity of explosive, km/s	Powder heating temperature, °C	Pressure in reflected waves, GPa
70	7.0	1.5	4.2	777	11.5
85				831	12.5

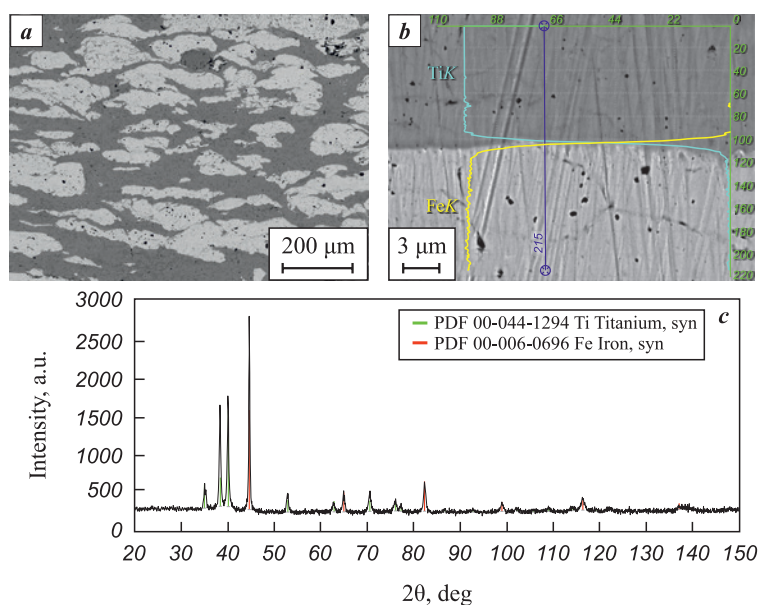


Fig. 3. Structure (a), chemical composition (b), and phase composition (c) of materials obtained under loading conditions: $t = 777\text{ }^{\circ}\text{C}$, $P = 11.5\text{ GPa}$

Рис. 3. Структура (a), химический (b) и фазовый (c) составы материалов, полученных в режиме нагружения: $t = 777\text{ }^{\circ}\text{C}$, $P = 11,5\text{ ГПа}$

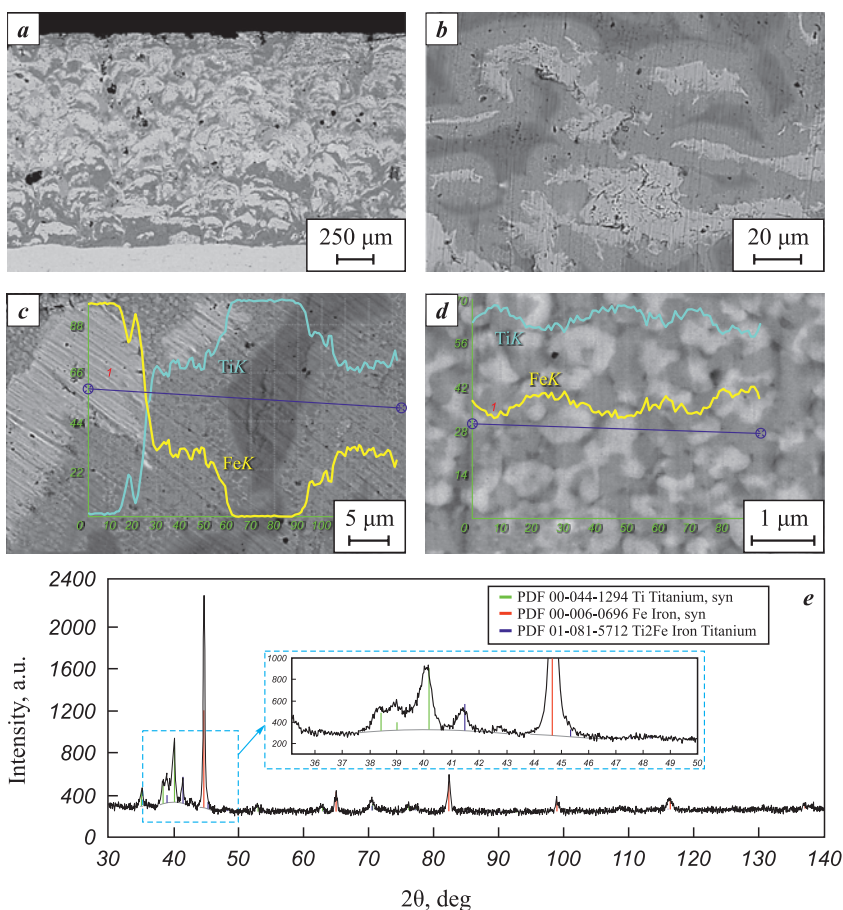


Fig. 4. Structure (a, b), chemical composition (c, d) and phase (e) composition of materials obtained under loading conditions: $t = 831\text{ }^{\circ}\text{C}$, $P = 12.5\text{ GPa}$

Рис. 4. Структура (a, b), химический (c, d) и фазовый (e) составы материалов, полученных в режиме нагружения: $t = 831\text{ }^{\circ}\text{C}$, $P = 12,5\text{ ГПа}$

Results and discussion

The data obtained from the conducted studies indicate that the mechanism of plastic deformation of titanium and iron particles during explosive compaction significantly influences the process of forming the metastable phase Ti_2Fe . Several hypotheses can be suggested about the nature of this influence. The most plausible hypothesis is that the intermetallic compound forms when a liquid phase is generated in the material during shock-wave treatment. This assertion is primarily supported by the experience of explosive welding of titanium alloys and steels [28; 29; 36].

Given that the contact melting temperature in the Ti–Fe system is low, at 1085 °C according to the phase diagram (see Fig. 1), achieving this temperature at particle boundaries during explosive compaction under conditions ensuring an average calculated heating temperature of 831 °C, combined with jet flows of metal and extreme temperature field heterogeneity, is quite likely. The heterogeneity of the formed intermetallic layer in this case could be a result of the simultaneous growth of its grains from a considerable number of crystallization centers within the liquid phase under rapid cooling due to heat dissipation into the “cold” areas of the structure and the metal substrate.

To test the proposed hypothesis, compacts obtained under loading conditions ensuring uniform plastic flow of the material particles without intermetallic phases were heated to 1100 °C in a vacuum with a holding time of 1 h, followed by cooling in an argon flow. As a result, the initial components of the compacts fully reacted with each other, forming a structure consisting of the intermetallic compounds $TiFe$ and Ti_2Fe (Fig. 5, *a, b*).

The associated impurity elements – carbon, oxygen, and nitrogen – were bound in titanium oxycarbonitrides (Fig. 5, *c*). Through coagulation and coalescence in the liquid phase, these formed relatively large inclusions that were uniformly distributed throughout the material (Fig. 5, *a, b*). The incorporation of part of the Ti into these inclusions appears to be the main reason why the $TiFe$ intermetallic phase formed in addition to the Ti_2Fe phase in the material’s structure. Addressing this issue requires increasing the Ti content (above stoichiometric) in the initial powder mixture.

Another factor likely contributing to the presence of the $TiFe$ intermetallic phase in the structure of compacts obtained by heat treatment is the significant increase in the duration of the interfacial interaction process when transitioning from purely explosive treatment to a combination of explosive and heat treat-

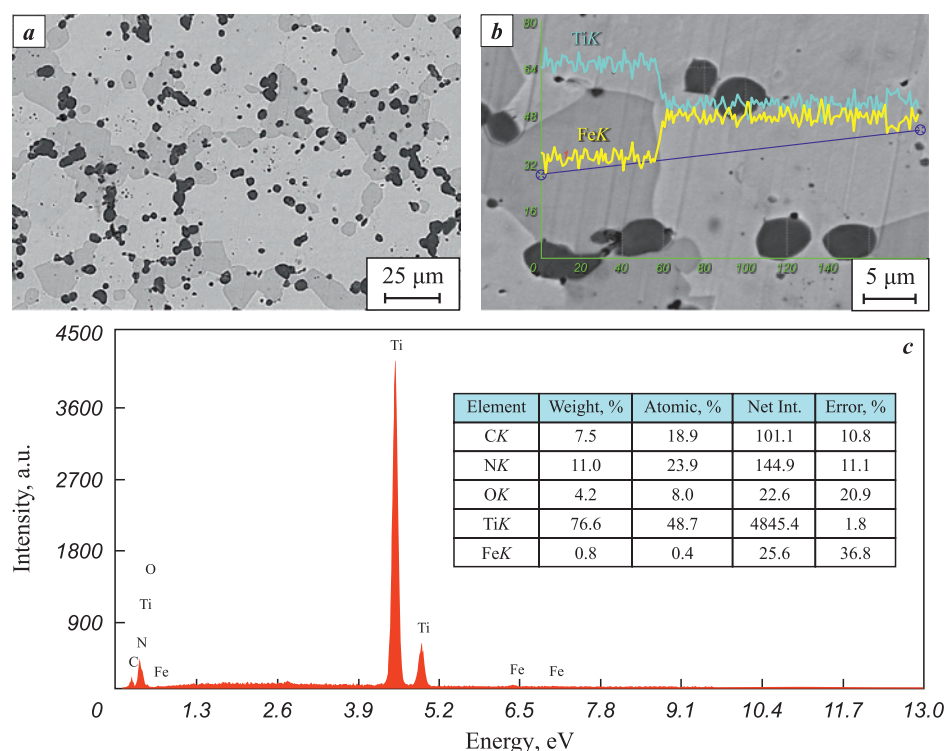


Fig. 5. Structure (*a*), chemical composition of intermetallic phases (*b*) and oxycarbonitride inclusions (*c*) of materials obtained by heat treatment of compacts

Рис. 5. Структура (*a*), химический состав интерметаллидных фаз (*b*) и оксикарбонитридных включений (*c*) материалов, полученных термической обработкой прессовок

ments. As a result, the likelihood of forming the stable TiFe phase and dissolving the metastable Ti_2Fe phase increased.

Conclusions

1. Under conditions of explosive compaction of iron and titanium powder mixtures that ensure uniform deformation of the initial particles without jet flows, the powder mixture compacts to an almost non-porous state while maintaining the original phase composition.

2. Using compaction regimes with localized plastic deformation and jet flows of the material particles in the original powder mixture forms a chemically heterogeneous metastable intermetallic Ti_2Fe as continuous layers between iron and titanium particles.

3. An effective method for producing materials with a high content of the metastable intermetallic Ti_2Fe is to combine explosive compaction of Fe and Ti powder mixtures with subsequent heat treatment in the intercritical temperature range (reactive sintering in the presence of a liquid phase).

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<https://doi.org/10.35211/1990-5297-2020-11-246-19-23>

Information about the Authors



Aleksander V. Krokhalev – Dr. Sci. (Eng.). Dean of the Faculty of Structural Materials Technology, Volgograd State Technical University (VSTU)

ORCID: 0000-0001-7677-0288

E-mail: kroch@vstu.ru

Valentin O. Kharlamov – Cand. Sci. (Eng.), Associate Professor at the Department "Equipment and Technology of Welding Production", Senior Engineer at the Shared Use Center "Physico-chemical research methods", VSTU

ORCID: 0000-0002-5039-4592

E-mail: harlamov_vo@mail.ru

Dmitry R. Chernikov – Postgraduate Student at the Department "Equipment and Technology of Welding Production", VSTU

ORCID: 0000-0003-2388-020X

E-mail: chernikovdr@yandex.ru

Sergey V. Kuzmin – Dr. Sci. (Eng.), Corresponding Member of the RAS, Professor at the Department "Equipment and Technology of Welding Production", First Vice-Rector of VSTU

ORCID: 0000-0003-2802-8497

E-mail: weld@vstu.ru

Vladimir I. Lysak – Dr. Sci. (Eng.), Academician of the RAS, Professor, Head of the Department "Equipment and Technology of Welding Production", Scientific Director of VSTU

ORCID: 0000-0003-3066-058X

E-mail: lysak@vstu.ru

Сведения об авторах

Александр Васильевич Крохалев – д.т.н., декан факультета технологии конструкционных материалов, Волгоградский государственный технический университет (ВолгГТУ)

ORCID: 0000-0001-7677-0288

E-mail: kroch@vstu.ru

Валентин Олегович Харламов – к.т.н., доцент кафедры «Оборудование и технология сварочного производства», вед. инженер Центра коллективного пользования «Физико-химические методы исследования», ВолгГТУ

ORCID: 0000-0002-5039-4592

E-mail: harlamov_vo@mail.ru

Дмитрий Романович Черников – аспирант кафедры «Оборудование и технология сварочного производства», ВолгГТУ

ORCID: 0000-0003-2388-020X

E-mail: chernikovdr@yandex.ru

Сергей Викторович Кузьмин – д.т.н., чл.-корр. РАН, профессор кафедры «Оборудование и технология сварочного производства», первый проректор ВолгГТУ

ORCID: 0000-0003-2802-8497

E-mail: weld@vstu.ru

Владимир Ильич Лысак – д.т.н., академик РАН, проф., зав. кафедрой «Оборудование и технология сварочного производства», научный руководитель ВолгГТУ

ORCID: 0000-0003-3066-058X

E-mail: lysak@vstu.ru

Contribution of the Authors



A. V. Krokhalev – analyzed the experimental data, wrote the article.

V. O. Kharlamov – conducted research using electron microscopy and X-ray diffraction analysis, participated in the discussion of the results.

D. R. Chernikov – conducted experiments on explosive compaction and heat treatment.

S. V. Kuzmin – carried out calculations of explosive compaction parameters, participated in the discussion of the results.

V. I. Lysak – determined the purpose of the work, participated in the discussion of the results.

Вклад авторов

А. В. Крохалев – анализ экспериментальных данных, написание текста статьи.

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Д. Р. Черников – проведение экспериментов по прессованию взрывом и термической обработке.

С. В. Кузьмин – расчеты параметров взрывного прессования, участие в обсуждении результатов.

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Research article

Научная статья



Dissolution-precipitation and cobalt grain growth during liquid phase sintering of Cu–Sn–Co and Cu–Sn–Co–W powder materials

E. G. Sokolov[✉], A. V. Ozolin, E. E. Bobylev,

D. A. Golius, S. A. Arefieva

Kuban State Technological University
2 Moskovskaya Str., Krasnodar 350072, Russia e_sokolov.07@mail.ru

Abstract. The study presents the results of the dissolution-precipitation process and cobalt grain growth during liquid phase sintering of Cu–Sn–Co and Cu–Sn–Co–W powder materials. The samples were obtained by static pressing of mixtures of technically pure copper, tin, cobalt, and tungsten powders. The average particle size of cobalt was 1.6 μm , and tungsten was 20 μm . Some of the samples contained mechanically activated tungsten with an average particle size of 0.14 μm . Sintering of the materials was carried out in a vacuum at temperatures of 820 and 1100 °C for durations of 5, 20, and 120 min. The structure of the sintered materials was studied using scanning electron microscopy and optical metallography. Elemental distribution maps in the materials were obtained through X-ray microanalysis. The grain sizes of cobalt were measured using specialized software. The largest grain size was observed in the Cu–Sn–Co material: after sintering at the specified temperatures and durations, it ranged from 8 to 46 μm . It was found that the most intensive grain growth occurred within the first 20 min of sintering. The addition of tungsten powder to the Cu–Sn–Co material contributed to the formation of finer cobalt grains. This is explained by the fact that tungsten particles, possessing high surface energy, act as nucleation centers for cobalt crystallization from the liquid phase. Mechanical activation of the tungsten powder increases its free surface area and enhances the mass transfer of Co through the liquid phase to the W particles. This helps to reduce the deposition of material on large Co particles and prevent their growth. As a result, in the Cu–Sn–Co–W material containing mechanically activated tungsten, the minimum average cobalt grain sizes were obtained, ranging from 3 to 25 μm .

Keywords: liquid phase sintering, dissolution-precipitation, mass transfer, nucleation centers, mechanical activation, grain size

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Растворение–осаждение и рост зерна кобальта при жидкофазном спекании порошковых материалов Cu–Sn–Co и Cu–Sn–Co–W

Е. Г. Соколов[✉], А. В. Озолин, Э. Э. Бобылев,
Д. А. Голиус, С. А. Арефьева

Кубанский государственный технологический университет
Россия, 350072, г. Краснодар, ул. Московская, 2

✉ e_sokolov.07@mail.ru

Аннотация. Представлены результаты исследования процесса растворения–осаждения и роста зерна кобальта при жидкофазном спекании порошковых материалов Cu–Sn–Co и Cu–Sn–Co–W. Образцы получали статическим прессованием смесей порошков технически чистых меди, олова, кобальта и вольфрама. Средний размер частиц кобальта составлял 1,6 мкм, вольфрама – 20 мкм. Часть образцов содержали механоактивированный вольфрам со средним размером частиц 0,14 мкм. Спекание материалов проводили в вакууме при температурах 820 и 1100 °С с выдержками 5, 20 и 120 мин. Структуру спеченных материалов исследовали методами сканирующей электронной микроскопии и оптической металлографии. Карты распределения элементов в материалах получали путем микрорентгеноспектрального анализа. Размеры зерна кобальта измеряли с помощью специализированного программного обеспечения. Наибольший размер зерна наблюдался в материале Cu–Sn–Co: после спекания при указанных температурах и выдержках он составлял 8–46 мкм. Установлено, что наиболее интенсивный рост зерна происходит в течение первых 20 мин спекания. Добавка порошка вольфрама в материал Cu–Sn–Co способствует формированию более мелкого зерна кобальта. Это объясняется тем, что частицы вольфрама, обладающего высокой поверхностной энергией, играют роль центров кристаллизации кобальта из жидкой фазы. Механическая активация порошка вольфрама увеличивает площадь его свободной поверхности и способствует усилению массопереноса Co через жидкую фазу к частицам W. Это позволяет ослабить осаждение вещества на крупных частицах Co и предотвратить их рост. В результате в материале Cu–Sn–Co–W, содержащем механоактивированный вольфрам, получены минимальные значения среднего размера зерна кобальта, находящиеся в диапазоне 3–25 мкм.

Ключевые слова: жидкофазное спекание, растворение–осаждение, массоперенос, центры кристаллизации, механическая активация, размер зерна

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Introduction

The production of sintered materials with a fine-grained structure and enhanced mechanical properties is a current challenge in powder metallurgy.

During the liquid phase sintering of various materials, a dissolution-precipitation process occurs, which is observed when the solid phase material is soluble in the liquid phase [1–3]. The dissolution-precipitation of the solid phase material contributes to the shrinkage and densification of the material, but it can also lead to the formation of a coarse-grained structure and deteriorate its mechanical properties [4–6].

Various methods are employed to achieve a fine-grained structure in sintered materials, including those aimed at suppressing the dissolution-precipitation process. These methods include homogenizing the sintered mixture by the size and shape of the powder par-

ticles [6; 7], reducing the sintering duration [8; 9], and introducing grain growth inhibitors into the powder material [10; 11].

To reduce the duration of the material's exposure to high temperatures, spark plasma sintering is used [8; 9]. However, this method is not applicable to all materials and products. During spark plasma sintering, the molds wear out rapidly, negatively affecting the dimensional accuracy of the products.

To inhibit grain growth, small amounts of chromium, vanadium, niobium, or other refractory metal carbides are added to tungsten-cobalt hard alloys [10; 11]. There is also evidence of grain growth inhibition in hard alloys with the addition of aluminum oxide nanoparticles [12]. During liquid phase sintering, these substances precipitate on the surface of tungsten carbide particles, inhibiting their growth. However, the addition of these substances leads to the formation

of brittle layers around the tungsten carbide particles, which negatively affects the mechanical properties of the sintered materials.

Some composite materials include diamond-graphite nanoparticles, which serve as nucleation centers for the liquid phase crystallization during cooling after sintering [13]. The addition of such particles allows for the formation of fine grains from the liquid phase, but it does not prevent dissolution-precipitation and grain growth of the solid phase during sintering. Thus, there is a need to develop new methods for forming a fine-grained structure in sintered materials.

The study [14] demonstrated that when two dissimilar solid metals, which are only partially soluble in the liquid phase, are placed in a melt, mass transfer occurs towards the metal with higher surface energy. This phenomenon provides opportunities to influence the dissolution-precipitation process by introducing particles with high surface energy into the powder material.

Cu–Sn–Co powder materials are used as metal binders in diamond abrasive tools [15–17], which exhibit resistance to abrasive wear and good adhesion to diamond grains [16]. During the liquid phase sintering of these materials, cobalt grain growth occurs, which negatively impacts their mechanical properties. To prevent this effect, it is advisable to introduce tungsten particles into the Cu–Sn–Co material. Compared to other components of this alloy, tungsten has a higher surface energy, ranging from 2.7 to 5.57 J/m² according to various sources [18; 19]. Additionally, tungsten is a carbide-forming metal, and its addition improves the adhesion of Cu–Sn–Co binders to diamond abrasive grains [17].

The objectives of this study were as follows:

- to identify the patterns of dissolution-precipitation and cobalt grain growth during the liquid phase sintering of Cu–Sn–Co and Cu–Sn–Co–W powder materials;
- to develop a new method for producing sintered materials with a fine-grained structure.

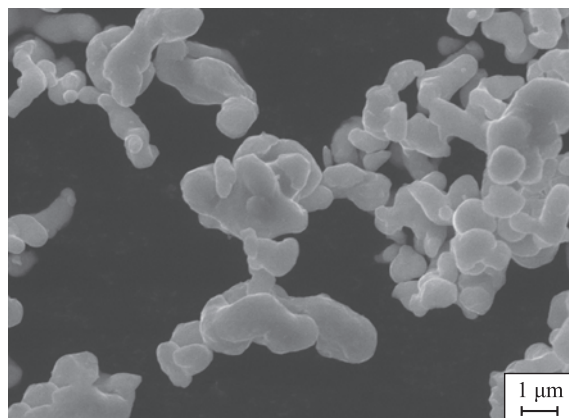


Fig. 1. Shape and size of Diacob-1600 cobalt powder particles

Рис. 1. Форма и размер частиц порошка кобальта Diacob-1600

Research methodology

For the research, the following metallic powders were used: PMS-1 copper powder (GOST 4960–75), PO1 tin powder (GOST 9723–73), and Diacob-1600 cobalt powder (Dr. Fritsch Kg., Germany). The latter was obtained by the carbonyl method, with rounded particles averaging 1.6 μm in size (Fig. 1).

W16.5 special tungsten powder from “Pobedit” JSC (Russia), consisting of equiaxed particles with an average size of about 20 μm, was mechanically activated using a AGO-2U planetary centrifugal mill (NPO “NOVITS”, Russia) for 60 min at a rotational speed of 800 rpm [20]. After treatment, the tungsten particles retained an equiaxed shape and ranged in size from 0.025 to 12.0 μm, with an average size of approximately 0.14 μm.

Mixtures were prepared from the specified powders, and their compositions are given in the Table.

Powder samples weighing 20 g were compacted by uniaxial static pressing under a load of 850 MPa. The resulting cylindrical samples, with a diameter of 21 mm, were sintered in a vacuum at temperatures of 820 and 1100 °C for 5, 20 and 120 min, and then microsections were prepared. To reveal the microstructure, an etchant containing 5 g of FeCl₃, 15 ml of HCl, and 100 ml of water was used.

Composition of powder materials

Состав порошковых материалов

Material composition	Content of powder components, wt. %				
	Copper PMS-1	Tin PO1	Cobalt Diacob-1600	Tungsten W16.5	Mechanically activated tungsten
Cu–Sn–Co	46	21	33	–	–
Cu–Sn–Co–W	43	20	30	7	–
Cu–Sn–Co–W(m)	43	20	30	–	7

The microstructure of the sintered alloys was studied using a scanning electron microscope EVO HD 15 and a metallographic microscope AxioObserver.A1m (both manufactured by Carl Zeiss AG, Germany) at magnifications of 50–1000×. Grain size measurements in the sintered materials were carried out using AxioVision Rel.4.8 software (Carl Zeiss AG).

The elemental distribution in the samples was investigated by *X*-ray microanalysis using the EVO HD 15 microscope.

Results and discussion

In Fig. 2, the microstructure of the Cu–Sn–Co–W material containing tungsten W16.5, sintered at 820 °C for 20 min, is shown. The phase composition of the Cu–Sn–Co and Cu–Sn–Co–W alloys has been investigated in studies [20; 21].

After sintering at temperatures of 820–1100 °C, the materials consist of the following phases: a copper-based solid solution (Cu), the intermetallic phase $\text{Cu}_{10}\text{Sn}_3$ (ξ -phase), and α -Co. In the Cu–Sn–Co–W samples, α -W and metastable β -W are present. Intermetallic compounds of Co–Sn and Co–W were not detected in the sintered materials. *X*-ray microanalysis showed that tungsten does not dissolve in the copper-tin phases (Cu and ξ) or in α -Co. The W particles observed in Fig. 2 retained their original shape characteristic of W16.5 powder. In the structure of the material containing mechanically activated tungsten powder, fine W particles remain after sintering, including some with transverse sizes less than 100 nm.

The structural formation of the materials during sintering consisted of several stages:

- formation of the liquid phase: melting of tin, its diffusion into copper particles, and subsequent melting of surface layers enriched with tin;
- viscous flow of the liquid and rearrangement of Co and W particles;

- dissolution-precipitation of cobalt;
- during subsequent cooling, crystallization of the liquid phase into a solid solution (Cu) and intermetallic ξ -phase.

According to *X*-ray microanalysis, the cobalt content in the (Cu) and ξ phases is 2 wt. % and 3 wt. %, respectively. This indicates its solubility in the liquid phase at sintering temperatures.

The dissolution-precipitation process leads to noticeable changes in the shape and size of Co particles. In Fig. 3–5, they appear as the brightest component. With increasing temperature and duration of sintering, Co particles become more equiaxed and more uniform in size.

Studies [22; 23] present an equation showing a non-linear relationship between the duration of liquid phase sintering and the size of the solid phase particle surrounded by the melt:

$$D^n - D_0^n = k\tau,$$

where D^n and D_0^n are the particle sizes after and before sintering; τ is the sintering duration; k is a constant; and the exponent n depends on which stage determines the intensity of the solid phase material's dissolution-precipitation:

- if the slowest process is the dissolution of the solid phase in the liquid, then $n = 2$;
- if the determining stage is the diffusion of the dissolved substance in the liquid phase, then $n = 3$.

The kinetic curves of Co particle growth, shown in Fig. 6, align well with the given equation if the parameter $n = 3$. This indicates that the rate of Co particle growth is limited by the diffusion rate of Co atoms through the liquid phase.

In Fig. 6, it is evident that the size of Co particles grows most intensively during the first 5–20 min of sintering. During the dissolution-precipitation process, Co

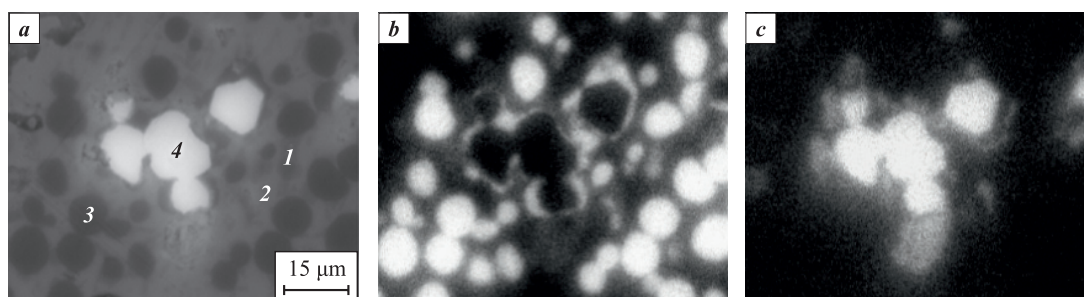


Fig. 2. Microstructure of the sintered Cu–Sn–Co–W material (a) and distribution maps of cobalt (b) and tungsten (c)
1 – solid solution (Cu); 2 – ξ -phase; 3 – α -Co; 4 – tungsten particles

Рис. 2. Микроструктура спеченного материала Cu–Sn–Co–W (a) и карты распределения кобальта (b) и вольфрама (c)
1 – твердый раствор (Cu); 2 – ξ -фаза; 3 – α -Co; 4 – частицы W

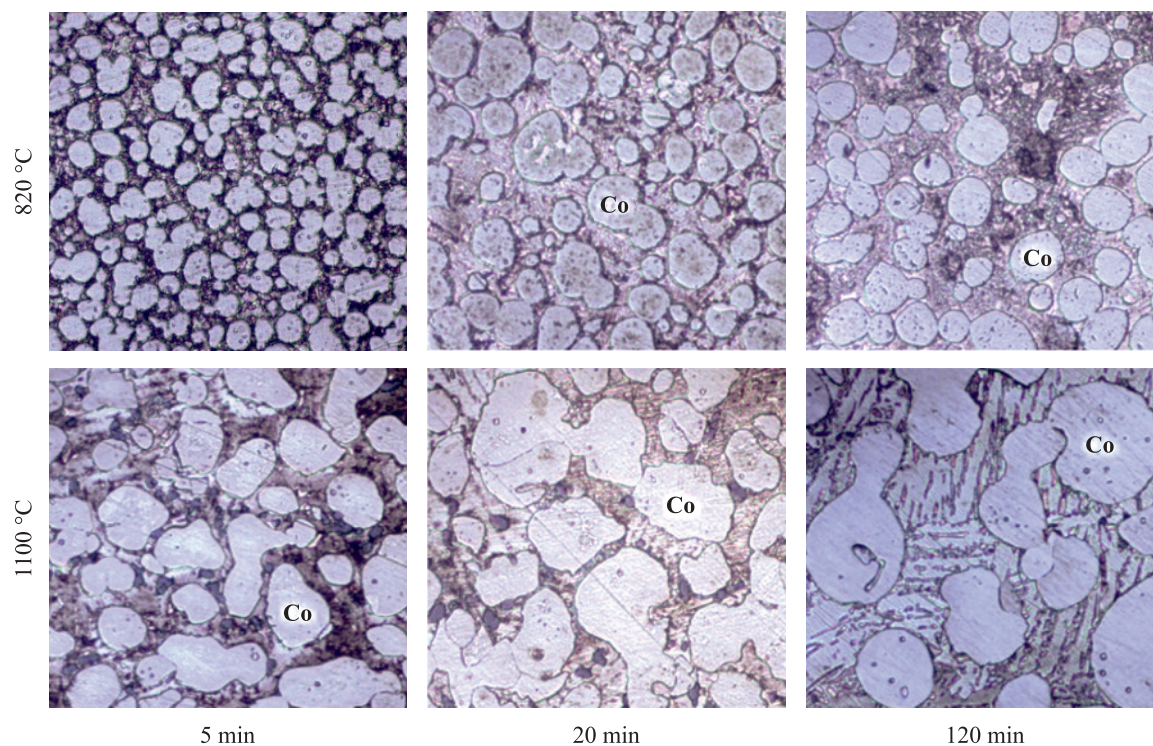


Fig. 3. Structure of Cu–Sn–Co alloys
Light image ($\times 500$)

Рис. 3. Структура сплавов Cu–Sn–Co
Световое изображение ($\times 500$)

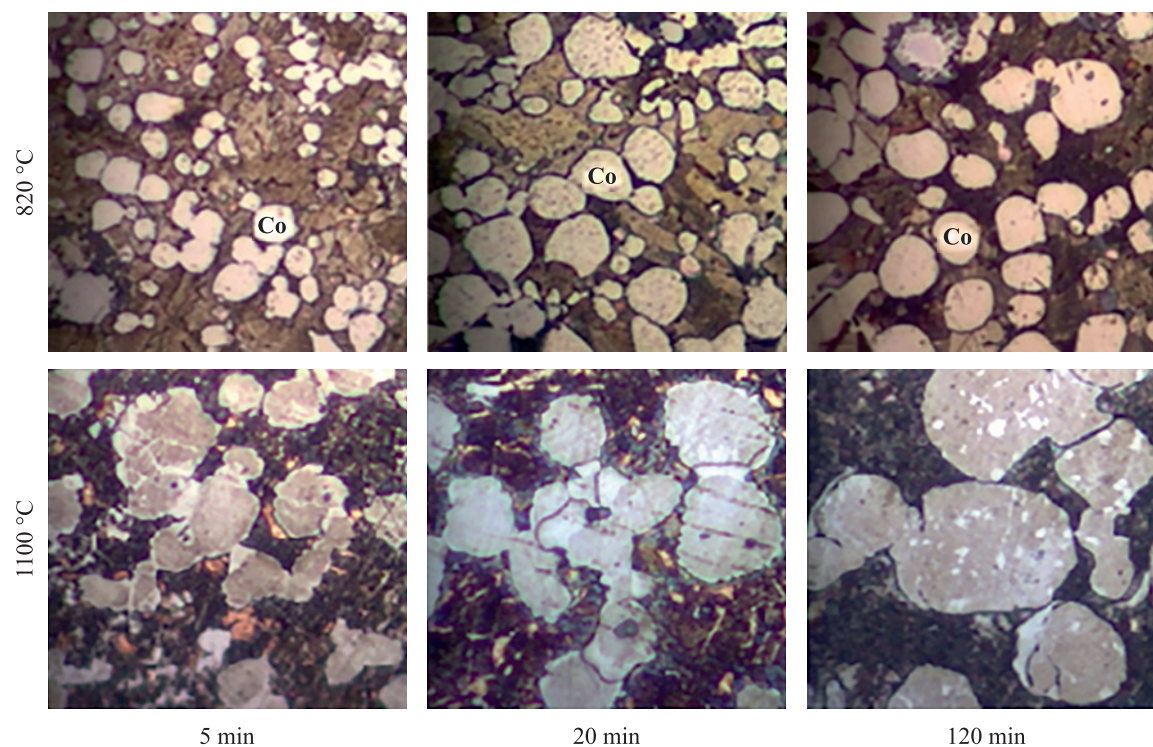


Fig. 4. Structure of Cu–Sn–Co–W alloys containing tungsten W16.5
Light image ($\times 1000$)

Рис. 4. Структура сплавов Cu–Sn–Co–W, содержащих вольфрам W16,5
Световое изображение ($\times 1000$)

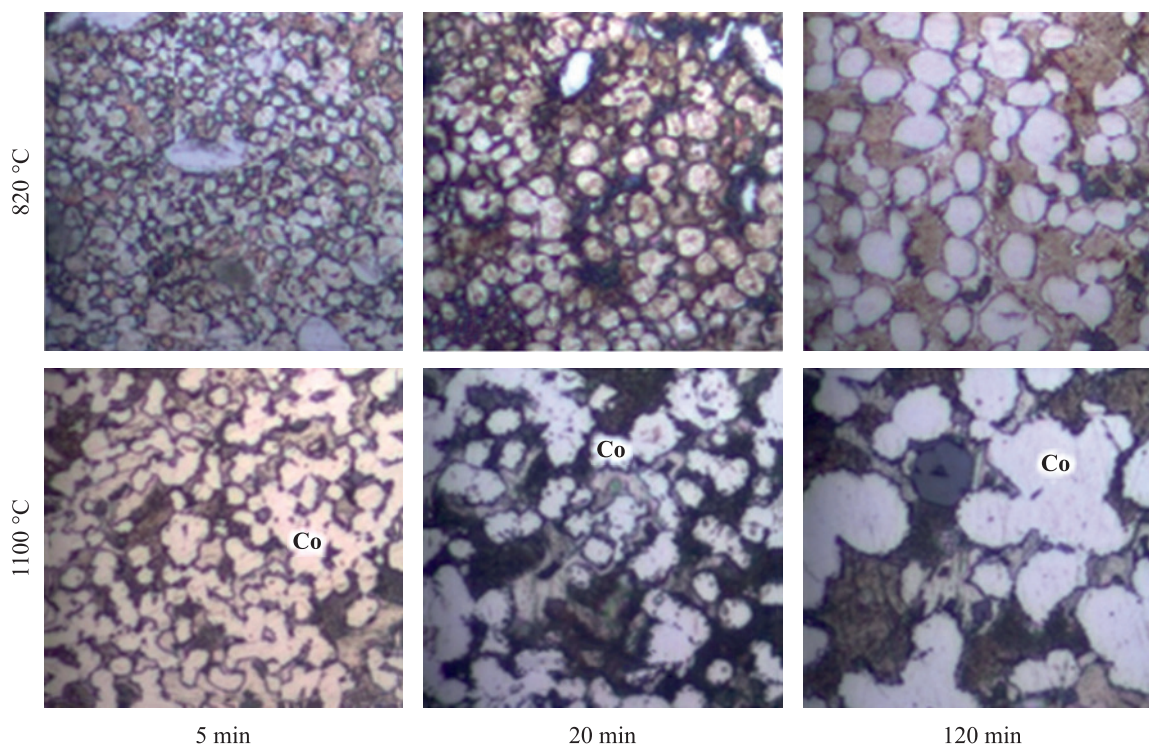


Fig. 5. Structure of Cu–Sn–Co–W(*m*) alloys containing mechanically activated tungsten
Light image ($\times 1000$)

Рис. 5. Структура сплавов Cu–Sn–Co–W(*m*), содержащих механоактивированный вольфрам
Световое изображение ($\times 1000$)

particles become more uniform in shape and size, leading to a decrease in the difference in chemical potentials of cobalt within the particles. As a result, during further isothermal holding, the driving force for mass transfer weakens, and the rate of Co grain growth slows down.

The addition of tungsten to the Cu–Sn–Co powder material significantly reduces the size of Co grains. X-ray microanalysis of the sintered material showed a cobalt layer on the surface of W particles (visible

in the component distribution maps, Fig. 2). It is known that tungsten has a higher surface energy than cobalt [18; 19], which facilitates the mass transfer of cobalt through the liquid phase to the surface of W particles during sintering. The thickness of the Co layer is predominantly uniform (Fig. 7, *a*). Some uneven areas with greater thickness formed due to the sintering of Co particles to W particles (Fig. 7, *b*). The probable mechanism of sintering is the dissolution of Co at con-

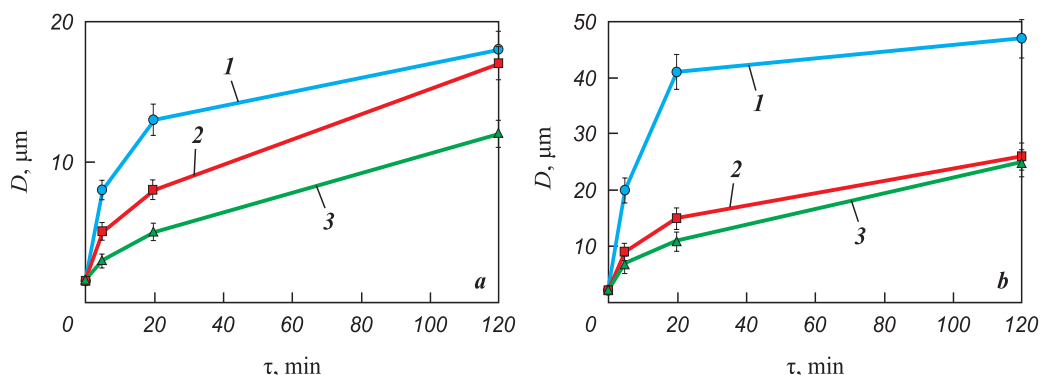


Fig. 6. Dependence of cobalt grain size on sintering duration at 820 °C (*a*) and 1100 °C (*b*)
1 – Cu–Sn–Co; 2 – Cu–Sn–Co–W; 3 – Cu–Sn–Co–W(*m*)

Рис. 6. Зависимость размера зерна кобальта от продолжительности спекания при $t = 820$ °C (*a*) и 1100 °C (*b*)
1 – Cu–Sn–Co; 2 – Cu–Sn–Co–W; 3 – Cu–Sn–Co–W(*m*)

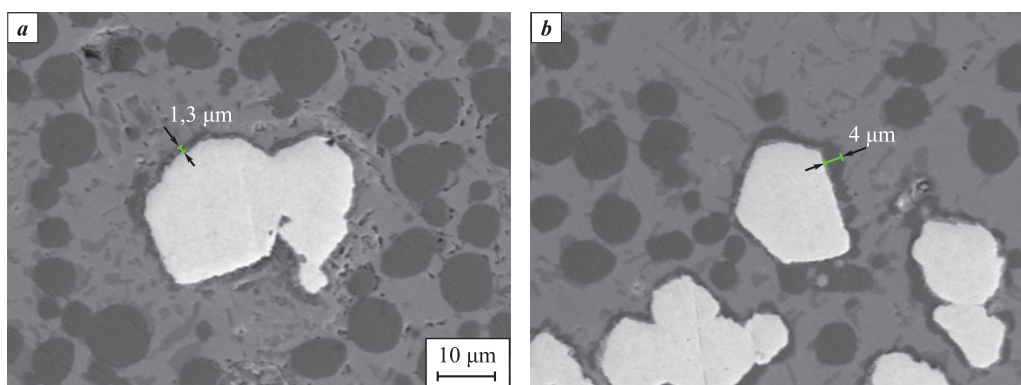


Fig. 7. Cobalt layer on tungsten particles formed by the precipitation of Co from the liquid phase (a) and sintering of Co particles (b)

Рис. 7. Кобальтовый слой на частицах вольфрама, сформированный за счет осаждения Co из жидкой фазы (a) и припекания частиц Co (b)

tact points and its precipitation on the free surface of W particles [1; 3].

It should be noted that, due to their high density, tungsten particles occupy only 2 % of the volume of the sintered material at a mass fraction of 7 %. As a result, the diffusion flux directed from Co particles to W particles is limited by the relatively small free surface area of the tungsten particles.

After mechanical activation under the above conditions, the free surface area of the tungsten powder increases significantly. In the mechanically activated powder, the average particle size of W is about 0.14 μm . Calculations using known geometric formulas show that reducing the diameter of equiaxed (spherical) particles from 20 to 0.14 μm increases the free surface area of the powder by approximately 140 times.

Increasing the free surface area of tungsten enhances the mass transfer of cobalt through the liquid phase to the W particles. As a result, deposition on large Co particles decreases, leading to the formation of a fine-grained structure in the material (see Fig. 5).

The identified patterns of cobalt mass transfer were utilized in developing a new method for producing sintered materials with a fine-grained structure [24]. This method involves introducing fine refractory particles with high surface energy into the powder material. The addition of these particles alters the direction of mass transfer during liquid phase sintering and inhibits the growth of solid phase grains.

The positive effect of introducing mechanically activated tungsten powder into the Cu–Sn–Co material is evident in the following example. At a sintering temperature of 820 $^{\circ}\text{C}$ and a holding time of 20 min, Co grains with an average size of 13 μm form in the material. The introduction of 7 wt. % mechanically activated tungsten powder under the same sintering

conditions results in Co grains with an average size of 5 μm .

Conclusions

1. The study determined the patterns of the dissolution-precipitation process of cobalt during the liquid phase sintering of Cu–Sn–Co and Cu–Sn–Co–W powder materials.
2. It was found that the addition of tungsten powder to the Cu–Sn–Co alloy promotes the formation of finer cobalt grains. This is explained by tungsten particles with high surface energy acting as nucleation centers for cobalt crystallization from the liquid phase.
3. Mechanical activation of tungsten powder increases its free surface area and enhances the mass transfer of cobalt through the liquid phase to the W particles. This helps to reduce the deposition of material on large Co particles and further decreases the size of the cobalt grains.
4. Based on the identified patterns, a new method for producing sintered materials with a fine-grained structure was proposed. The essence of this method is that the addition of fine refractory particles with high surface energy to the powder material changes the direction of mass transfer and inhibits the growth of the solid phase grains during liquid phase sintering.

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Information about the Authors



Сведения об авторах

Evgeny G. Sokolov – Cand. Sci. (Eng.), Assistant Professor at the Department of Control Systems Engineering, Materials, and Technologies in Mechanical Engineering (CSEMTME), Kuban State Technological University (KubSTU)

 **ORCID:** 0000-0002-7229-228X

 **E-mail:** e_sokolov.07@mail.ru

Alexander V. Ozolin – Cand. Sci. (Eng.), Junior Research at the Center for Advanced Technologies and Nanomaterials, KubSTU

 **ORCID:** 0000-0002-0173-1716

 **E-mail:** ozolinml@yandex.ru

Eduard E. Bobylev – Cand. Sci. (Eng.), Assistant Professor at the Department of CSEMTME, KubSTU

 **ORCID:** 0000-0001-7754-1807

 **E-mail:** ebobylev@mail.ru

Dmitry A. Golius – Postgraduate student at the Department of CSEMTME, KubSTU

 **ORCID:** 0000-0002-5467-4372

 **E-mail:** da-golius@ya.ru

Svetlana A. Arefieva – Cand. Sci. (Eng.), Assistant Professor at the Department of CSEMTME, KubSTU

 **ORCID:** 0000-0002-5894-4595

 **E-mail:** 4492698@mail.ru

Евгений Георгиевич Соколов – к.т.н., доцент кафедры инженерии систем управления, материалов и технологий в машиностроении (ИСУМиТМ), Кубанский государственный технологический университет (КубГТУ)

 **ORCID:** 0000-0002-7229-228X

 **E-mail:** e_sokolov.07@mail.ru

Александр Витальевич Озолин – к.т.н., мл. науч. сотрудник НОЦ «Центр перспективных технологий и наноматериалов», КубГТУ

 **ORCID:** 0000-0002-0173-1716

 **E-mail:** ozolinml@yandex.ru

Эдуард Эдуардович Бобылев – к.т.н., доцент кафедры ИСУМиТМ, КубГТУ

 **ORCID:** 0000-0001-7754-1807

 **E-mail:** ebobylev@mail.ru

Дмитрий Александрович Голиус – аспирант кафедры ИСУМиТМ, КубГТУ

 **ORCID:** 0000-0002-5467-4372

 **E-mail:** da-golius@ya.ru

Светлана Александровна Арефьева – к.т.н., доцент кафедры ИСУМиТМ, КубГТУ

 **ORCID:** 0000-0002-5894-4595

 **E-mail:** 4492698@mail.ru

Contribution of the Authors



Вклад авторов

E. G. Sokolov – defined the research objective, analyzed experimental data, developed the concept, and wrote the article.

A. V. Ozolin – investigated experimental samples using SEM and X-ray microanalysis, performed graphical processing of experimental data, prepared illustrations, and participated in the discussion of experimental results.

E. E. Bobylev – investigated experimental samples using optical metallography, participated in the discussion of results, and formulated conclusions.

D. A. Golius – planned experiments, prepared powder mixtures, pressed and sintered experimental samples, and prepared micro-sections.

S. A. Arefieva – conducted a critical literature review and prepared the manuscript

Е. Г. Соколов – определение цели работы, анализ экспериментальных данных, разработка концепции и написание статьи.

А. В. Озолин – исследование экспериментальных образцов методами сканирующей электронной микроскопии и микрорентгеноспектрального анализа, графическая обработка экспериментальных данных, подготовка иллюстраций, участие в обсуждении результатов экспериментов.

Э. Э. Бобылев – исследование экспериментальных образцов методом оптической металлографии, участие в обсуждении результатов и формулировке выводов.

Д. А. Голиус – планирование экспериментов, подготовка порошковых смесей, прессование и спекание экспериментальных образцов, подготовка микрошлифов.

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Research article

Научная статья



Phase transformations, microstructure formation, and magnetic properties of a hysteresis alloy based on the Fe–Cr–Co–Mo system doped with Sm, Zr, and Cu

M. A. Beltyukova , A. A. ShatsovPerm National Research Polytechnic University Russia
29 Komsomolskiy Prosp., Perm 614990, Russia marievamar@rambler.ru

Abstract. The development of new hard magnetic materials (HMM) is crucial for meeting the ever-increasing demands of industry. Today, the advancement of energy, electrical engineering, and instrumentation sectors requires manufacturers of HMM products to enhance the energy efficiency and power of devices while reducing their size and weight, which increases scientists' interest in these alloys. Among HMM, magnets derived from rare-earth elements such as Sm and Nd ($\text{Nd}_2\text{Fe}_{14}\text{B}$, SmCo_5 , $\text{Sm}_2\text{Co}_{17}$) possess the highest magnetic energy at smaller sizes and weights. Alloys based on the Fe–Cr–Co system offer the best reliability, strength, corrosion resistance, and manufacturability, making them particularly in demand among HMM. Creating a magnet based on two alloying systems, Sm–Co and Fe–Cr–Co, may yield a material with unique properties that combine the advantages of both systems. This study investigates the powder hysteresis alloy 22Kh15K4MS (22 % Cr–15 % Ni–4 % Mo–Co–Si) doped with the rare-earth magnet KS25DTs in amounts ranging from 1.5 to 9.0 %. The microstructure, transformation kinetics, phase composition, and magnetic properties of the developed alloys were examined. It was found that the magnetic characteristics of the alloys depend on the concentration of the rare-earth magnet additive and the thermal treatment regime. It was demonstrated that the introduction of 3 % KS25DTs achieves the maximum magnetic properties of the alloy: $H_c = 55.6$ kA/m, $B_r = 1.33$ Tl, $(BH)_{\max} = 41$ kJ/m³. The combination of the developed alloy composition and the thermal treatment regime allows for an increase in the rectangularity coefficient of the magnetic hysteresis loop (K_l) – one of the most important characteristics of precision hysteresis electric motors.

Keywords: hard magnetic material (HMM), powder alloy, magnetic properties, rectangularity coefficient of the magnetic hysteresis loop, Fe–Cr–Co–Mo, Sm–Co.

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Особенности фазовых превращений, формирования микроструктуры и магнитных свойств гистерезисного сплава на основе системы Fe–Cr–Co–Mo, легированного Sm, Zr и Cu

М. А. Бельтюкова[✉], А. А. Шацов

Пермский национальный исследовательский политехнический университет
Россия, 614990, г. Пермь, Комсомольский пр-т, 29

✉ marievamar@rambler.ru

Аннотация. Разработка новых магнитотвердых материалов (МТМ) важна для удовлетворения постоянно растущих требований промышленности. Сегодня развитие энергетической, электротехнической и приборостроительной отраслей требует от производителей изделий из МТМ повышения энергоэффективности, мощности приборов при уменьшении их размеров и массы, что увеличивает интерес ученых к этим сплавам. Среди МТМ наибольшей магнитной энергией при меньших размерах и массе обладают магниты, полученные из редкоземельных элементов, таких как Sm и Nd ($\text{Nd}_2\text{Fe}_{14}\text{B}$, SmCo_5 , $\text{Sm}_2\text{Co}_{17}$). Наилучшие характеристики надежности, прочности, коррозионной стойкости и высокую технологичность изготовления имеют сплавы на основе системы Fe–Cr–Co, что также делает их особенно востребованными среди МТМ. Создание магнита, в основе которого лежат две системы легирования Sm–Co и Fe–Cr–Co, может способствовать получению материала с уникальными свойствами, сочетающего в себе достоинства каждой из указанных систем. В работе исследован порошковый гистерезисный сплав 22X15K4MC, легированный добавкой редкоземельного магнита марки KC25ДЦ в количестве от 1,5 до 9,0 %. Изучены микроструктура, кинетика превращений, фазовый состав и магнитные свойства разработанных сплавов. Установлено, что магнитные характеристики сплавов зависят от концентрации добавки редкоземельного магнита и режима термической обработки. Показано, что введение сплава KC25ДЦ в количестве 3 % позволяет достичь максимальных магнитных свойств легированного материала: $H_c = 55,6$ кА/м, $B_r = 1,33$ Тл, $(BH)_{\max} = 41$ кДж/м³. Сочетание разработанного состава сплава и режима термической обработки позволяет повысить коэффициент прямоугольности петли магнитного гистерезиса (K_H) – одной из важнейших характеристик прецизионных гистерезисных электрических двигателей.

Ключевые слова: магнитотвердый материал (МТМ), порошковый сплав, магнитные свойства, коэффициент прямоугольности петли магнитного гистерезиса, Fe–Cr–Co–Mo, Sm–Co

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Introduction

Recently, there has been a global trend towards producing magnetic materials with enhanced consumer qualities at a lower cost. When comparing rare-earth metal (REM) magnets with magnets from the Fe–Cr–Co system, the former appear less attractive due to their high cost, expensive extraction processes, import dependencies, low mechanical strength, and environmental restrictions during production [1–3]. Research on Fe–Cr–Co-based alloys mainly focuses on reducing the content of expensive elements such as Co [4; 5], and the introduction of micro-additives like Si, Mo, Ti, Dy, Nd, Y, and Sm [6–11].

The greatest interest lies in studies where FCC alloys are doped with REM and W [8; 9–11]. In [9], a cast alloy 43Fe–28Cr–23Co–3Mo–2V–1Zr¹ was doped with 0–3 % yttrium. The best magnetic properties were

achieved in the alloy with 2 % Y: the maximum magnetic energy $(BH)_{\max}$ increased from 51.3 to 61.6 kJ/m³, residual magnetic induction (B_r) increased from 0.71 to 1.05 T, and coercive force (H_c) increased from 97 to 130 kA/m compared to the original alloy. Further increase in yttrium content to 3 % led to a decrease in magnetic properties due to phase coarsening and structural heterogeneity. In [10], adding up to 2 % samarium during metallurgical production of cast ingots $(BH)_{\max}$ increased by 86 %, B_r by 47 %, and H_c by 28.7 %. The authors attributed this growth in magnetic properties to enhanced shape magnetic anisotropy and magnetic field anisotropy due to intermetallic compounds of the rare-earth magnet SmCo_5 . Additionally, X-ray phase analysis revealed that samarium atoms concentrate in the α_1 -phase, thereby increasing the lattice parameter of the strongly magnetic Fe–Co phase and its volume fraction.

Alloys SmCo_5 and $\text{Sm}_2\text{Co}_{17}$ were developed in the 1960s–1980s and are still widely used in valve

¹ Here and throughout the text, mass percent (wt. %) is implied unless otherwise specified.

motors of submersible pumps, flaw detector magnets, magnetic lenses, and couplings [13]. According to research, SmCo_5 and $\text{Sm}_2\text{Co}_{17}$ alloys have high values of magnetocrystalline anisotropy (up to $(15 \div 20) \cdot 10^6 \text{ J/m}^3$) [14], corrosion resistance (0.1 mg/cm^2 in Na_2S and NaCl , 20 mg/cm^2 in HCl) [15], Curie temperature (727°C for SmCo_5 and 920°C for $\text{Sm}_2\text{Co}_{17}$), and exceed Nd–Fe–B magnets in temperature stability [16–17].

Fe–Cr–Co alloys have already found wide application in mechatronic systems, rotors of high-speed and ultra-high-speed electromechanical energy converters, hysteresis motors, and even microwave radiation absorbers [18–20]. Introducing elements with shape anisotropy of ferromagnetic anisotropic particles, high values of crystal anisotropy constant, and saturation magnetization into Fe–Cr–Co alloys can improve the magnetic properties of the alloy: H_c , B_r , $(BH)_{\max}$ [21], and K_l – the rectangularity coefficient of the magnetic hysteresis loop, related by the formula

$$K_l = \frac{B_r}{B_{\max}},$$

where B_r is the residual magnetic induction, and $B_{\max}$ is the maximum magnetic induction (GOST 19693-74).

Increasing the residual induction of the magnet will allow achieving greater excitation flux while maintaining the torque value in the electric motor with lower armature current, thus increasing the device's efficiency. Due to the demagnetizing factor, the induction at the operating point is lower than B_r , so ensuring the convexity and rectangularity of the magnetic hysteresis loop is essential [22]. Enhancing the power of Fe–Cr–Co hard magnetic alloys will expand their application areas.

The aim of this study is to determine the possibility of improving the magnetic properties of a powder hysteresis hard magnetic alloy based on the Fe–Cr–Co system by doping it with the KS25DTs alloy.

Materials and methods

The study investigated the powder alloy 22Kh15K4MS, doped with the KS25DTs additive in amounts ranging from 0 to 9 % as a substitute for iron (Table 1). The following metal and alloy powders were used as the initial batch components:

– chromium PKh-1S (TU 14-5-298-99) with an average particle size $d = 10 \mu\text{m}$ and a standard deviation $\sigma = 5 \mu\text{m}$;

– cobalt GP-OK (TU 1793-008-92), $d = 24 \mu\text{m}$, $\sigma = 13 \mu\text{m}$;

– carbonyl iron OSCh 6-2 (TU 6-09-05808008-262-92), $d = 2 \mu\text{m}$, $\sigma = 2 \mu\text{m}$;

– ferrosilicon FS50 (GOST 1415-93), $d = 8 \mu\text{m}$, $\sigma = 4 \mu\text{m}$;

– molybdenum MPCh (TU 48-19-69-80), $d = 2 \mu\text{m}$, $\sigma = 1 \mu\text{m}$.

Pure samarium powder has low corrosion resistance and a relatively high sintering temperature, so the KS25DTs alloy powder (GOST 21559-76), containing 24–27 % Sm, 1.5–3.5 % Zr, 13–20 % Fe, 4–6 % Cu, and 57.5–43.5 % Co, obtained by crushing magnet scrap, was used in the experiments. Recycling of the sintered SmCo_5 alloys, crushed in a hydrogen environment, allows for the production of magnets with an improved microstructure and enhanced magnetic properties compared to the original magnets [23].

All components of the charge were sieved through a $63 \mu\text{m}$ mesh and homogenized in a mixer with an offset rotation axis for 8 h. The sample billets were obtained by cold pressing in a metal mold in two stages with an intermediate pre-sintering operation. Pressing was carried out at a pressure of 29.4 MPa, followed by pre-sintering at a temperature of 860°C and holding for 3 h in a hydrogen environment. The samples were then calibrated at a pressure of 34.3 MPa and finally sintered in a vacuum with a residual pressure of 10^{-2} Pa according to the regime $t = 1350^\circ\text{C}$, $\tau = 4 \text{ h}$. The density after all sintering stages was determined hydrostatically using a VLR-200 device (Gosmer, Russia) according to GOST 25281-82.

Quenching of all samples was carried out from a temperature of 1250°C in a 15 % aqueous NaCl solution. Aging of the billets was performed sequentially in 7 stages with the application of an external magnetic field of 150 kA/m. The processing parameters are specified in Table 2. Phase transitions in the studied samples were examined using differential scanning calorimetry (DSC) during the heating and cooling of samples weighing 3–4 g on an STA 449 F3 Jupiter (Netzsch,

Table 1. Chemical composition of experimental alloys

Таблица 1. Химический состав опытных сплавов

Composition No.	Content, wt. %					
	Fe	Cr	Co	Mo	Si	KS25DTs (Sm)
1	57.5	22.5	15.0	4.0	1.0	0
2	55.5					1.5 (0.36)
3	54.5					3.0 (0.77)
4	53.0					4.5 (1.15)
5	51.5					6.0 (1.53)
6	48.5					9.0 (2.30)

Germany). The heating rate was 10 °C/min. The main parameters and shape of the magnetic hysteresis loop of the experimental samples were determined after quenching and multistage aging using a Permagraph L hysteresis graph (Magnet Physik, Germany) with PERMA software. Experimental data were processed using Fityk and Proteus Analyses software packages (Marcin Wojdyr, Poland).

X-ray phase analysis of the samples was performed using XRD on a D8 Advance ECO powder diffractometer (Bruker, Germany) under the following conditions: cobalt radiation with a wavelength $\lambda = 1,78897 \text{ \AA}$, an accelerating voltage of 35 kV, and an X-ray tube current of 25 mA.

Qualitative and semi-quantitative analyses were carried out using the Diffrac.Eva software. The PDF-2 2013 powder diffraction database was used for phase identification.

Hardness was measured using a Rockwell hardness tester (Tochpribor, Russia) according to GOST 9013-59 with a load of 150 kg. The microstructure of the samples was investigated using a GX-51 metallographic microscope (Olympus, Japan) with SIAMS 800 software. For high-resolution structural analysis, VEGA 3 (TESCAN, Czech Republic) and FEI Quanta 650FEG (FEI, USA) electron microscopes were used.

Research results

The magnetic characteristics of the 22Kh15K4MS powder alloy are shown in Fig. 1. The base alloy, processed through stages 1 to 7 (Table 2) with the application of an external magnetic field, exhibits the following maximum properties: $H_c = 38.9 \text{ kA/m}$, $B_r = 1.16 \text{ T}$, $(BH)_{\max} = 20 \text{ kJ/m}^3$. These properties increased in samples containing KS25DTs additives (with Sm concentrations ranging from 0.36 to 0.77 %), reaching a maximum with the introduction of 0.77 % Sm: $H_c = 55.6 \text{ kA/m}$, $B_r = 1.33 \text{ T}$, $(BH)_{\max} = 41 \text{ kJ/m}^3$. However, the magnetic properties deteriorated with

an increase in the Sm content from 1.15 to 2.3 % due to phase coarsening [10] and the segregation of samarium at grain boundaries (see Fig. 2, c).

Multistage aging of the alloys with the application of an external magnetic field led to the spinodal decomposition of the α -solid solution into the α_1 -phase, enriched with iron and cobalt, and the α_2 -phase, enriched with chromium. The alternation of the strongly mag-

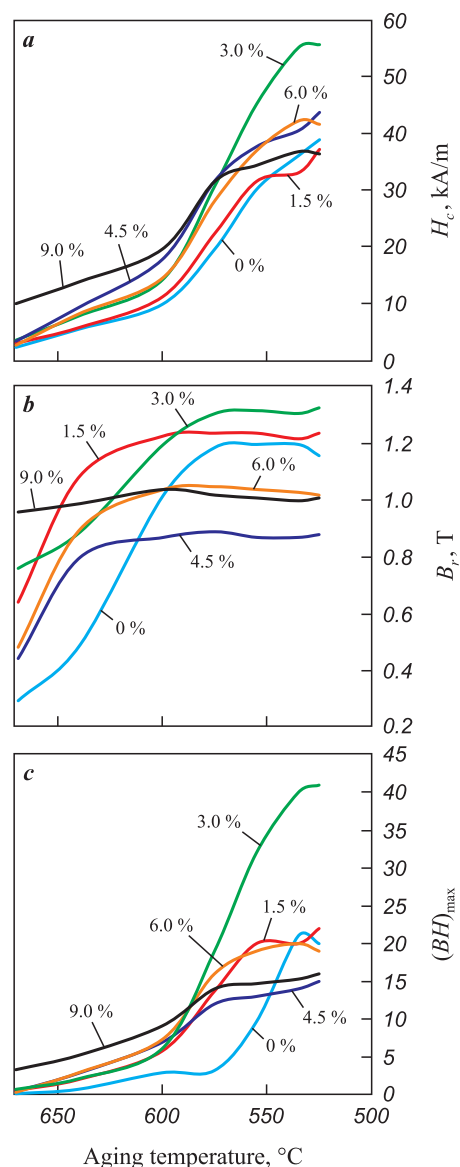


Fig. 1. Dependence of coercive force H_c (a), magnetic induction B_r (b) and maximum magnetic energy $(BH)_{\max}$ (c) on the aging temperature of the base alloy 22Kh15K4MS and samples with KS25DTs additive in concentrations ranging from 0 to 9 % (values indicated on the curves)

Рис. 1. Зависимость коэрцитивной силы H_c (a), магнитной индукции B_r (b) и максимальной магнитной энергии $(BH)_{\max}$ (c) от температуры старения исходного сплава 22Х15К4МС и образцов с добавкой КС25ДЦ от 0 до 9 % (цифры у кривых)

Table 2. Aging mode

Таблица 2. Режимы старения

Stage No.	t , °C	τ , min
1	670	15
2	640	40
3	600	40
4	575	40
5	555	30
6	535	30
7	525	30

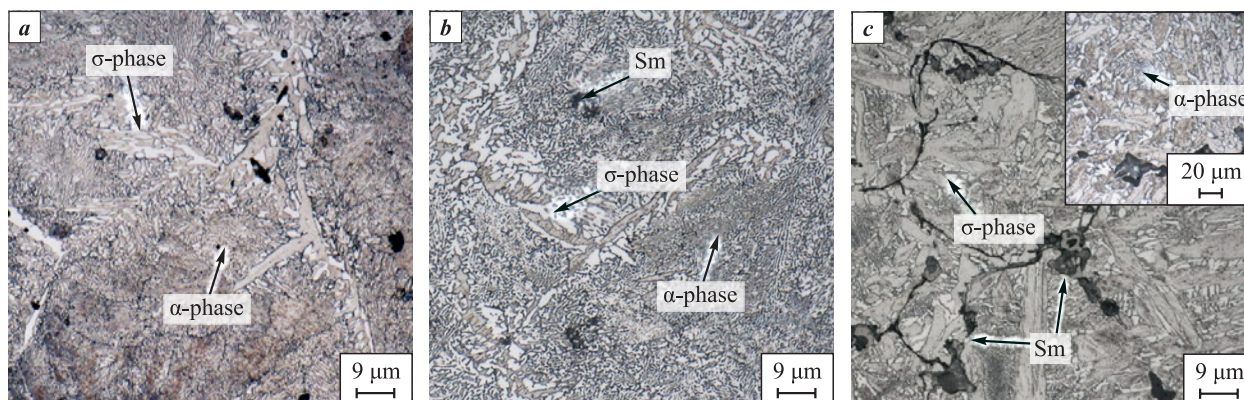


Fig. 2. Microstructure of the alloys after sintering ($\times 1000$)

Composition 1 (without additive) (a), 3 (b) and 6 (c) (see Table 1)

Рис. 2. Микроструктура сплавов после спекания ($\times 1000$)

Состав 1 (без добавки) (a), 3 (b) и 6 (c) (см. табл. 1)

netic α_1 -phase in the weakly magnetic α_2 -matrix, along with the presence of samarium-containing phase inclusions that enhance the magnetic anisotropy of the alloy, resulted in increased magnetic properties (H_c , B_r , $(BH)_{\max}$) compared to the original sample (see Fig. 1).

The structure of the samples after sintering consists of a lamellar σ -phase, constituting 70–80 vol. %, primarily located at the grain boundaries, with interlayers of the α -phase (Fig. 2). Samarium, appearing as dark areas in the photographs in Fig. 2, b and c, is also predominantly observed at the grain boundaries.

Due to the presence of the σ -phase, the hardness of the samples after sintering was 35–42 HRC. However, with an increase in the concentration of the KS25DTs additive from 0 to 9 %, the hardness decreased, as did the density (Table 3). The change in porosity exhibited the opposite trend accordingly.

The heating temperature for quenching was selected based on available research results [24] and DSC data. The microstructure of the base alloy after quenching represented an α -solid solution (Fig. 3, a). In samples containing the KS25DTs additive, in addition to the α -phase, undissolved Sm inclusions were present (Fig. 3, b, c).

The hardness of the samples after quenching ranged from 20 to 24 HRC and decreased with an increase in the KS25DTs concentration.

To determine the distribution pattern of the KS25DTs additive in the structure of the 22Kh15K4MS alloy, a sample after quenching was examined using a scanning electron microscope. It was found that the basis of the quenched alloy's structure is an α -solid solution with inclusions containing samarium and zirconium. According to the distribution maps (Fig. 4, b), sama-

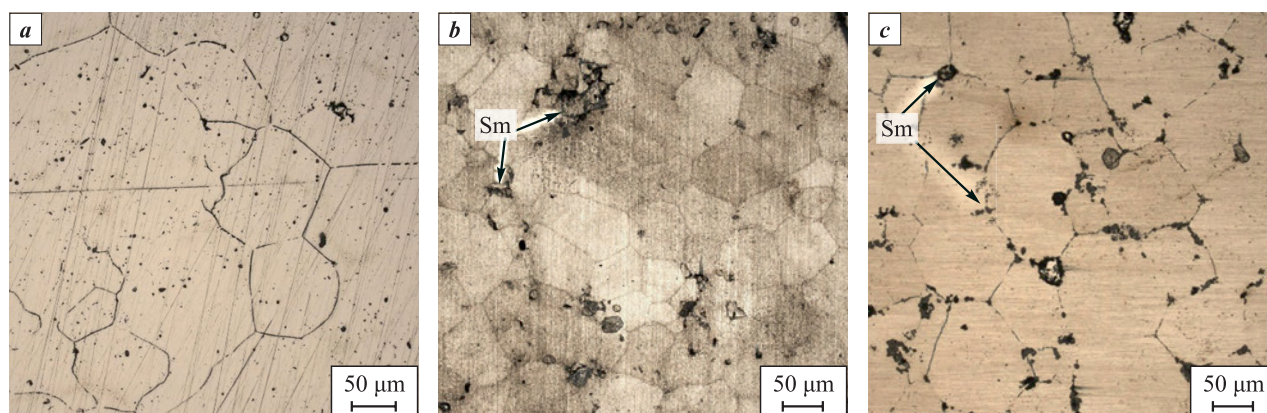


Fig. 3. Microstructure of the alloys after quenching ($\times 1000$)

Composition 1 (without additive) (a), 3 (b) and 6 (c) (see Table 1)

Рис. 3. Микроструктура сплавов после закалки ($\times 1000$)

Состав 1 (без добавки) (a), 3 (b) и 6 (c) (см. табл. 1)

rium is unevenly distributed within the structure, with areas of accumulation present.

The regions of Sm and Zr distribution overlap when the inclusion size is greater than 1 μm (see Fig. 4, *b*). The authors attribute this to the hindered diffusion processes in the larger initial KS25DTs particles. When the particle size of the additive is below 1 μm , Zr is not detected (Fig. 4, *d*), indicating its uneven distribution in the initial charge material. Regions enriched with Sm are depleted in Co, suggesting partial redistribution of samarium from KS25DTs into the α -solid solution.

The thermal effects during heating of quenched samples, both of the base composition and with

the addition of 3 % KS25DTs, exhibited similar kinetics (Fig. 5 *a, b*): transformations in both alloys occurred in the temperature range of 500–1100 °C. At 500 °C, spinodal decomposition of the α -phase into strongly magnetic and weakly magnetic phases began, characterized by heat absorption. The addition of 3 % KS25DTs did not significantly affect the position of the first local extremum at around 520 °C. The precipitation of the σ -phase from the solid solution began at 670–680 °C, with the corresponding local extremum recorded at around 700 °C in both samples. The temperature of the third local extremum for the base alloy without the additive was 830 °C, and with the additive, it was 848 °C.

For the alloy with 3 % KS25DTs (Fig. 5, *b*), a curve inflection was observed at 300 °C, which was absent in the base sample. The same peak appeared on the DSC curve of the KS25DTs alloy (Fig. 5, *d*) at 275 °C. According to the study [25], the eutectoid decomposition of SmCo_5 into Sm_2Co_7 and $\text{Sm}_2\text{Co}_{17}$ phases occurs at temperatures below 750 °C, as confirmed by the DSC curve of the KS25DTs alloy (Fig. 5, *d*). When the concentration of the additive in the 22Kh15K4MS alloy was increased to 9 %, an unusual peak at 800 °C was observed on the DSC curve (Fig. 5, *c*).

Thus, the addition of 3 % samarium does not significantly affect the decomposition temperatures of the α -solid solution based on Fe–Cr–Co; however, increasing its concentration to 9 % leads to the appearance of atypical phase transitions in the 22Kh15K4MS alloy.

Table 3. Density, porosity and hardness of sample blanks after sintering

Таблица 3. Плотность, пористость и твердость заготовок образцов после спекания

Concentration of the KS25DTs, %	Density, g/cm^3	Porosity, %	Hardness, HRC
0	7.9	0.3	42
1.5	7.9	0.5	41
3.0	7.8	1.4	38
4.5	7.7	2.7	39
6.0	7.7	2.7	38
9.0	7.6	4.2	35

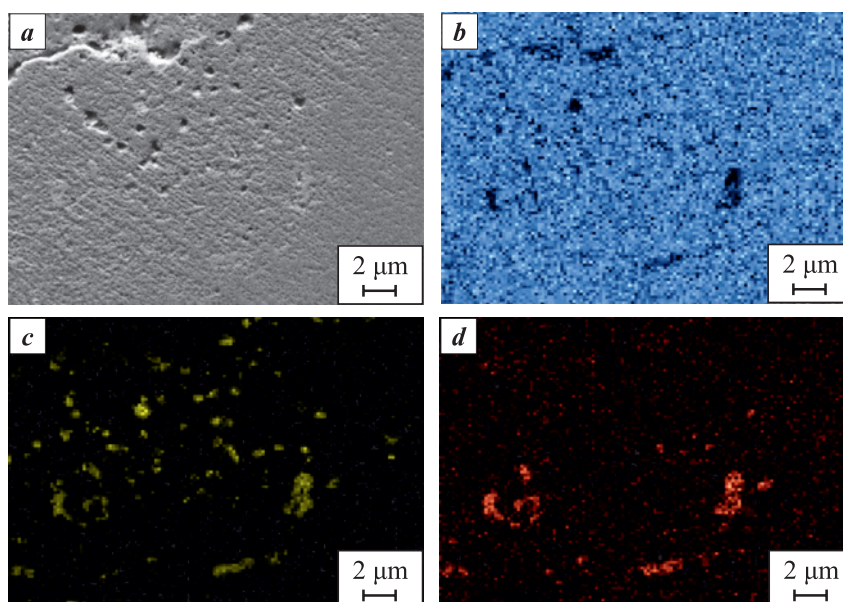


Fig. 4. Microstructure of alloy composition 3 (see Table 1) after quenching (*a*) and distribution maps of Sm (*b*), Co (*c*) and Zr (*d*) in the structure

Рис. 4. Микроструктура сплава состава 3 (см. табл. 1) после закалки (*a*) и карты распределения Sm (*b*), Co (*c*) и Zr (*d*) в структуре

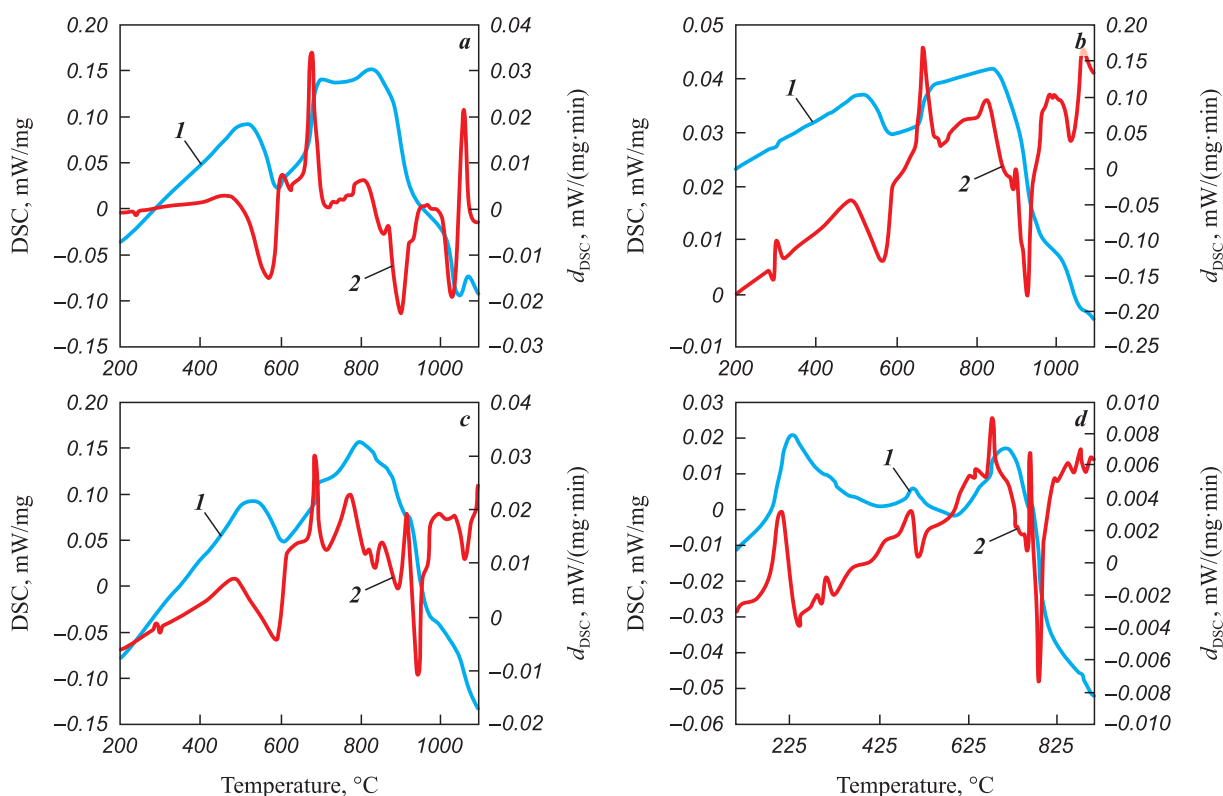


Fig. 5. DSC (1) and d_{DSC} (2) curves of alloys 22Kh15K4MS (a), 22Kh15K4MS + 3 % KS25DTs (b), 22Kh15K4MS + 9 % KS25DTs (c) and KS25DTs (d) when heated at a rate of 10 °C/min

Рис. 5. Кривые ДСК (1) и $d_{ДСК}$ (2) сплавов 22Х15К4МС (а), 22Х15К4МС + 3 % КС25ДЦ (б), 22Х15К4МС + 9 % КС25ДЦ (с) и КС25ДЦ (д) при нагреве со скоростью 10 °С/мин

To evaluate the changes in the phase composition of the 22Kh15K4MS alloy when doped with 3 % KS25DTs, an X-ray phase analysis was conducted on the samples after quenching and aging. The results are shown in Fig. 6. The X-ray diffraction pattern

of the initial sample after quenching shows the presence of the α -phase ($2\theta = 52.2^\circ$). Multistage aging led to a significant increase in magnetic properties. The phase composition after 7 stages of aging underwent the following changes.

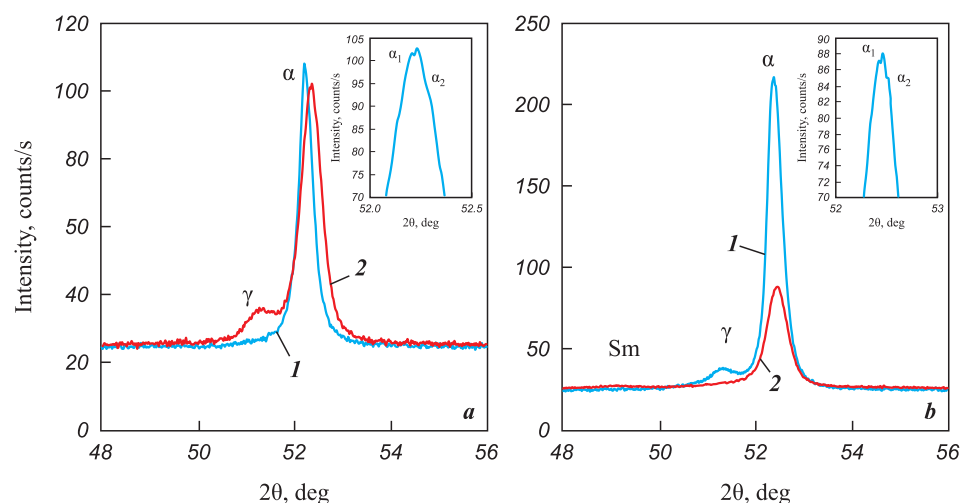


Fig. 6. X-ray diffraction patterns of the base 22Kh15K4MS sample (a) and with the addition of 3 % KS25DTs (b) after quenching (1) and thermomagnetic treatment (2)

Рис. 6. Рентгенограммы исходного образца 22Х15К4МС (а) и с добавкой 3 % КС25ДЦ (б) после закалки (1) и термомагнитной обработки (2)

During aging, the α -phase peak split into two isomorphous phases: α_1 , enriched with FeCo, and α_2 , based on FeCr. This is noticeable in the 22Kh15K4MS alloy (Fig. 6, a) by the increased half-width of the α -phase intensity peaks in the region of $2\theta = 52.24^\circ$, which is not observed in samples with the KS25DTs additive (Fig. 6, b). In the X-ray diffraction pattern of the alloy containing the KS25DTs additive, a γ -phase peak ($2\theta = 51.36^\circ$) was detected after quenching, which was absent in the undoped sample (see Fig. 6, a). This may indicate a narrowing of the α -solid solution region and a decrease in its stability due to the introduction of alloying additives. A weak peak of the samarium phase with a hexagonal crystal lattice was found at $2\theta = 49.2^\circ$, which can be explained by its low concentration (23–25 %) in the KS25DTs alloy. This, along with the high values of the crystal anisotropy constant and the saturation magnetization of samarium, led to an increase in the magnetic anisotropy of the doped alloy, contributing to the enhancement of its magnetic properties [10; 21].

Based on X-ray phase analysis data, the lattice parameters of the α -phase of the base alloy and the alloy with a 3 % KS25DTs additive are equal and amount to $a = 2.87 \text{ \AA}$. The interplanar distance decreased when doping the 22Kh15K4MS alloy: after quenching, it was $2.032 \text{ \AA}$, and in the alloy with a 3 % KS25DTs additive – $2.027 \text{ \AA}$. The invariance of the lattice parameter and the decrease in the interplanar distance indicate the absence of Sm dissolution in the α -phase of Fe–Cr–Co system alloys.

To determine the rectangularity coefficient of the magnetic hysteresis loop in the 22Kh15K4MS +

+ 3 % KS25DTs alloy, a sample with a coercive force of 10 kA/m was tested under a remagnetizing field intensity of 100 A/cm (10 kA/m), corresponding to the field intensity of the stator of the hysteresis experimental motor (Fig. 7). The alloy with a 3 % KS25DTs additive was aged according to the first 3 stages of the regime presented in Table 2, with the application of an external magnetic field. The holding time at each stage ranged from 5 to 40 min. The combination of the alloy composition and the thermomagnetic treatment regime ensured high K_I values – up to 0.87.

Thus, increasing the content of the KS25DTs additive from 1.5 to 3 % contributes to changes in the magnetic properties of the 22Kh15K4MS alloy.

Conclusions

The best combination of magnetic hysteresis loop parameters was achieved with a 3 % KS25DTs content in conjunction with thermomagnetic treatment: $H_c = 55.6 \text{ kA/m}$, $B_r = 1.33 \text{ T}$, and $(BH)_{\max} = 41 \text{ kJ/m}^3$. However, increasing the KS25DTs additive content from 4.5 % to 9 % results in a decrease in the alloy's magnetic characteristics due to phase coarsening, increased porosity, and the segregation of samarium at the grain boundaries.

Adding up to 3 % KS25DTs does not significantly affect the transformation kinetics of the 22Kh15K4MS alloy. In contrast, increasing the additive concentration from 4.5 % to 9 % leads to the emergence of transformations not typical for this alloy. The presence of Sm phases with high crystal anisotropy constants and saturation magnetization enhances the magnetic characteristics of the doped 22Kh15K4MS alloy.

The combination of the alloy composition with 3 % KS25DTs and the thermomagnetic treatment regime allows for an increased K_I value of 0.87, which may positively influence the dynamic characteristics of precision hysteresis motors in the future.

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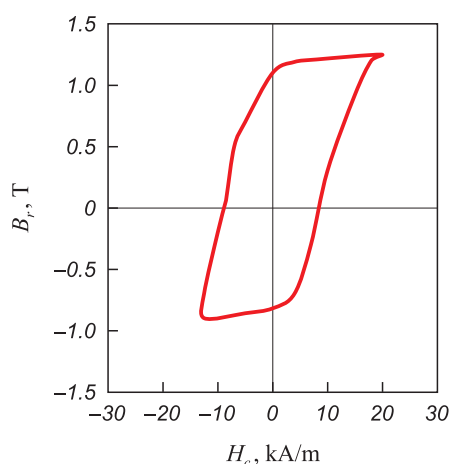


Fig. 7. Magnetic hysteresis loop of the 22Kh15K4MS alloy with 3 % KS25DTs at a magnetizing field intensity $H_m = 100 \text{ A/cm}$ after aging

Рис. 7. Петля магнитного гистерезиса сплава 22Х15К4МС с 3 % КС25ДЦ при намагниченности магнитного поля $H_m = 100 \text{ А/см}$ после старения

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Information about the Authors

Maria A. Beltyukova – Postgraduate Student of the Department of Metal Science, Thermal and Laser Processing of Metals, Perm National Research Polytechnic University

 **ORCID:** 0000-0002-6599-5091

 **E-mail:** marievamar@rambler.ru

Alexander A. Shatsov – Dr. Sci. (Eng.), Professor of the Department “Metal science, heat and laser treatment of metals”, Perm National Research Polytechnic University

 **ORCID:** 0000-0002-2723-964X

 **E-mail:** shatsov@pstu.ru

Сведения об авторах

Мария Александровна Бельтюкова – аспирант кафедры «Металловедение, термическая и лазерная обработка металлов», Пермский национальный исследовательский политехнический университет (ПНИПУ)

 **ORCID:** 0000-0002-6599-5091

 **E-mail:** marievamar@rambler.ru

Александр Аронович Шацов – д.т.н., профессор кафедры «Металловедение, термическая и лазерная обработка металлов», ПНИПУ

 **ORCID:** 0000-0002-2723-964X

 **E-mail:** shatsov@pstu.ru

Contribution of the Authors

M. A. Beltyukova – preparation of the mixture and initial samples, conducting experiments, writing the manuscript.

A. A. Shatsov – defining the study's objective, participating in the discussion of results, editing the manuscript.

Вклад авторов

М. А. Бельтюкова – подготовка смеси и исходных образцов, проведение экспериментов, написание текста статьи.

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Научная статья

Dispersion strengthening of powder high-speed steel R6M5K5 with particles of SHS ceramics $\text{MoSi}_2\text{--MoB--HfB}_2$

A. S. Akhmetov[✉], S. K. Mukanov, M. E. Samoshina,
V. Yu. Lopatin, Zh. V. Ereemeeva

National University of Science and Technology “MISIS”
4 bld. 1 Leninskiy Prosp., Moscow 119049, Russia

✉ aman1aotero@gmail.com

Abstract. The possibility of dispersion strengthening of powder high-speed steel R6M5K5 with $\text{MoSi}_2\text{--MoB--HfB}_2$ heterophase ceramics particles was investigated. A mechanically alloyed powder mixture with an average particle size of $d = 10 \mu\text{m}$ was used as the base material; the ceramic powder additive ($d = 5 \mu\text{m}$), obtained by the SHS method, was also used. Mixing was carried out in a high planetary ball mill. As a result, powder mixture particles with sizes of 2–25 μm were obtained, close to spherical in shape, with larger particles being agglomerates. Cold pressing and sintering were performed, achieving a density of up to 92.7 % and a hardness of 62 HRA, as well as hot pressing with a density of 97.2 % and a hardness of 65 HRC. The hot-pressed billet had a bending strength of 1141 MPa and a compressive strength of 2157 MPa. The prospects of using heterophase ceramics as a strengthening additive was shown, which contributes to lowering the temperature of the liquid phase formation and creates a pronounced heterogeneous microstructure, similar to the microstructure of metallic glass materials. The matrix is a solid solution based on iron (with an average grain size of 14–34 μm) with a network of eutectic carbide Me_6C and ceramic additive inclusions in the form of HfO_2 , SiO_2 , and HfSiO_4 compounds. This provided a twofold reduction in wear during tribological tests against a counterbody made of VK6 hard alloy. The obtained composite material, demonstrating high red hardness, may find application in the production of wear-resistant products operating at temperatures up to 630 °C.

Keywords: high-speed steel, powder metallurgy, dispersion hardening, ceramics, tribology, wear

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Дисперсное упрочнение порошковой быстрорежущей стали Р6М5К5 частицами СВС-керамики $\text{MoSi}_2\text{--MoB--HfB}_2$

А. С. Ахметов[✉], С. К. Муканов, М. Е. Самошина,
 В. Ю. Лопатин, Ж. В. Еремеева

Национальный исследовательский технологический университет «МИСИС»
 Россия, 119049, г. Москва, Ленинский пр-т, 4, стр. 1

✉ aman1aotero@gmail.com

Аннотация. Исследована возможность дисперсного упрочнения порошковой быстрорежущей стали Р6М5К5 частицами гетерофазной керамики $\text{MoSi}_2\text{--MoB--HfB}_2$. В качестве исходного материала использованы: механически легированная порошковая смесь со средним размером частиц $d = 10$ мкм; измельченная порошковая керамическая добавка ($d = 5$ мкм), полученная методом самораспространяющегося высокотемпературного синтеза (СВС). Смешивание осуществлялось в планетарной центробежной мельнице. В результате получены частицы порошковой смеси размером 2–25 мкм, по форме, близкой к округлой, более крупные частицы представляли собой агломераты. Проведены холодное прессование и спекание с достижением плотности до 92,7 % и твердости 62 HRA, а также горячее прессование с плотностью заготовки 97,2 % и твердостью 65 HRC. Горячепрессованная заготовка имела прочность на изгиб 1141 МПа и на сжатие 2157 МПа. Показана перспективность применения гетерофазной керамики в качестве упрочняющей добавки, которая способствует снижению температуры образования жидкой фазы и образует ярко выраженную гетерогенную микроструктуру, схожую с микроструктурой металлокерамических материалов. Матрица – твердый раствор на основе железа (со средним размером зерен 14–34 мкм) с сеткой из эвтектического карбида Me_6C и включениями керамической добавки в виде соединений HfO_2 , SiO_2 и HfSiO_4 . Это обеспечило уменьшение в 2 раза приведенного износа при трибологических испытаниях в паре с контртелом из твердого сплава ВК6. Полученный композиционный материал, продемонстрировавший высокую красностойкость, может найти применение в изготовлении износостойких изделий, эксплуатируемых при температурах до 630 °С.

Ключевые слова: быстрорежущая сталь, порошковая металлургия, дисперсное упрочнение, керамика, трибология, износ

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Introduction

Effective combinations of type and content of additives for strengthening powder high-speed steel (HSS) by introducing dispersed hard particles have been widely studied. Generally [1], when selecting strengthening additives, important criteria include their stability at the operating temperatures of the material being strengthened and minimal solubility in the matrix. Carbides such as NbC, TiC, VC, etc. [2–7], and nitrides like VN [8], meet these requirements for HSS. However, compounds that actively interact with the matrix can also be used as dispersed additives. For example, studies [9; 10] investigated the effect of adding boron carbide (B_4C) on the properties of M3/2 powder steel (analogous to 10R6M5), consolidated by hot pressing. It was found that dispersion strengthening led to an increase in hardness up to 85 HRA, with B_4C particles interacting with the matrix. At optimal concentrations, such an additive can ensure high density at rela-

tively low sintering temperatures ($t = 1150\div 1190$ °С) due to the interaction of both boron and carbon with the matrix. As a result, these characteristics significantly enhance the physical and mechanical properties of the material [10].

The consolidation of powder high-speed steel with strengthening additives is often performed by pressing and supersolidus sintering or hot pressing (HP), without resorting to hot isostatic pressing [2–11].

Another important aspect in the dispersion strengthening of powder HSS, in addition to the choice of additive and its content, is the method of mixing. Incorrect selection of the method and conditions can lead to particle segregation [12]. Usually, for mixing metal powders with dispersed additives, a planetary ball mill is used, which ensures not only high-quality mixing and uniform distribution of strengthening dispersed particles throughout the charge but also additional grinding of both the strengthening and base

powder particles [13]. As a result, with a proper selection of the mixing mode in the planetary ball mill, a fine-grained structure of the material can be obtained, enhancing its physical and mechanical properties. High dispersion of the powder mixture particles can lead to activated sintering [14]. This also allows for maintaining a fine-grained structure by achieving high density with shorter sintering times, preventing grain growth due to prolonged holding.

The heterophase ceramic $\text{MoSi}_2\text{--MoB--HfB}_2$, produced using self-propagating high-temperature synthesis (SHS), is of interest as a strengthening additive due to its high hardness (19.5 GPa) and heat resistance, particularly its resistance to oxidation at elevated temperatures across a wide range [15; 16]. The boron in the ceramic composition can help form a liquid phase at relatively low temperatures and activate the sintering process [10; 17].

Such complex compounds are rarely used as strengthening additives, making the study of their effect on the physical and mechanical properties and microstructure of HSS a pertinent task.

The aim of this work was to produce consolidated samples from a powder mixture of high-speed steel with the addition of heterophase ceramic $\text{MoSi}_2\text{--MoB--HfB}_2$ and to study their properties to identify promising areas of application for this material.

Materials and methods

The mechanically alloyed powder mixture of HSS grade R6M5K5 was used as the base material, with the following composition by mass percentage:

W	6.0
Mo	5.0
Co	5.0
Cr	4.0
V	2.0
C	0.9
Fe	Rest.

This mixture was obtained by milling in a Planetary ball mill “Activator – 4M” (Russia) at a drum rotation speed of 800 rpm, with a ball-to-powder ratio of 10:1 and a milling time of 30 min. The characteristics of the initial powder components used to produce this mixture are presented in Table 1.

The size range of the main fraction of the mechanically alloyed powder mixture was 3–20 μm , with an average particle diameter of 10 μm and $D_{50} = 9 \mu\text{m}$. The mixture consists of solid solutions based on Fe, W, and Mo, as well as WC carbide. The ceramic powder additive had a composition

of 60 % (90 % MoSi_2 –10 % MoB) + 40 % HfB_2 , with an average particle size of 5 μm . The method of its production is described in [15].

The powder steel was mixed with 3 vol. % of the strengthening additive and processed in the Planetary ball mill “Activator – 4M” at a drum rotation speed of 800 rpm, a ball-to-powder ratio of 10:1, and processing times of 15, 30, and 45 min.

The microstructure of the samples was examined using a scanning electron microscope (SEM) S-3400N (Hitachi, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS) NORAN System 7 X-ray Microanalysis System (Thermo Scientific, USA).

X-ray diffraction phase analysis (XRD) of the samples was performed on a D2 PHASER diffractometer (Bruker AXS GmbH, Germany) using CuK_α radiation (1.5418 Å).

Particle size distribution was assessed using an ANALYSETTE 22 MicroTec plus (Fritsch GmbH, Germany). The flowability and bulk density of the powder mixture were determined according to GOST 20899-98 and GOST 19440-94, respectively. Additionally, the compressibility during cold pressing and the change in density after sintering were investigated.

Cold pressing of the obtained mixture with and without the ceramic additive was carried out in a steel mold with an inner diameter of 12 mm at pressures ranging from 200 to 900 MPa, and the sintering of the billets was conducted at 1200 °C for 60 min. Hot pressing was performed in a graphite mold with an inner diameter of 20 mm in a Direct Hot Pressing DSP-515 SA press (Dr. Fritsch Sondermaschinen GmbH, Germany) under vacuum at 1000 °C and 50 MPa. The heating and cooling rates were 50 °C/min, with an isothermal holding time of 3 min. The mass of the charge during pressing was calculated to ensure that the height of the pore-free

Table 1. Characteristics of the initial powder components

Таблица 1. Характеристики исходных порошковых компонентов

Powder grade	Element	GOST/TU	Purity, %
PZhRV 2.200.26	Fe	TU 14-5365-98	99.24
PVCh	W	TU 48-19-57-91	99.99
PM	Mo	TU 14-22-160-2002	99.90
PK	Co	GOST 9721-79	99.95
ERKh-1	Cr	GOST 5905-2004	99.99
FVd50U0,5	V	GOST 27130-94	99.00
P-803	C	GOST 7885-86	99.90

billets was 0.5 times the diameter. Heat treatment (HT) of the obtained hot-pressed billets was carried out under the following conditions: annealing at 800 °C, quenching in oil from 1210 °C, and double tempering at 560 °C [18].

The compressive and flexural strength were evaluated using an LF-100KN testing machine (Walter + Bai, Switzerland). Hardness after hot pressing, heat treatment, and annealing at 630 °C for 4 h (red hardness) was measured using a TR5006 hardness tester (Tochpribor, Russia).

Comparative tribological tests were conducted at room temperature using a Tribometer friction machine (CSM Instruments, Switzerland) in accordance with ASTM G 99-17 and DIN 50324. The tests were performed in a reciprocating motion mode with a “pin-on-disc” configuration. A ball made of WC–Co hard alloy (VK6) was used as the counterbody. The test conditions were as follows: linear speed – 10 cm/s, applied load – 2 N, track length – 4 mm, and total running distance – 10,000 cycles. The profiles of the wear tracks were studied using a WYKO NT 1100 optical profilometer (Veeco, USA).

Results and discussion

After processing (mixing) in the planetary ball mill for 15, 30 and 45 min, the technological properties of each powder mixture were determined: flowability, bulk density, and particle size distribution. The results are presented in Table 2.

The obtained powder mixtures did not exhibit flowability when tested according to GOST 20899-98. Minor variations in bulk density values are associated with differences in particle sizes. The lack of flowability and low bulk density are due to the high dispersion of the powder mixture (average particle size 10–16 µm). Changes in particle size distribution are explained by the different milling durations: 15, 30 and 45 min. In the latter case, the particles tend to agglomerate. Further studies were conducted on the powder mixture processed in the planetary ball mill for 30 min,

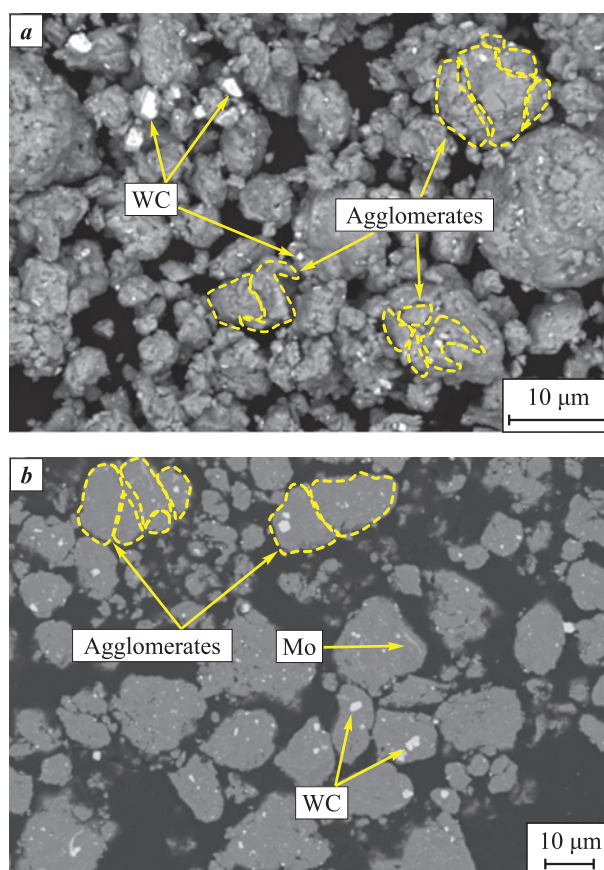


Fig. 1. SEM images of the morphology of HSS powder mixture particles (a) and their microstructure in cross-section (b)

Рис. 1. РЭМ-изображения морфологии частиц (a) порошковой смеси БРС и их микроструктуры на поперечном шлифе (b)

which is optimal for achieving a dispersed particle size distribution.

Figure 1 shows SEM images of the morphology of the powder mixture particles and their microstructure on a cross-section. It can be seen that the powder mixture particles range in size from 2 to 25 µm, with a near-spherical shape, and larger particles are agglomerates. The images were obtained in backscattered electron detection mode, which highlights heavy alloying elements (tungsten and molybdenum) by contrast,

Table 2. Technological properties of the HSS powder mixture at different processing durations of the PBM

Таблица 2. Технологические свойства порошковой смеси БРС при различной длительности обработки в ПЦМ

Processing duration, min	Flowability, s	Bulk density, g/cm ³	Particle size distribution range, µm	Average particle size, µm	Distribution quantile D_{50} , µm
15	Does not flow	2.66	6–30	12	11
30		2.50	3–30	10	8
45		2.90	4–30	16	12

distributed both on the surfaces and within the iron particles.

The presence of the introduced ceramic is detected only through general EDS analysis of the observed areas, indicating a high uniformity of the dispersion of the additive within the powder mixture, without the formation of separate agglomerates.

Figure 2 shows the dependence of the relative density of the billets on the compaction pressure after pressing and sintering. The dependencies show that during cold pressing, the powder mixtures are compacted to achieve a relative density of up to 69.8 % at a pressure of 900 MPa. After sintering, the density increases to 92.7 %. The highest hardness (62.0 ± 1.0 HRA) is observed in the densest sintered billets, pressed at $P = 900$ MPa. The high level of compressibility during cold pressing is provided by the iron-based matrix powder.

The significant increase in density during sintering indicates an intense process at 1200 °C. This is due to the high initial dispersion of the powder mixture, which provides an increased specific surface area and promotes the activation of sintering. The presence of boron lowers the temperature of liquid phase formation in the steel, further activating the sintering process [10; 17]. This may result in the formation of some amount of liquid phase.

Figure 3 shows SEM images of the microstructure of the sintered sample of R6M5K5 steel with ceramic additive, pressed at $P = 900$ MPa. The microstructure of the sintered billet is quite homogeneous and porous, with alloying elements not forming carbide compounds Me_6C and MeC , which ensure the red hardness of HSS. The effect of the ceramic additive on the microstructure images and EDS analysis results is difficult to assess. In

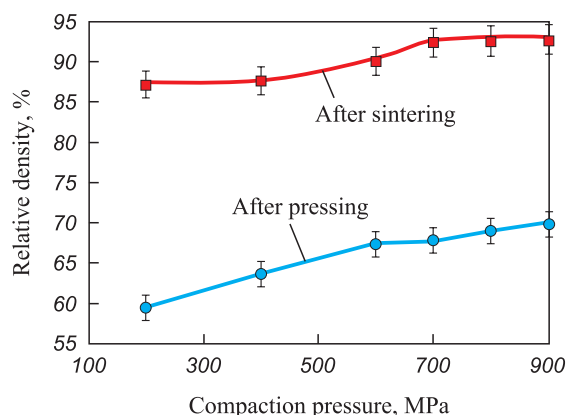


Fig. 2. Dependence of relative density of billets on compaction pressure before and after sintering

Рис. 2. Зависимость относительной плотности заготовок от давления прессования до и после спекания

Fig. 3, *b*, grains of the matrix with a size of 3–8 μm can be distinguished. The general elemental EDS analysis (integral area in Fig. 3, *a*) shows the presence of Hf and Si, which are part of the ceramic but not included in the composition of R6M5K5 steel itself (Table 3). This indicates significant dissolution of the ceramic additive in the steel matrix.

After hot pressing the powder mixture, the obtained billet had a hardness of 64.0 ± 0.3 HRC with a relative density of 97.2 %, and after heat treatment, the hardness changed slightly to 64.7 ± 0.2 HRC. The high hardness of the hot-pressed billet is due to the low temperature of hot pressing, which preserves a finer grain structure. During prolonged holding during annealing and austenitization at high temperatures, inevitable grain growth occurs. The increase in hardness after heat treatment is largely due to the formation of a carbide network during quenching and secondary carbides during tempering [19].

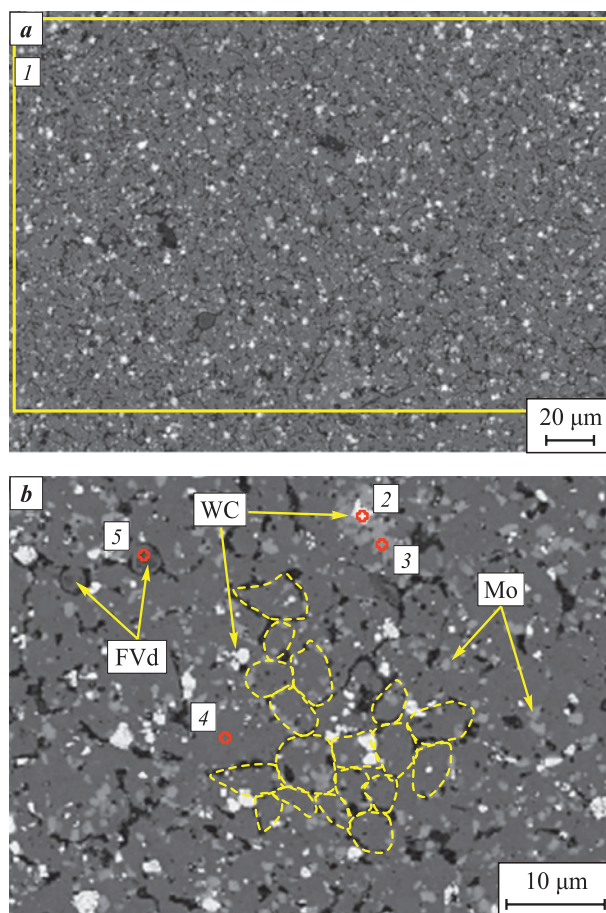


Fig. 3. SEM images of the microstructure of the sintered sample at 500× (*a*) and 2000× (*b*) magnification

Рис. 3. РЭМ-изображения микроstructuresпеченного образца при увеличении 500× (*a*) и 2000× (*b*)

Table 3. Results of general and EDS analyses of microstructural components of the sintered HSS billet (see Fig. 3)

Таблица 3. Результаты общего и ЭДС анализов микроструктурных составляющих спеченной заготовки БРС (см. рис. 3)

Area (component)	Content, at. %									
	C	V	Cr	Fe	Mo	Hf	W	Co	O	Si
1 (General)	20.4	2.4	3.8	58.4	4.0	0.4	1.8	2.5	3.7	2.7
2 (WC)	81.5	—	—	2.4	—	—	16.2	—	—	—
3 (Mo)	62.0	3.3	2.4	14.5	16.2	—	1.8	—	—	—
4 (Matrix)	17.2	0.4	2.4	78.6	1.2	—	0.3	—	—	—
5 (FVd)	27.1	37.3	2.4	25.4	2.9	—	4.8	—	—	—

Figure 4 shows SEM images of the microstructure of the hot-pressed billet after heat treatment. As seen from the data, carbide Me_6C with characteristic morphology is distributed along the grain boundaries, which is more typical for cast HSS [18; 20]. This may indicate the formation of a significant amount of liquid phase due to the melting of eutectic as a result of the influence of boron with the precipitation of eutectic carbide Me_6C , necessitating quenching at lower temperatures [17; 19]. In the matrix, represented by a solid solution based on iron, alloying elements are dissolved. After hot pressing followed by heat treatment, the introduced ceramic particles are fixed in the micro-

structure (marked in Fig. 4, *b* according to the presumed phases). The average grain size is 14–34 μm , and the size of the ceramic particles is 2–4 μm . Secondary carbide Me_6C is not detected, and vanadium, according to EDS results (Table 4), is contained in the matrix and Me_6C carbide. Secondary carbide Me_6C is not observed in the studied microstructure areas and XRD results (Table 5), as evidenced by the slight increase in hardness after heat treatment.

According to XRD data, the following phases are identified: $\alpha\text{-Fe}$ (matrix), carbide Me_6C ($\text{W}_3\text{Fe}_3\text{C}/\text{Mo}_3\text{Fe}_3\text{C}$), as well as HfO_2 and HfSiO_4 , which is consistent with

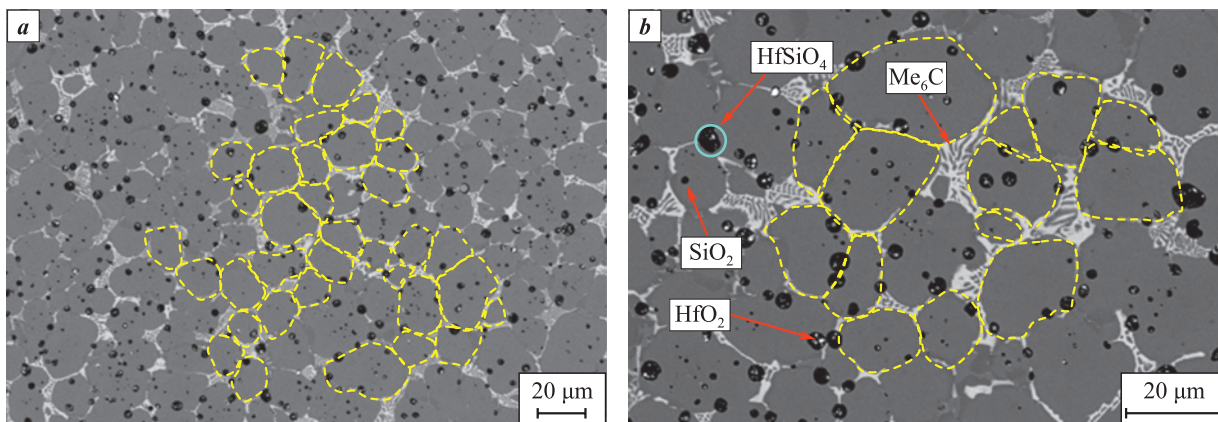


Fig. 4. SEM images of the microstructure of the hot-pressed biller after heat treatment

Рис. 4. РЭМ-изображения микроструктуры горячепрессованной заготовки после термообработки

Table 4. Results of EDS analysis of microstructural components of the hot-pressed HSS billet

Таблица 4. Результаты ЭДС-анализа микроструктурных компонентов горячепрессованной заготовки БРС

Component	Content, at. %										
	C	O	Si	V	Cr	Mn	Fe	Co	Mo	Hf	W
Matrix	14.3	—	—	1.4	3.7	—	74.5	2.8	2.1	—	1.3
HfSiO_4	9.8	60.2	20.0	0.9	—	0.4	2.6	0.1	0.4	5.6	—
HfO_2	18.5	57.9	—	—	0.5	—	3.6	0.4	1.3	17.7	—
SiO_2	11.2	61.3	20.6	1.3	0.6	0.2	4.3	—	0.5	—	—
Me_6C	31.9	—	—	4.8	3.9	—	32.8	1.6	15.6	—	9.4

Table 5. XRD results of the hot-pressed R6M5K5 billet with ceramic additive**Таблица 5. Результаты РФА горячепрессованной заготовки Р6М5К5 с керамической добавкой**

Phase	Structural type	Volume fraction, %	Lattice parameter, Å
α -Fe	<i>cI2/1</i>	82.4	$a = 2.890$
Me_6C	<i>cF112/2</i>	9.9	$a = 11.026$
HfSiO_4	<i>tI24/3</i>	1.6	–
HfO_2	<i>mP12/3</i>	1.5	–
Austenite	<i>cF4/1</i>	4.5	$a = 3.612$

the microstructure analysis results. Ceramic inclusions (Fig. 5) may represent hafnium silicate, which could form during the hot-pressing process or subsequent heat treatment [15; 21]. White particles in the structure of the ceramic additive (see Fig. 4, Table 4) in some areas are similar in composition to HfO_2 , indicating incomplete interaction of HfO_2 with SiO_2 , which forms HfSiO_4 [21]. Accordingly, the black areas are similar in composition to SiO_2 .

The strength characteristics of the hot-pressed billets were studied: the bending and compressive strength values were 1141 ± 50 and 2157 ± 42 MPa, respectively. Additionally, the red hardness of the hot-pressed samples was determined by annealing in air for 4 h at 630 °C. The hardness after annealing was 59.5 ± 0.8 HRC, meeting the requirements of GOST 19265-73.

Figure 5 shows the effect of the ceramic additive on the friction coefficient dependence on the running distance and the 2D profile of the wear track of hot-pressed powder high-speed steel R6M5K5 billets. It was found that they have a consistently low friction coefficient (0.20–0.22) when sliding against a VK6 alloy ball. The specific wear values calculated from the 2D profiles of the wear tracks were $5.40 \cdot 10^{-6}$ and $2.56 \cdot 10^{-6}$ $\text{mm}^3/(\text{N} \cdot \text{m})$ for the R6M5K5 and R6M5K5 + ceramic billets, respectively. Thus, the ceramic additive doubles the wear resistance of R6M5K5 steel (see Table 5). This is primarily due to the high hardness (64.0 ± 0.3 HRC) of the sample, owing to the formation of a carbide network and hard particles of SiO_2 and HfO_2 . However, the specific wear of the counterbody (Table 6) is twice as high when testing R6M5K5 with the ceramic additive.

According to [22], the increase in the actual contact area of the tribopair is accompanied by an increase in the friction coefficient. However, when sliding the ball on the R6M5K5 sample with the ceramic additive, this parameter did not change. The wear track of the R6M5K5 billet with the ceramic additive was studied using SEM (Fig. 6). At its edge, corresponding products in the form of flake-like agglomerates are present. According to EDS data (Table 7), they represent a mixture of oxidized counterbody and steel particles. Also, an adhered layer of oxidized wear products from the sample and counterbody was found in the wear track area. The pronounced heterogeneous

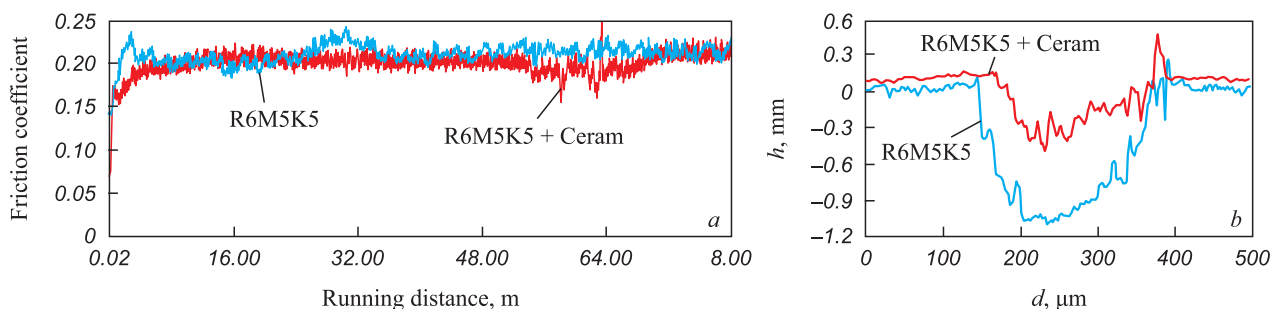
**Fig. 5.** Dependence of friction coefficient on running distance (*a*) and 2D profiles of wear tracks (*b*) of hot-pressed R6M5K5 steel billets and R6M5K5 steel billets with ceramic additive

Рис. 5. Зависимость коэффициента трения от длины пробега (*a*) и изображение 2D-профилей дорожек износа (*b*) горячепрессованных заготовок из стали Р6М5К5 и Р6М5К5 + керамическая добавка

Table 6. Results of tribological tests**Таблица 6. Результаты трибологических испытаний**

Sample	Specific wear, $10^{-6} \text{ mm}^3/(\text{N} \cdot \text{m})$		Friction coefficient		
	Sample	Counterbody	Initial	Average	Final
R6M5K5	5.40	0.20	0.41	0.22	0.23
R6M5K5 + ceramic	2.56	0.47	0.40	0.20	0.20

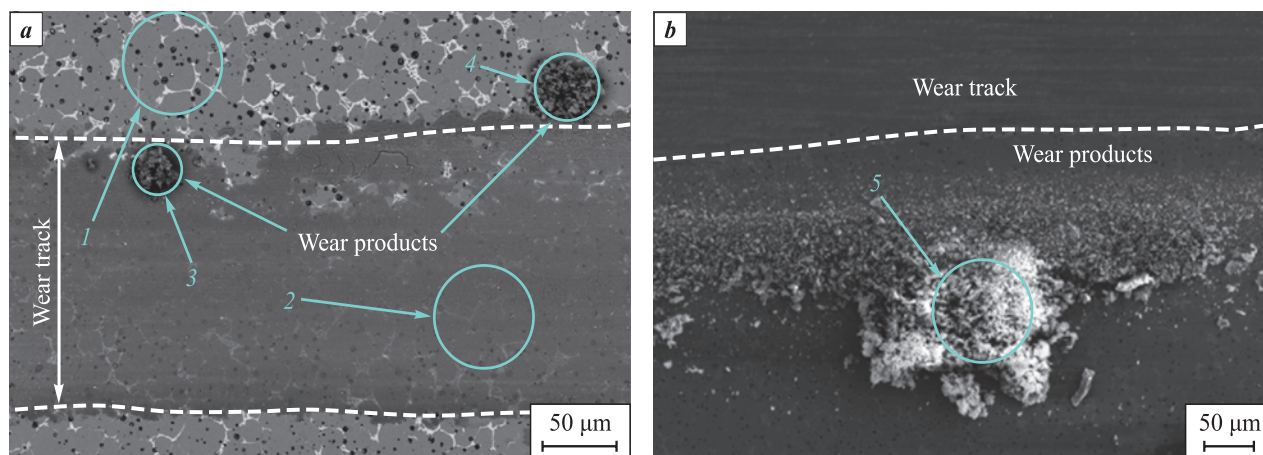


Fig. 6. SEM images of the wear track of the hot-pressed sample (a) and wear products (b)

Рис. 6. РЭМ-изображения дорожки износа горячепрессованного образца (a) и продуктов износа (b)

Table 7. Results of EDS analysis of wear track components

Таблица 7. Результаты ЭДС-анализа компонентов дорожки износа

Area No. in Fig. 6	Content, at. %									
	C	O	Si	V	Cr	Fe	Co	Mo	Hf	W
1	19.5	—	2.3	2.2	3.5	64.0	3.8	3.0	0.2	1.6
2	9.8	54.3	—	1.2	1.6	27.0	1.6	1.3	0.1	3.1
3	12.6	51.7	—	0.9	1.7	28.1	1.6	—	0.1	3.3
4	12.9	46.3	2.3	1.2	2.2	28.5	1.9	0.4	1.9	2.4
5	44.9	38.9	0.5	0.5	0.7	11.9	0.6	0.6	0.1	1.3

structure with ceramic inclusions is similar to the structure of powder metallic glass materials [23].

During wear, HfO_2 , SiO_2 and HfSiO_4 particles may contribute to its reduction [24]. The formed carbide structure is more preferable from the wear resistance perspective compared to dispersed carbides [25]. It can be assumed that the obtained composite material, demonstrating high red hardness, can also find application in the production of wear-resistant products operating at temperatures up to 630 °C.

Conclusions

1. Sintered and hot-pressed billets of HSS grade R6M5K5 with a 3 % addition of heterophase ceramic $\text{MoSi}_2\text{--MoB--HfB}_2$ were obtained, achieving relative densities of up to 92.7 % and 97.2 %, respectively. The hardness of the sintered billet was 62.0 HRA, while the hot-pressed billet reached 64.7 HRC. Both billets exhibited a bending strength of 1141 MPa and a compressive strength of 2157 MPa.

2. It was established that the hot-pressed billet is characterized by a pronounced heterogeneous microstructure, similar to that of metallic glass materials.

3. Tribological tests showed that the addition of the ceramic $\text{MoSi}_2\text{--MoB--HfB}_2$ to the hot-pressed R6M5K5 high-speed steel billet resulted in more than a twofold increase in wear resistance.

4. A method for further improvement of the physical and mechanical properties is proposed by introducing a smaller amount of boron-containing ceramic additive and performing quenching at lower temperatures.

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Information about the Authors

Сведения об авторах

Amankeldy S. Akhmetov – Scientific Project Engineer, Department of Powder Metallurgy and Functional Coatings (PM&FC), National University of Science and Technology “MISIS” (NUST MISIS)

 **ORCID:** 0000-0002-1606-838X

 **E-mail:** aman1aotero@gmail.com

Samat K. Mukanov – Cand. Sci. (Eng.), Junior Research Scientist, Laboratory “*In situ* Diagnostics of Structural Transformations”, Scientific Educational Center of Self-Propagating High-Temperature Synthesis, MISIS-ISMAN

 **ORCID:** 0000-0001-6719-6237

 **E-mail:** sam-mukanov@mail.ru

Vladimir Yu. Lopatin – Cand. Sci. (Eng.), Associate Professor, Department of PM&FC, NUST MISIS

 **ORCID:** 0000-0002-1294-9198

 **E-mail:** lopatin63@mail.ru

Marina E. Samoshina – Cand. Sci. (Eng.), Head of the Division of Academic Degrees, Academic Secretary of the Dissertation Board, NUST MISIS

 **ORCID:** 0009-0000-2773-3122

 **E-mail:** samoshina@list.ru

Zhanna V. Ereemeeva – Dr. Sci. (Eng.), Professor, Department of PM&FC, NUST MISIS

 **ORCID:** 0000-0002-1790-5004

 **E-mail:** ereemeeva-shanna@yandex.ru

Аманкельды Серикбаевич Ахметов – инженер научного проекта, кафедра порошковой металлургии и функциональных покрытий (ПМиФП), Национальный исследовательский технологический университет «МИСИС» (НИТУ МИСИС)

 **ORCID:** 0000-0002-1606-838X

 **E-mail:** aman1aotero@gmail.com

Самат Куандыкович Муканов – к.т.н., мл. науч. сотрудник лаборатории «*In situ* диагностика структурных превращений» Научно-учебного центра СВС, МИСИС-ИСМАН

 **ORCID:** 0000-0001-6719-6237

 **E-mail:** sam-mukanov@mail.ru

Владимир Юрьевич Лопатин – к.т.н., доцент кафедры ПМиФП, НИТУ МИСИС

 **ORCID:** 0000-0002-1294-9198

 **E-mail:** lopatin63@mail.ru

Марина Евгеньевна Самошина – к.т.н., начальник отдела учебных степеней, ученый секретарь диссертационного совета, НИТУ МИСИС

 **ORCID:** 0009-0000-2773-3122

 **E-mail:** samoshina@list.ru

Жанна Владимировна Еремеева – д.т.н., профессор кафедры ПМиФП, НИТУ МИСИС

 **ORCID:** 0000-0002-1790-5004

 **E-mail:** ereemeeva-shanna@yandex.ru

Contribution of the Authors

Вклад авторов

A. S. Akhmetov – conducted experiments, prepared the manuscript of the article.

S. K. Mukanov – participated in editing the text of the article, studied the features of tribological tests, and discussed the results.

M. E. Samoshina – participated in editing the text of the article, participated in the discussion of the results.

V. Yu. Lopatin – participated in the discussion of the results.

Zh. V. Ereemeeva – conceptualization of the study, participated in the discussion of the results.

А. С. Ахметов – проведение экспериментов, подготовка текста статьи.

С. К. Муканов – исследование особенностей трибологических испытаний, участие в обсуждении результатов, подготовка текста статьи.

М. Е. Самошина – участие в обсуждении результатов, корректировка текста статьи.

В. Ю. Лопатин – участие в обсуждении результатов.

Ж. В. Еремеева – концептуализация исследования, участие в обсуждении результатов.

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Research article

Научная статья



Oxidation-resistant Zr–Mo–Si–B coatings deposited by DCMS and HIPIMS methods

A. D. Chertova¹ , F. I. Chudarin¹, I. O. Vakhrusheva¹,
Yu. Yu. Kaplansky¹, X. Ren², P. Feng³, E. A. Levashov¹,
Ph. V. Kiryukhantsev-Korneev¹

¹ National University of Science and Technology “MISIS”

4 Leninsky Prospekt, Moscow 119049, Russia

² Henan Academy of Sciences

Zhengzhou 450046, China

³ China University of Mining and Technology

Xuzhou 221116, China

alina-sytchenko@yandex.ru

Abstract. This study focuses on the development of high-temperature oxidation-resistant coatings within the Zr–Mo–Si–B system. It addresses the deposition processes using direct current magnetron sputtering (DCMS) and high-power impulse magnetron sputtering (HIPIMS). The research includes an analysis of gas discharge plasma, investigation of the coating structure, and determination of the mechanical properties and high-temperature oxidation resistance of the resulting coatings. The coatings were found to be X-ray amorphous, characterized by a dense, defect-free structure with a uniform distribution of elements throughout their thickness. All coatings demonstrated high oxidation resistance at temperatures of 1100 and 1300 °C. The transition from DCMS to HIPIMS mode resulted in a 16–21 % reduction in oxidation depth at 1300 °C. The coating obtained via DCMS exhibited the greatest thickness and the best oxidation resistance at 1500 °C. The high-temperature oxidation resistance of the coatings is attributed to the formation of a protective surface oxide film of Si:B:O₂, with dispersed nanocrystallites *t*-ZrSiO₄ and *m*-ZrO₂ phases.

Keywords: direct current magnetron sputtering, high-power impulse magnetron sputtering, coatings, high-temperature oxidation resistance

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Жаростойкие покрытия Zr–Mo–Si–B, полученные методом магнетронного распыления в режимах DCMS и HIPIMS

А. Д. Чертова¹, Ф. И. Чударин¹, И. О. Вахрушева¹,
Ю. Ю. Капланский¹, Х. Ren², Р. Feng³, Е. А. Левашов¹,
Ф. В. Кирюханцев-Корнеев¹

¹ Национальный исследовательский технологический университет «МИСИС»
Россия, 119049, г. Москва, Ленинский пр-т, 4

² Henan Academy of Sciences
Zhengzhou 450046, China

³ China University of Mining and Technology
Xuzhou 221116, China

✉ alina-sytchenko@yandex.ru

Аннотация. Работа посвящена созданию жаростойких покрытий системы Zr–Mo–Si–B. Рассматриваются вопросы, связанные с процессом осаждения покрытий методами магнетронного распыления на постоянном токе (DCMS, *direct current magnetron sputtering*) и в высокомоощном импульсном режиме (HIPIMS, *high-power impulse magnetron sputtering*). Выполнен анализ плазмы газового разряда, исследована структура, определены механические характеристики и жаростойкость полученных покрытий. Установлено, что они являются рентгеноаморфными и характеризуются плотной малodefектной структурой с равномерным распределением элементов по толщине. Все покрытия обладают высокой стойкостью к окислению при температурах 1100 и 1300 °C. Переход от режима DCMS к HIPIMS привел к снижению глубины окисления на 16–21 % при температуре 1300 °C. Покрытие, полученное в режиме DCMS, имело максимальную толщину и показало лучшую стойкость к окислению при температуре 1500 °C. Высокая жаростойкость покрытий обусловлена образованием защитной поверхностной оксидной пленки Si:B:O с диспергированными в ней нанокристаллитами фаз *t*-ZrSiO₄ и *m*-ZrO₂.

Ключевые слова: магнетронное распыление на постоянном токе, высокомоощное импульсное магнетронное распыление, покрытия, жаростойкость

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Introduction

Zirconium disilicide (ZrSi₂), owing to its high strength characteristics and oxidation resistance, is a promising material for use as a base in the development of high-temperature oxidation and wear-resistant coatings [1; 2]. The protective properties of ZrSi₂ are due to the formation of a surface layer of silicon dioxide (SiO₂), which prevents the diffusion of oxygen atoms into the material and possesses high viscosity, aiding in the healing of cracks formed during heating. In multicomponent and multiphase materials, the local rearrangement of particles caused by the phase transition from monoclinic zirconium oxide (ZrO₂) to tetragonal ZrO₂ serves as an additional mechanism for defect healing [3]. Moreover, ZrO₂, formed as a result of ZrSi₂ oxidation, has a high melting point and can react with SiO₂ to form zirconium silicate (ZrSiO₄),

which is highly chemically stable and has low oxygen permeability [2; 4; 5].

Despite the high potential for practical application, information on the development of materials based on ZrSi₂ is limited. Known works [6; 7] describe ZrSi₂–MoSi₂–ZrB₂, ceramics obtained by self-propagating high-temperature synthesis (SHS). Due to the formation of a multilayer structure consisting of a ZrSiO₄ layer and sublayers based on ZrO₂ and SiO₂, these ceramics exhibit high oxidation resistance at 1650 °C.

In addition to the development of bulk materials based on ZrSi₂, researchers are also focusing on creating coatings with a similar composition. ZrSi₂-based coatings are widely used to protect zirconium alloys [8–10], C/C composites [11–14], and graphite [15; 16] from oxidation at high temperatures.

Studies [8; 9] have shown that the deposition of ZrSi_2 coatings reduces the thickness of the oxide layer on zirconium alloys by a factor of 10 at temperatures of 1000 and 1200 °C. The introduction of molybdenum disilicide (MoSi_2), which has self-healing properties, into ZrSi_2 coatings is of interest [3]. The addition of MoSi_2 reduces the likelihood of the phase transition of ZrO_2 from the tetragonal to monoclinic phase, which causes volume expansion and leads to coating cracking [12]. In a study [17], ZrSi_2 – MoSi_2 – ZrB_2 coatings obtained by slip-firing method exhibited record oxidation resistance at temperatures of 1500–1700 °C. This can be explained by the following factors:

- formation of a thermally stable heterogeneous oxide film;
- dissolution of ZrO_2 in the borosilicate layer forming ZrSiO_4 ;
- formation of thermally stable molybdenum-based particles that hinder oxygen diffusion;
- high melting point and low thermal conductivity of the ZrO_2 -based oxide layer, protecting the inner layers.

Despite the high oxidation resistance of ZrSi_2 – MoSi_2 – ZrB_2 coatings obtained by the slip-firing method, the application of this method is limited by the size of the treated parts. Additionally, it is not possible to accurately control the phase composition and thickness of the coating. In this regard, the direct current magnetron sputtering (DCMS) method appears promising, as it allows the production of defect-free coatings with a specified phase composition, uniform thickness, high adhesive strength, and the ability to reinforce complex-shaped products [18; 19].

The application of high-power impulse magnetron sputtering (HIPIMS) opens up additional possibilities for applying ceramic coatings [20; 21]. Due to its higher power, HIPIMS significantly increases the plasma density from $\sim 10^{10}$ ions/cm³ for DCMS to 10^{13} – 10^{14} ions/cm³ for HIPIMS [22]. In the latter case, sputtered atoms are intensely ionized while passing through the plasma, and the flow consists predominantly of ions rather than atoms, as in DCMS. The increased ion/atom ratio in the flow characteristic of HIPIMS leads to a significant enhancement in the adhesive strength of the deposited coatings due to the formation of pseudo-diffusion layers and ion implantation effects during the preliminary etching of the substrate surface [22]. The increased density of the structure and adhesive strength improve the mechanical properties, wear resistance, and oxidation resistance of the coatings [23; 24].

The aim of this study was to develop Zr–Mo–Si–B system coatings using DCMS and HIPIMS methods, and to investigate their structure, mechanical properties, and high-temperature oxidation resistance.

Materials and methods

The coatings were produced using the DCMS and HIPIMS methods with a functionally graded target (ZrSi_2 – ZrB_2 – MoSi_2)/Cr [25]. The coatings were produced using the DCMS and HIPIMS methods with a functionally graded target (ZrSi_2 – ZrB_2 – MoSi_2)/Cr [25]. Deposition was carried out in a vacuum chamber based on the UVN-2M pumping system (Quartz JSC, Russia) [26]. For the DCMS mode, a Pinnacle Plus power supply (Advanced Energy, USA) was used, while HIPIMS deposition was performed using a TruPlasma 4002 system (Trumpf, Germany). The average power for coating deposition using both methods was $P = 1$ kW. To compensate for the lower growth rate in the HIPIMS mode, experiments were conducted at an increased power of $P = 2$ kW. The HIPIMS frequency was 1 kHz, with a pulse duration of 50 µs, and the residual and working pressures of Ar (99.9995 %) were $3 \cdot 10^{-3}$ and $1 \cdot 10^{-1}$ Pa, respectively. Polycrystalline Al_2O_3 plates (VOK-100-1 grade) and Si (KEF-100 grade) were used as substrates. To remove surface contaminants before sputtering, the substrates were cleaned ultrasonically in isopropyl alcohol for 5 min and then cleaned with Ar^+ ions at 2 keV for 20 min using an ion source. The deposition time was 60 min for both modes ($P = 1$ kW) and 30 min for HIPIMS at $P = 2$ kW.

The magnetron discharge plasma was studied using optical emission spectroscopy with a PlasmaScope spectrometer (Horiba Jobin Yvon, France). The composition and structure of the coatings were analyzed using a scanning electron microscope (SEM) S-3400N (Hitachi, Japan) equipped with a Noran-7 Thermo energy-dispersive spectroscopy (EDS) attachment. The surface topography of the coatings was investigated using a WYKO-NT1100 optical profilometer (Veeco, USA). The phase composition of the coatings was determined by X-ray diffraction (XRD) using a D2 Phaser diffractometer (Bruker, Germany) with CuK_α radiation. Elemental profiles of the coatings were obtained by optical emission spectroscopy with a glow discharge (GDOES) using a Profiler 2 instrument (Horiba JY, France) [27].

Mechanical properties such as hardness (H), elastic modulus (E), and elastic recovery (W) were evaluated by nanoindentation using a Nanohardness Tester (CSM Instruments, Switzerland) at a load of 4 mN. To determine the oxidation kinetics, stepwise annealing

Designations, deposition modes, elemental composition, growth rate, and mechanical characteristics of the coatings

Обозначения, режимы осаждения, элементный состав, скорость роста и механические характеристики покрытий

Sample	Mode	Composition, at. %				Growth rate, nm/min	<i>H</i> , GPa	<i>E</i> , GPa	<i>W</i> , %
		Zr	Si	Mo	B				
1	DCMS	31	49	8	12	140	11 ± 0.9	177 ± 8	37
2	HIPIMS <i>P</i> = 1 kW	26	54	8	12	95	12 ± 0.5	181 ± 12	37
3	HIPIMS <i>P</i> = 2 kW	26	55	8	11	95	14 ± 1.2	208 ± 19	42

was performed in air in a muffle furnace SNOL-7.2/1200 (AB Umega, Lithuania) at 1000 °C with hold times of 10, 30, 60, and 180 min. To assess the high-temperature oxidation resistance of the coatings, non-isothermal annealing was conducted in a muffle furnace TK 15.1800.DM.1F (Thermoceramics LLC, Russia) at temperatures of 1100, 1300, and 1500 °C with a hold time of 10 min. After annealing, the coatings were examined using SEM, EDS, and XRD methods. The designations of the coatings and their deposition modes are presented in the Table below.

Results and discussion

Plasma diagnostics during coating deposition

Fig. 1 presents the plasma spectra obtained by sputtering of a Zr–Si–Mo–B target in DCMS and HIPIMS modes at an average power of 1 kW, as well as in HIPIMS mode at *P* = 2 kW.

Plasma analysis in the wavelength range of 200 to 880 nm was conducted for the elements present in the target, as well as for the working gas (Ar).

The main characteristic line positions, according to the Quantum XP software (Horiba JY, France), are 252, 288, and 386 nm for Si; 399 nm for Zr; 313 and 380 nm for Mo; 250 nm for B; and 603, 697, 707, 750, 801, 811, and 842 nm for Ar. When transitioning from DCMS to HIPIMS mode (with an average power of 1 kW in both cases), the intensities of the Mo, B, and Si peaks increased by 1.7, 3.7, and 2.5 times, respectively. The most significant change was observed for the Zr signal, with peak intensities increasing 14-fold, reaching a maximum when transitioning from DCMS to HIPIMS at *P* = 1 kW. The intensity of the Ar peaks during HIPIMS deposition decreased by 1.3 to 3.7 times compared to DCMS. Increasing the power from 1 to 2 kW during HIPIMS deposition resulted in an increase in the intensity of the Si, Mo, and B lines by 1.6, 1.7, and 1.5 times, respectively, while the intensity of the Zr remained unchanged.

Thus, transitioning from DCMS to HIPIMS at an average power of 1 kW allows for the generation of plasma predominantly consisting of target material ions [28; 29], with the integrated intensity, calculated using MagicPlot Pro software, increasing threefold. Increasing the power from 1 to 2 kW during HIPIMS

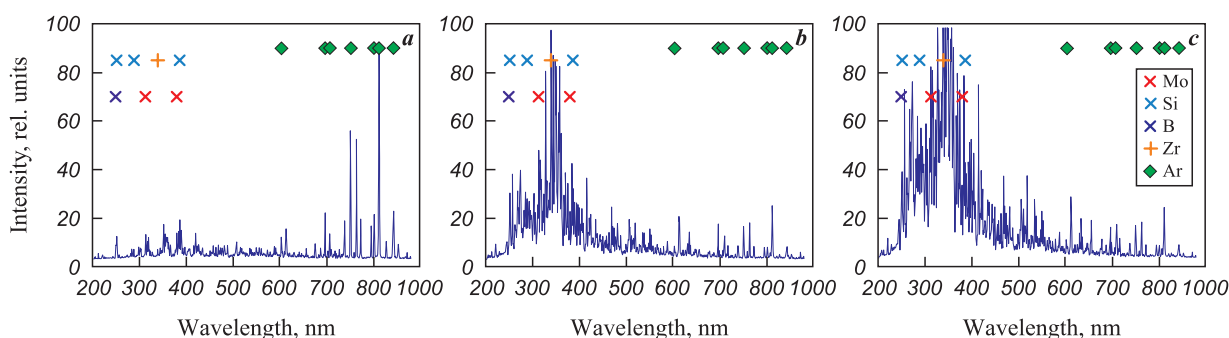


Fig. 1. Plasma spectra obtained by sputtering a Zr–Si–Mo–B target in the DCMS (a) and HIPIMS (b, c) modes at an average power of 1 (a, b) and 2 kW (c)

Рис. 1. Спектры плазмы, полученные при распылении мишени Zr–Si–Mo–B в режимах DCMS (a) и HIPIMS (b, c) при средней мощности 1 кВт (a, b) и 2 кВт (c)

operation results in a further twofold increase in this indicator.

Study of coating structure and mechanical characteristics

Typical SEM images of the structure, elemental profiles, and three-dimensional surface images (using coating 1 as an example) are shown in Fig. 2.

All samples exhibited a dense, defect-free structure and a similar roughness parameter R_a in the range of 7–8 nm. The structure of the initial coatings was studied in more detail in [25]. According to GDOES

data (Fig. 2, *b*), all elements were uniformly distributed across the thickness of the coatings (refer to the Table).

The thickness of coatings 1, 2, and 3 reached 8.4, 5.7, and 5.6 μm , respectively. The growth rate of sample 1 was 140 nm/min, but switching to HIPIMS mode reduced it by 1.5 times. This reduction can be attributed to self-sputtering effects and the decreased overall sputtering time in HIPIMS pulse mode [30; 31]. It is worth noting that increasing the power during coating deposition under these conditions does not affect the composition or growth rate of the coatings.

According to our previously obtained data [25], all coatings, regardless of the deposition mode, are X-ray amorphous.

Nanoindentation results (refer to the Table) showed that all samples had similar mechanical characteristics: hardness of 11–14 GPa, elastic modulus of 177–208 GPa, and elastic recovery of 37–42 %. It is noteworthy that a hardness level of 10–15 GPa is characteristic of silicide ceramics based on ZrSi_2 [1; 32].

Study of high-temperature oxidation resistance of coatings

Fig. 3 shows the specific mass change ($\Delta m/S$) of the coatings as a function of holding time, as well as the appearance of the coatings before and after annealing at 1000 °C. For all samples, an increase in the parameter $\Delta m/S$ was observed for holding times up to 30 min, associated with the growth of the oxide film on the surface of the coatings. The decrease in this parameter observed for all coatings during the holding period of 30–60 min may be related to the partial evaporation of MoO_x . In the range of 60–180 min, the value of $\Delta m/S$ increased by 25 and 50 % for samples 1 and 3, respectively, while for coating 2 it remained unchanged. The maximum values of $\Delta m/S$, 11.2 and 10.5 mg/cm^2 , were recorded for samples 1 and 2, while coating 3, produced in HIPIMS mode at an average power of 2 kW, exhibited the lowest specific mass change of 5.3 mg/cm^2 , indicating its superior oxidation resistance under stepwise annealing at 1000 °C. The visual analysis of the samples (Fig. 3, *b*) showed that coatings 1 and 3 maintained their integrity during the tests, with no visible damage (delamination or cracking), whereas coating 2 partially delaminated during the testing.

To determine the maximum working temperature at which the coatings retain their protective properties, non-isothermal annealing was conducted in the temperature range of 1100–1500 °C. Fig. 4 presents SEM images of the coating surfaces after annealing at 1100 °C. All samples showed areas of damage

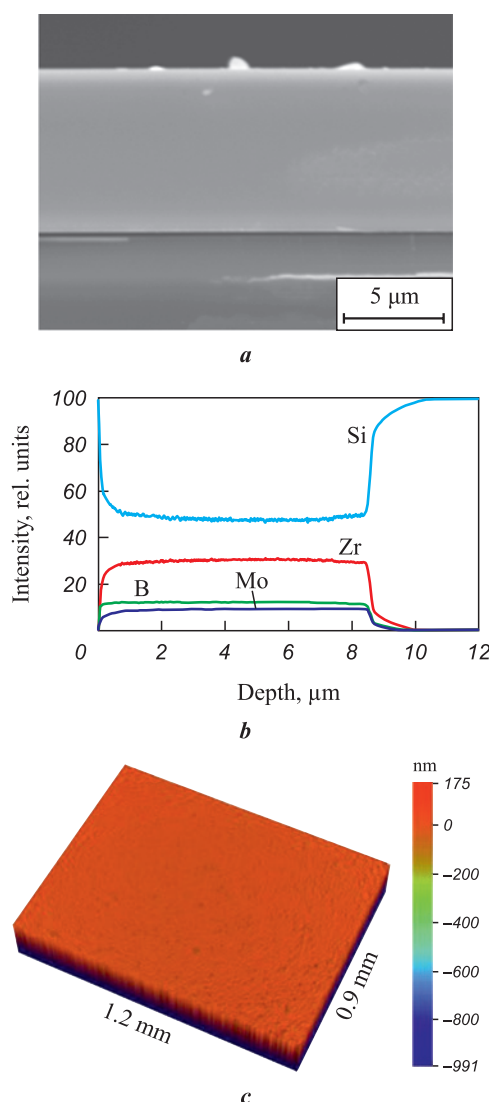


Fig. 2. Typical SEM micrograph of the cross-sectional fracture (*a*), elemental profile (*b*), and 3D surface image (*c*) of coating 1 obtained by the DCMS method

Рис. 2. Типичные СЭМ-микрофотография поперечного излома (*a*), элементный профиль (*b*) и трехмерное изображение поверхности (*c*) покрытия 1, полученного методом DCMS

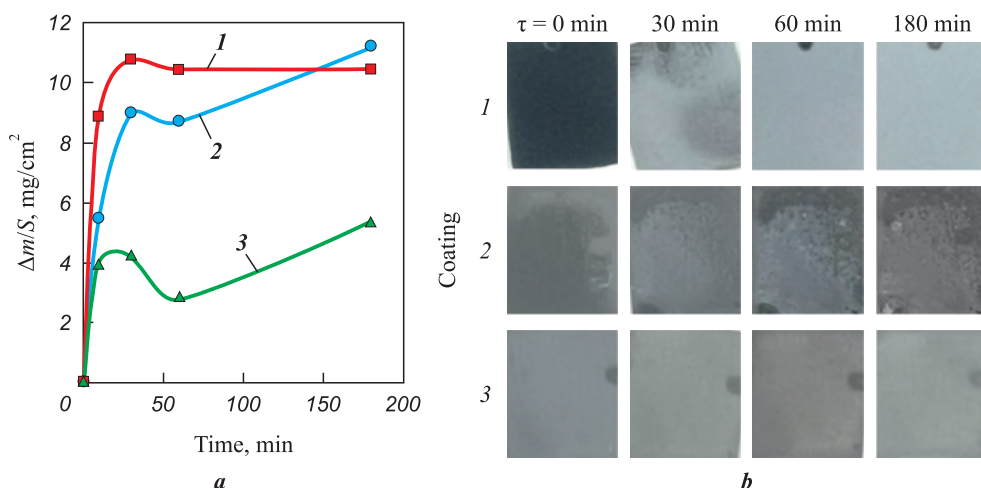


Fig. 3. Specific mass change ($\Delta m/S$) of the coatings as a function of holding time (a) and the appearance of the coatings before and after annealing at 1000 °C (b)

Рис. 3. Зависимость удельного изменения массы покрытий от времени выдержки (a) и внешний вид покрытий до и после отжига при температуре 1000 °C (b)

(blistering), which could be due to the formation and evaporation of MoO_x , as well as phase transformations accompanied by volume changes of the structural components. Similar effects were previously observed in studies of Mo–(Hf, Zr)–Si–B coatings [26]. The size

of the local damage areas decreased by 1.3 and 4.0 times when transitioning from coating 1 to coatings 2 and 3, respectively. Particles of ZrO_x and ZrSiO_x , sized 0.4–1.2 μm , were identified on the surfaces of all samples. According to EDS analysis at points on

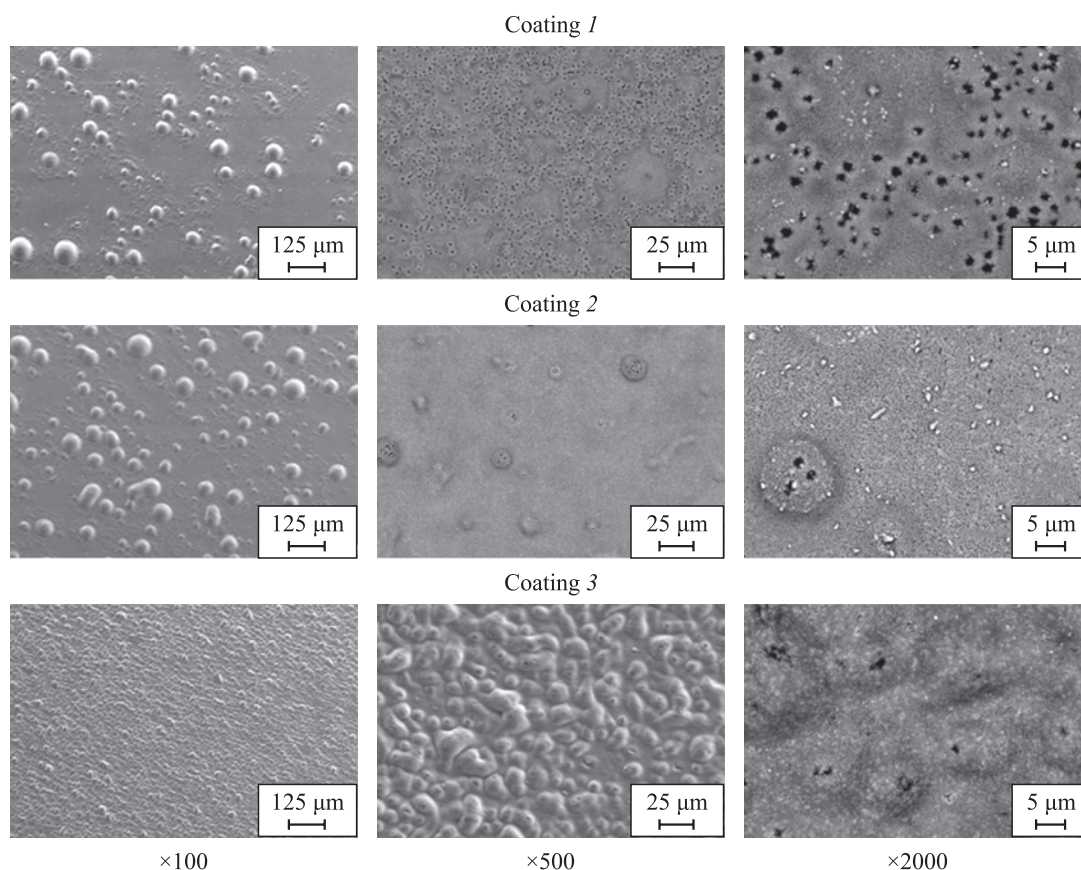


Fig. 4. SEM images of the surface of coatings 1, 2, and 3 after annealing at 1100 °C

Рис. 4. СЭМ-микрофотографии поверхности покрытий 1, 2 и 3 после отжига при температуре 1100 °C

the surfaces of coatings 1 and 2, the formation of MoO_x particles was observed.

Cross-sectional SEM images and EDS maps of the studied coatings after annealing at 1100 °C are presented in Fig. 5. The obtained data showed that an oxide film of equal thickness ($\sim 5.0 \mu\text{m}$) formed on the surfaces of coatings 1 and 2, consisting of two layers:

- the upper layer ($\sim 2.6 \mu\text{m}$ thick) consisting of an amorphous phase $a\text{-Si:B}$ and nanocrystallites of $nc\text{-ZrO}_2$, $nc\text{-ZrSiO}_4$;
- the $a\text{-Si:B:O}$ layer ($\sim 2.4 \mu\text{m}$ thick).

A porous oxide layer of $a\text{-Si:B:O} + nc\text{-ZrO}_2 + nc\text{-ZrSiO}_4$ with a thickness of $4.8 \mu\text{m}$ formed on the surface of sample 3. Notably, the formation of ZrSiO_x and ZrO_2 effectively enhances the protective properties of the oxide film by increasing stability and reducing defects in the borosilicate glass layer [33; 34]. After annealing at 1300 °C, the surfaces of samples 1, 2, and 3 exhibited blistering areas of approximately 500, 250, and 15 μm , respectively (Fig. 6), as well as cracks, which could be attributed

to oxidation and crystallization processes occurring in the coatings during heating [35; 36]. It is worth mentioning that the presence of cracks facilitates oxygen diffusion into the material, potentially compromising its oxidation resistance [37; 38]. It is worth noting that particles of ZrSiO_4 formed in the crack area on the surface of coating 1, which may provide additional healing effects [33].

Fig. 7 shows cross-sectional SEM images of the coatings after annealing at 1300 °C. According to EDS data (mapping and point analysis), the cross-sectional fracture of sample 1 revealed three layers in the oxide film with a thickness of $\sim 6.2 \mu\text{m}$:

- the upper porous layer of $a\text{-Si:B:O} + nc\text{-ZrO}_2 + nc\text{-ZrSiO}_4$ with a thickness of $\sim 3.0 \mu\text{m}$ and pore sizes of 0.2–0.6 μm ;
- a 200 nm thick layer containing MoO_x particles;
- a layer at the “oxide film-coating” interface, consisting $a\text{-Si:B:O}$ and $nc\text{-ZrO}_2$.

The oxide film on the surface of sample 2 consisted of $a\text{-Si:B:O} + nc\text{-ZrO}_2 + nc\text{-ZrSiO}_4$ with a thickness of $\sim 5.2 \mu\text{m}$. The layer near the surface had

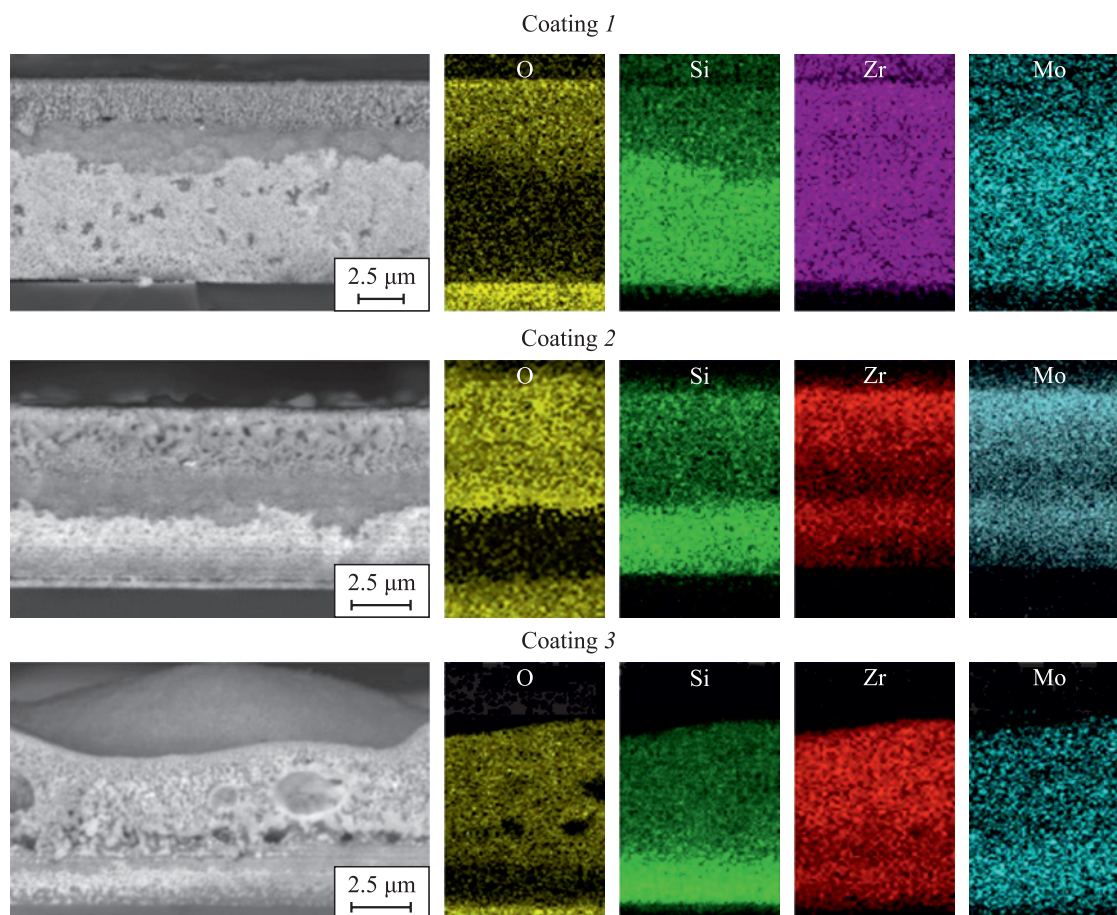


Fig. 5. Cross-sectional SEM images and EDS maps of coatings 1, 2, and 3 after annealing at 1100 °C

Рис. 5. СЭМ-микрофотографии поперечных изломов и ЭДС-карты покрытий 1, 2 и 3 после отжига при температуре 1100 °C

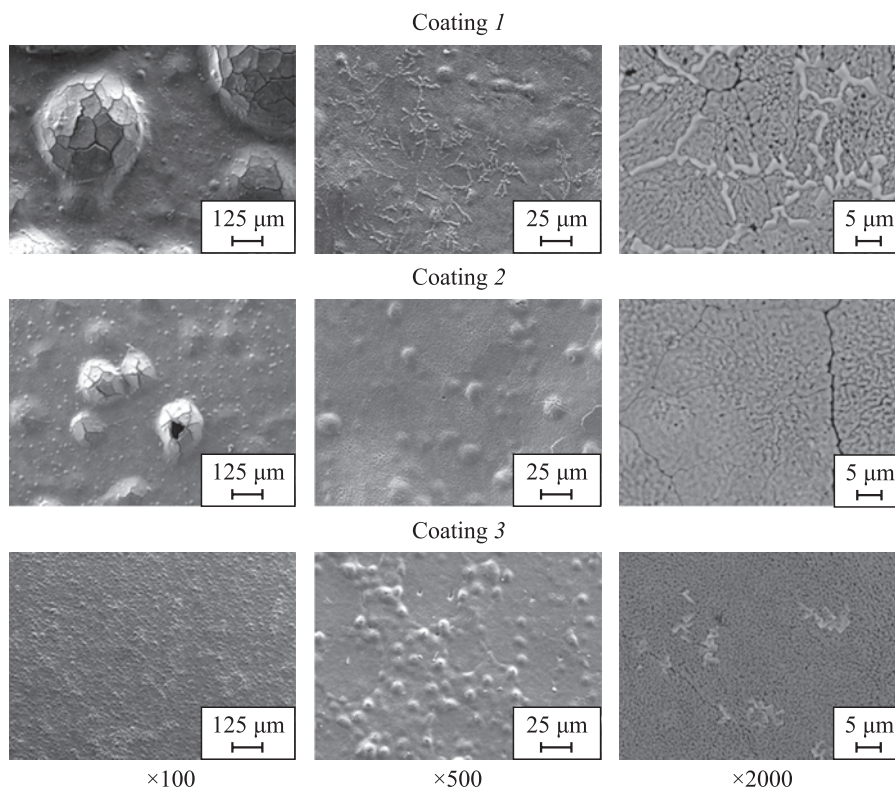


Fig. 6. SEM images of the surface of coatings 1, 2, and 3 after annealing at 1300 °C

Рис. 6. СЭМ-микрофотографии поверхности покрытий 1, 2 и 3 после отжигов при температуре 1300 °C

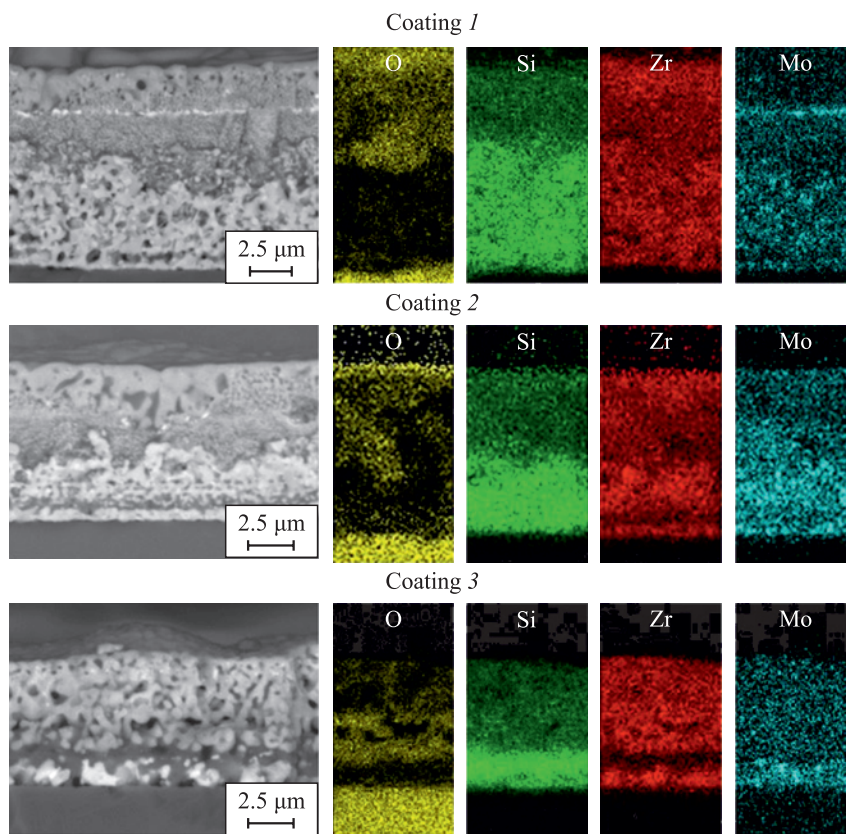


Fig. 7. Cross-sectional SEM images and EDS maps of coatings 1, 2, and 3 after annealing at 1300 °C

Рис. 7. СЭМ-микрофотографии поперечных изломов и ЭДС-карты покрытий 1, 2 и 3 после отжигов при температуре 1300 °C

a porous structure with pore sizes of 0.2–1.2 μm , while the lower layer was dense (see Fig. 7). For coating 3, the thickness of the porous oxide layer $\alpha\text{-Si:B:O} + nc\text{-ZrO}_2 + nc\text{-ZrSiO}_4$ was minimal, measuring 4.9 μm . The unoxidized layers of all samples contained crystallites of ZrSi_2 and MoSi_2 phases.

The results after oxidation annealing at 1300 $^{\circ}\text{C}$ demonstrated that using the HIPIMS method instead of DCMS reduced the thickness of the surface oxygen-containing layer by 16 %. Increasing the power from 1 to 2 kW during HIPIMS deposition further reduced the thickness of the oxide layer by 6 %. This effect may be related to the densification of the structure and the elimination of structural defects in the coatings when transitioning from DCMS to HIPIMS [39; 40]. It is noteworthy that increasing the power during HIPIMS sputtering enhances ionization rates and ion energy, which positively affects the quality of the resulting coatings [41; 42].

Increasing the annealing temperature to 1500 $^{\circ}\text{C}$ led to the complete oxidation of coatings 2 and 3 due to their small thickness. On the surface of sample 1, in addition to characteristic blistering areas, crack formation was observed (Fig. 8). At higher SEM magnification ($\times 2000$), grains of ZrO_2 (the brightest areas in the SEM images) with sizes of 0.6–1.8 μm and grains

of ZrSiO_4 with sizes of 1.2–5.0 μm were identified in an amorphous Si:B matrix (the darkest areas).

According to SEM images and EDS maps of the cross-sectional fracture (Fig. 8), coating 1 retained an oxygen-free layer, indicating its high oxidation resistance at 1500 $^{\circ}\text{C}$. The thickness of the protective layer $\alpha\text{-Si:B:O} + nc\text{-ZrO}_2 + nc\text{-ZrSiO}_4$, formed on the surface during oxidation was $\sim 8.0 \mu\text{m}$. The unoxidized layer contained MoSi_2 grains sized 3.6 to 5.0 μm and Zr_5Si_3 grains sized 0.2 to 1.0 μm . The superior oxidation resistance of coating 1, produced in DCMS mode, can be attributed to its maximum thickness.

X-ray diffractograms of coatings 1–3 annealed at 1100 $^{\circ}\text{C}$ are presented in Fig. 9, a. Peaks corresponding to the phases $o\text{-ZrSi}_2$ (ICDD 032-1499) and $t\text{-MoSi}_2$ (ICDD 41-0612), indicative of the unoxidized layer, were identified in all samples. Peaks corresponding to the oxide phases $m\text{-ZrO}_2$ (ICDD 07-0343) and $t\text{-ZrSiO}_4$ (ICDD 06-0266) were also observed. Coatings 1 and 2 exhibited peaks from the $m\text{-MoO}_2$ phase (ICDD 76-1807).

The crystallite sizes of the main phases, determined using the Debye–Scherrer formula, were similar for all coatings: 50–57 nm for $o\text{-ZrSi}_2$ (131) and $t\text{-MoSi}_2$ (200), 47–50 nm and 57–70 nm for $m\text{-ZrO}_2$ (111) and $t\text{-ZrSiO}_4$ (200), respectively. The crystallite sizes

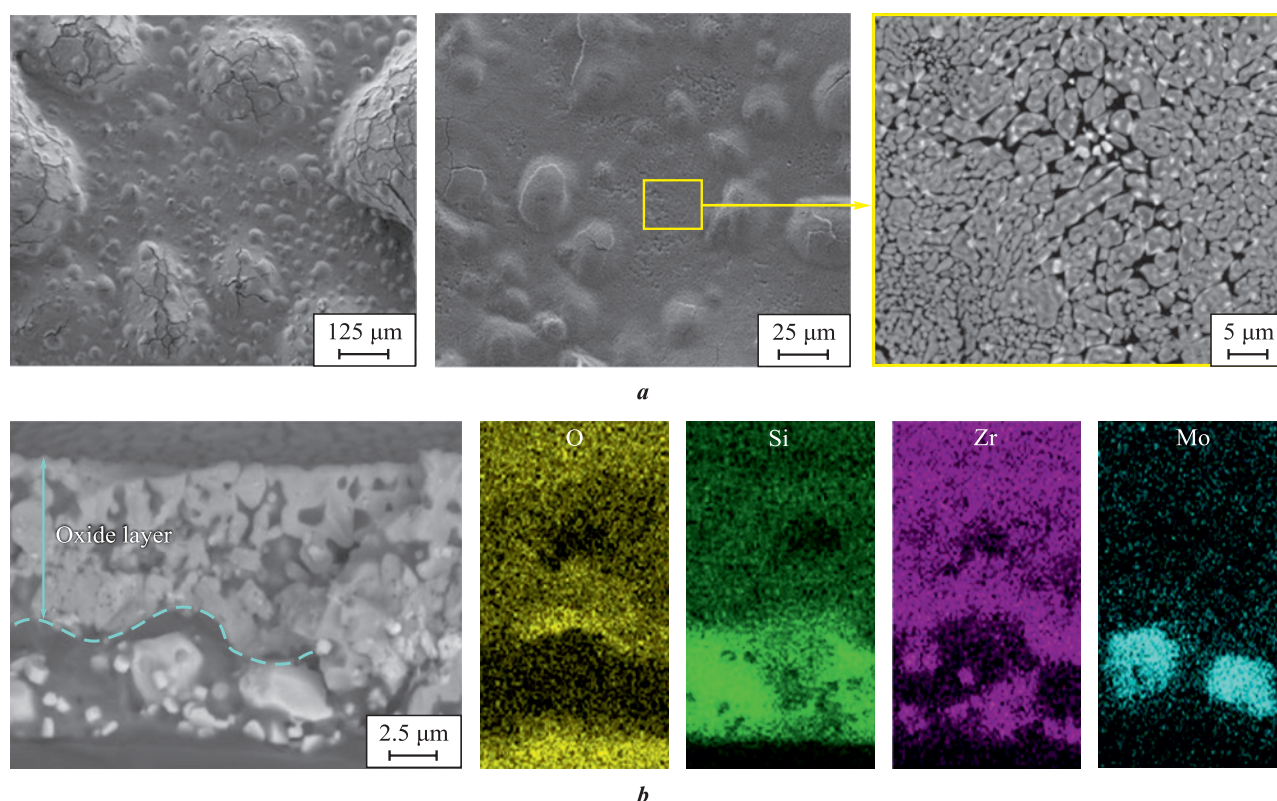


Fig. 8. SEM images of the surface (a) and cross-sectional fracture (b) of coating 1 after annealing at 1500 $^{\circ}\text{C}$

Рис. 8. СЭМ-изображения поверхности (a) и поперечного излома (b) покрытия 1 после отжига при температуре 1500 $^{\circ}\text{C}$

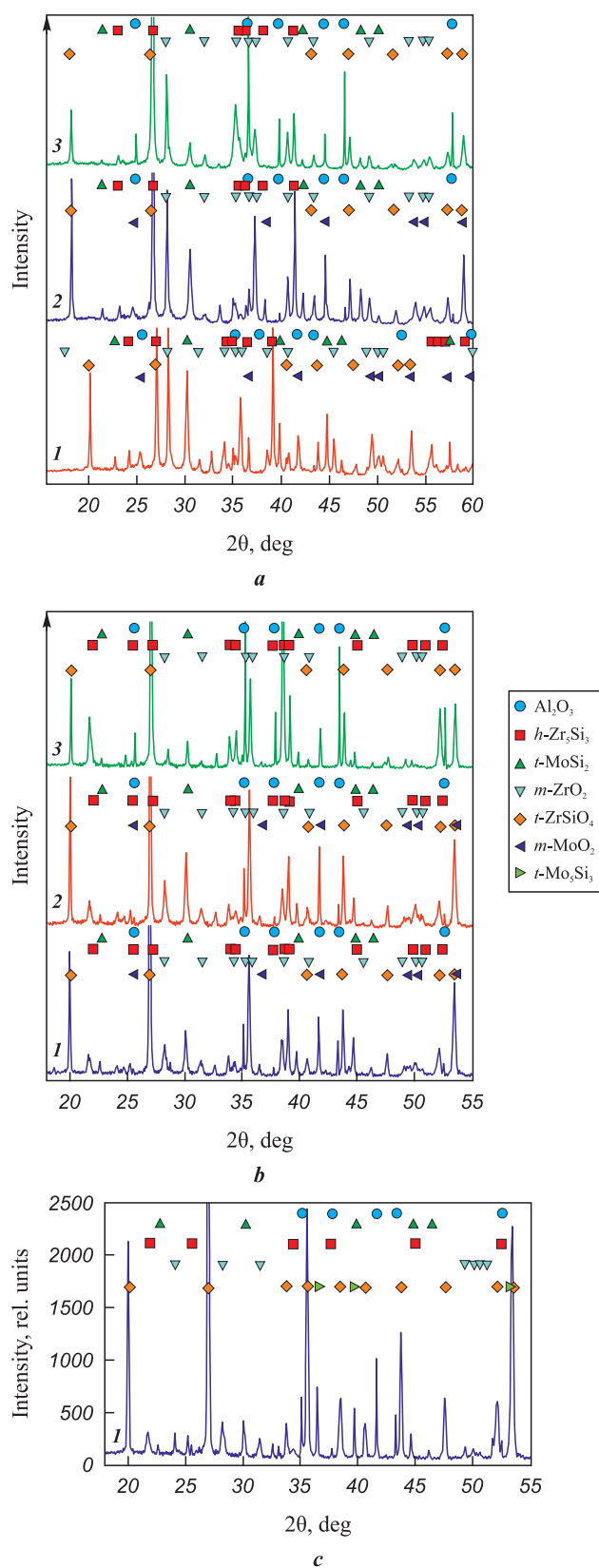


Fig. 9. X-ray diffractograms of coatings 1, 2, and 3 after annealing at 1100 °C (a) and 1300 °C (b), as well as coating 1 after annealing at 1500 °C (c)

Рис. 9. Рентгенограммы покрытий 1, 2 и 3 после отжига при температурах 1100 °C (a) и 1300 °C (b), а также покрытия 1 после отжига при 1500 °C (c)

of the $m\text{-MoO}_2$ (200) phase for coatings 1 and 2 were 61 and 68 nm, respectively.

X-ray diffractograms of coatings annealed at 1300 °C (Fig. 9, b) revealed peaks from the hexagonal phase $h\text{-Zr}_5\text{Si}_3$ (ICDD 79-4988), in addition to the phases $t\text{-MoSi}_2$, $m\text{-ZrO}_2$, and $t\text{-ZrSiO}_4$, indicating a phase transition from the orthorhombic $o\text{-ZrSi}_2$ phase to the hexagonal $h\text{-Zr}_5\text{Si}_3$ phase. The crystallite size of $h\text{-Zr}_5\text{Si}_3$ phase increased from 57 to 77 nm when transitioning from coating 1 to coatings 2 and 3.

After heating sample 1 to 1500 °C, the crystallite sizes of the $t\text{-ZrSiO}_4$ and $m\text{-ZrO}_2$ phases were 50 and 43 nm, respectively, and the sizes of the $h\text{-Zr}_5\text{Si}_3$ and $t\text{-MoSi}_2$ phases were 85 and 77 nm, respectively. A partial transition of the $t\text{-MoSi}_2$ phase to $t\text{-Mo}_5\text{Si}_3$ was observed (Fig. 9, c). The crystallite size of the $t\text{-Mo}_5\text{Si}_3$ phase, determined from the (002) line, was 57 nm.

Thus, among all the samples studied, coating 1 exhibited the smallest crystallite sizes for both the main phases ($h\text{-Zr}_5\text{Si}_3$ and $t\text{-MoSi}_2$) and the oxygen-containing phases ($t\text{-ZrSiO}_4$ and $m\text{-ZrO}_2$), indicating its higher thermal stability and enhanced protective properties. This assertion is well supported by the fact that only this sample withstood annealing at 1500 °C. It is noteworthy that Zr–Mo–Si–B coatings are comparable in oxidation resistance to previously studied ZrB_2 and ZrSiB coatings [43; 44].

Conclusions

1. Coatings of the Zr–Mo–Si–B system were produced using DCMS and HIPIMS methods with a functionally graded SHS target $(\text{ZrSi}_2\text{--ZrB}_2\text{--MoSi}_2)/\text{Cr}$. Transitioning from DCMS to HIPIMS at $P = 1$ kW led to an increase in the ionization degree of target component atoms and a threefold rise in the integral intensity of the spectra. Increasing the power from 1 to 2 kW during HIPIMS deposition further doubled this parameter.

2. Regardless of the deposition method (DCMS or HIPIMS), the coatings were X-ray amorphous with a homogeneous structure and uniform elemental distribution throughout their thickness. They exhibited similar values of hardness (11–14 GPa), elastic modulus (177–208 GPa), and elastic recovery (37–42 %). All coatings demonstrated high oxidation resistance in air at $t = 1100$ and 1300 °C. Transitioning from DCMS to HIPIMS reduced defectiveness and decreased the oxidation depth by 16–21 % at 1300 °C.

3. The 8 μm thick coating showed the highest oxidation resistance at 1500 °C, which is attributed to its thermal stability and the formation of a dense oxide

film on the surface with an amorphous matrix of α -Si₃N₄ and nanocrystallites of t -ZrSiO₄ and m -ZrO₂.

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Information about the Authors



Сведения об авторах

Alina D. Chertova – Cand. Sci. (Eng.), Junior Researcher, Laboratory “*In situ* Diagnostics of Structural Transformations”, Scientific-Educational Center of Self-Propagating High-temperature Synthesis of MISIS–ISMAN (SHS-Center), National University of Science and Technology MISIS (NUST MISIS)

 **ORCID:** 0000-0002-8668-5877

 **E-mail:** alina-sytchenko@yandex.ru

Fedor I. Chudarin – Laboratory Assistant, SHS-Center of MISIS–ISMAN

 **ORCID:** 0009-0001-2791-5732

 **E-mail:** theodor2000@yandex.ru

Irina O. Vakhrusheva – Project Engineer, SHS-Center of MISIS–ISMAN

 **ORCID:** 0000-0002-0572-5030

 **E-mail:** 89896231497i@gmail.com

Yuri Yu. Kaplansky – Cand. Sci. (Eng.), Researcher, Laboratory “*In situ* diagnostics of structural transformations”, SHS-Center of MISIS–ISMAN

 **ORCID:** 0000-0002-2153-0743

 **E-mail:** ykaplansky@mail.ru

Xuanru Ren – Dr. Sci., Professor, Henan Academy of Sciences

 **ORCID:** 0000-0002-9390-2825

 **E-mail:** renxuanru1986@163.com

Peizhong Feng – Dr. Sci., Professor, China University of Mining and Technology

 **ORCID:** 0000-0002-9853-6457

 **E-mail:** pzfeng@cumt.edu.cn

Evgeniy A. Levashov – Dr. Sci. (Eng.), Professor, Academician of the Russian Academy of Natural Sciences, Head of the Department of Powder Metallurgy and Functional Coatings, NUST MISIS; Head of SHS-Center of MISIS–ISMAN

 **ORCID:** 0000-0002-0623-0013

 **E-mail:** levashov@shs.misis.ru

Philipp V. Kiryukhantsev-Korneev – Dr. Sci. (Eng.), Professor of the Department of Powder Metallurgy and Functional Coatings, Head of the Laboratory “*In situ* Diagnostics of Structural Transformations”, SHS-Center of MISIS–ISMAN

 **ORCID:** 0000-0003-1635-4746

 **E-mail:** kiruhancev-korneev@yandex.ru

Алина Дмитриевна Чертова – к.т.н, мл. науч. сотрудник лаборатории «*In situ* диагностика структурных превращений» Научно-учебного центра (НУЦ) СВС МИСИС–ИСМАН, Национальный исследовательский технологический университет «МИСИС» (НИТУ МИСИС)

 **ORCID:** 0000-0002-8668-5877

 **E-mail:** alina-sytchenko@yandex.ru

Фёдор Ильич Чударин – лаборант учебной лаборатории НУЦ СВС МИСИС–ИСМАН

 **ORCID:** 0009-0001-2791-5732

 **E-mail:** theodor2000@yandex.ru

Ирина Олеговна Вахрушева – инженер научного проекта НУЦ СВС МИСИС–ИСМАН

 **ORCID:** 0000-0002-0572-5030

 **E-mail:** 89896231497i@gmail.com

Юрий Юрьевич Капланский – к.т.н, науч. сотрудник лаборатории «*In situ* диагностика структурных превращений» НУЦ СВС МИСИС–ИСМАН

 **ORCID:** 0000-0002-2153-0743

 **E-mail:** ykaplansky@mail.ru

Xuanru Ren – Dr. Sci., Professor, Henan Academy of Sciences

 **ORCID:** 0000-0002-9390-2825

 **E-mail:** renxuanru1986@163.com

Peizhong Feng – Dr. Sci., Professor, China University of Mining and Technology

 **ORCID:** 0000-0002-9853-6457

 **E-mail:** pzfeng@cumt.edu.cn

Евгений Александрович Левашов – д.т.н, проф., акад. РАЕН, зав. кафедрой порошковой металлургии и функциональных покрытий НИТУ МИСИС; директор НУЦ СВС МИСИС–ИСМАН

 **ORCID:** 0000-0002-0623-0013

 **E-mail:** levashov@shs.misis.ru

Филипп Владимирович Кирюханцев-Корнеев – д.т.н, проф. кафедры порошковой металлургии и функциональных покрытий, зав. лабораторией «*In situ* диагностика структурных превращений» НУЦ СВС МИСИС–ИСМАН

 **ORCID:** 0000-0003-1635-4746

 **E-mail:** kiruhancev-korneev@yandex.ru

Contribution of the Authors



Вклад авторов

A. D. Chertova – conducted structural investigations, analyzed research results, and prepared the manuscript.

F. I. Chudarin – conducted high-temperature annealing.

I. O. Vakhrusheva – analyzed research results.

Yu. Yu. Kaplansky – analyzed research results.

X. Ren – conducted research.

P. Feng – analyzed research results.

E. A. Levashov – set the research objectives, provided overall supervision, revised the manuscript, and formulated the conclusions.

Ph. V. Kiryukhantsev-Korneev – applied coatings using the magnetron sputtering method, revised the manuscript, and discussed the results.

А. Д. Чертова – проведение структурных исследований, анализ результатов исследований, подготовка текста статьи.

Ф. И. Чударин – проведение высокотемпературных отжигов.

И. О. Вахрушева – анализ результатов исследований.

Ю. Ю. Капланский – анализ результатов исследований.

X. Ren – проведение исследований.

P. Feng – анализ результатов исследований.

Е. А. Левашов – постановка цели, общее руководство, корректировка текста статьи, формулировка выводов.

Ф. В. Кирюханцев-Корнеев – нанесение покрытий методом магнетронного распыления, корректировка текста, обсуждение результатов.

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Research article

Научная статья



Structural characteristics and mechanical properties of heat-resistant TNM-B1 alloy obtained by selective laser melting from SHS powder spheroidized in thermal plasma

G. M. Markov¹ , A. A. Fadeev^{1, 2}, A. A. Skirpichnikova¹,
P. A. Loginov¹, M. G. Khomutov¹, A. V. Samokhin², E. A. Levashov¹

¹ National University of Science and Technology “MISIS”

4 Bld. 1 Leninskiy Prosp., Moscow 119049, Russia

² A. A. Baikov Institute of Metallurgy and Materials Science of the Russian Academy of Sciences

49 Leninskiy Prosp., Moscow 119334, Russia

markov.sci@gmail.com

Abstract. The TNM-B1 + Y₂O₃ alloy powders obtained by the method of self-propagating high-temperature synthesis were studied. The influence of particle processing parameters in thermal plasma, generated by a DC (direct current) arc plasma torch, on the morphology and structure of spherical particles was considered. It was established that plasma treatment significantly changes the shape of the particles and allows obtaining a product with a high degree of spheroidization (from 88 to 97 %), which depends on the plasma stream temperature, the composition of the plasma-forming gas, and the amount of processed material. Using hydrogen-containing thermal plasma, the degree of spheroidization can reach 99 %. At the same time, the concentrations of impurity oxygen decrease from 0.8 to 0.13 wt. %, nitrogen decreases by 2 times, and the concentration of hydrogen significantly drops. Studies were conducted to develop selective laser melting regimes, resulting in samples with minimal defects. The optimal volumetric energy density of the laser was 40–50 J/mm³. The gasostatic treatment process allowed achieving almost complete uniformity of the samples' structure and the absence of pores. Additionally, thermal treatment at $t = 1380$ °C and $\tau = 120$ min contributed to the transformation of the initial equiaxed structure of the alloy into a lamellar one. According to the results of thermomechanical tests under the scheme of uniaxial compression in the temperature range from 800 to 1100 °C, it was established that the alloy with a lamellar structure after selective laser melting, hot isostatic pressing, and thermal treatment has increased strength values by 80–100 MPa compared to the globular structure. The mechanical properties of the alloy with a lamellar structure at $t = 800$ °C are: modulus of elasticity $E = 115.2$ GPa, yield strength $\sigma_{0.2} = 528$ MPa, compressive strength $\sigma_u = 1148$ MPa, and at $t = 1100$ °C: $E = 48.2$ GPa, $\sigma_{0.2} = 98$ MPa, $\sigma_u = 149$ MPa.

Keywords: titanium alloys, plasma spheroidization, powder metallurgy, self-propagating high-temperature synthesis, combustion synthesis, hot isostatic pressing (HIP), mechanical properties

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Особенности структуры и механические свойства жаропрочного сплава TNM-B1, полученного селективным лазерным сплавлением из сфероидизированного в термической плазме СВС-порошка

Г. М. Марков¹✉, А. А. Фадеев^{1, 2}, А. А. Скирпичникова¹,
П. А. Логинов¹, М. Г. Хомутов¹, А. В. Самохин², Е. А. Левашов¹

¹ Национальный исследовательский технологический университет «МИСИС»

Россия, 119049, г. Москва, Ленинский пр-т, 4, стр. 1

² Институт металлургии и материаловедения им. А.А. Байкова Российской академии наук

Россия, 119334, г. Москва, Ленинский пр-т, 49

✉ markov.sci@gmail.com

Аннотация. Исследованы порошки из сплава TNM-B1 + Y₂O₃, полученные методом самораспространяющегося высокотемпературного синтеза. Рассмотрено влияние параметров обработки частиц в термической плазме, генерируемой электродуговым плазматроном постоянного тока, на морфологию и структуру сферических частиц. Установлено, что плазменная обработка существенно изменяет форму частиц и позволяет получить продукт с высокой степенью сфероидизации (от 88 до 97 %), которая зависит от температуры потока плазмы, состава плазмообразующего газа и количества обрабатываемого материала. При использовании водородсодержащей термической плазмы степень сфероидизации может достигать 99 %. При этом снижаются концентрации примесного кислорода с 0,8 до 0,13 мас. %, азота в 2 раза и существенно падает концентрация водорода. Проведены исследования по отработке режимов селективного лазерного сплавления, в результате чего были построены образцы с минимальным количеством дефектов. При этом оптимальная объемная плотность энергии лазера составила 40–50 Дж/мм³. Процесс газостатической обработки позволил достичь практически полной однородности структуры образцов и отсутствия пор. Дополнительно проведенная термическая обработка при $t = 1380$ °C и $\tau = 120$ мин способствовала преобразованию исходной равноосной структуры сплава в ламеллярную. По результатам термомеханических испытаний по схеме одноосного сжатия в диапазоне температур от 800 до 1100 °C установлено, что сплав с ламеллярной структурой после операций селективного лазерного сплавления, горячего изостатического прессования и термической обработки имеет повышенные на 80–100 МПа значения прочности по сравнению с глобулярной структурой. Механические свойства сплава с ламеллярной структурой составили при $t = 800$ °C: модуль упругости $E = 115,2$ ГПа, предел текучести $\sigma_{0,2} = 528$ МПа, предел прочности при сжатии $\sigma_{\text{в}} = 1148$ МПа, а при $t = 1100$ °C – $E = 48,2$ ГПа, $\sigma_{0,2} = 98$ МПа, $\sigma_{\text{в}} = 149$ МПа.

Ключевые слова: титановые сплавы, плазменная сфероидизация, порошковая металлургия, самораспространяющийся высокотемпературный синтез, синтез горением, горячее изостатическое прессование (ГИП), механические свойства

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Introduction

Heat-resistant alloys based on titanium aluminides TiAl/Ti₃Al are of significant interest for technical applications in mechanical engineering [1; 2]. They are characterized by high heat resistance, corrosion resistance, and creep resistance. Under the influence of high temperatures and aggressive environments, these alloys maintain thermodynamic stability and, in addition, have low density (~5 g/cm³), which makes their spe-

cific strength superior to that of modern nickel-based superalloys of similar purpose (~9 g/cm³) [3–5].

The primary challenges hindering the use of TiAl/Ti₃Al-based alloys in the manufacture of complex-shaped parts include high sensitivity of the phase composition to process parameters, impurities, and variations in the concentrations of alloying elements, as well as the difficulty of processing at room temperature. Producing such parts through traditional metal-

lurgical methods followed by mechanical processing involves high capital costs and significant material losses [6]. Modern additive manufacturing technologies, such as selective laser melting (SLM), can address these issues by minimizing the need for mechanical processing [4; 5]. Active research is underway to optimize the compositions and production methods of heat-resistant alloy powders [6–9].

One method for producing TiAl/Ti₃Al-based alloy powders utilizes the technology of self-propagating high-temperature synthesis (SHS) [10; 11]. The potential of this method lies in the heterogeneity scale of powder particles with increased reactive surface area due to the high speed of combustion wave propagation, allowing the production of powder materials of the required composition [12–14]. Using this technology, products from basic TiAl/Ti₃Al alloys have been manufactured [15].

The development of the SLM process opens up prospects for the creation of complex-shaped products from TiAl/Ti₃Al-based materials [5; 12]. In the SLM technology, narrow particle size distribution spherical powders, are used as raw materials, which must meet specific requirements for chemical composition, impurity content, and properties such as bulk density, flowability, granulometric composition, and sphericity.

Based on these requirements, spheroidized powders from TiAl/Ti₃Al-based alloys can be obtained using gas atomization, plasma rotating electrode process (PREP method) and plasma spheroidization technologies [16–20], which ensure rapid melt crystallization, contributing to the reduction of grain size and the formation of a homogeneous structure in the solid state. Producing such powders by gas atomization and PREP methods involves using pre-manufactured cast billets and rods, increasing the process cost [18; 21–23]. Plasma spheroidization allows the use of precursor powders as raw materials, significantly simplifying the technology. Under high temperatures and the influence of surface tension forces, particles of arbitrary shape melt, acquire a spherical shape, and crystallize. This processing method improves many powder characteristics for further use in additive technologies: it increases flowability and bulk density; reduces impurity oxygen content; and helps remove internal pores formed in the original particles [24–27].

The aim of this work was to produce spherical powders in the 10–65 μm fraction from the TNM-B1 + Y₂O₃ alloy based on titanium aluminide, to study the influence of particle processing parameters in thermal plasma generated by a DC arc plasma torch on the morphology, structure, and properties of the powders,

and to use these powders in selective laser melting technology.

Materials and methods

As the starting material, powders of a reactive mixture of pure elements were used to produce the TNM-B1 alloy modified with yttrium oxide (Y₂O₃) by the SHS method in a thermal explosion mode [14]. Pressed billets of the reactive mixture were placed in a tube furnace heated to 900 °C to initiate bulk combustion. The synthesis products were sequentially ground to a powder with particle sizes <100 μm using a jaw crusher and a planetary ball mill Activator-4M (Russia). Narrow particle size distribution spherical powders with grain sizes of 10–65 μm were obtained using an air classifier Golf-3 (Russia).

The classified powders were processed in a thermal plasma stream using a powder spheroidization unit developed by the Baikov Institute of Metallurgy and Materials Science (Moscow, Russia) [28]. The parameters for the spheroidization process of micropowders in the thermal plasma stream are as follows:

Plasma torch power (N_{pl}), kW	11–25
Plasma-forming gases	Ar, Ar + H ₂
Plasma gas flow rate ($G_{pl,g}$), m ³ /h	2.0–2.16
Plasma stream enthalpy (I_{pl}), kW·h/m ³	2.0–3.9
Precursor feed rate (G_{pr}), kg/h	0.6–2.4
Transport gas flow rate – Ar($G_{tr,g}$), m ³ /h	0.5

The plasma jet is generated by a DC arc plasma torch with a power of 30 kW and flows into a water-cooled plasma reactor with a diameter of 300 mm and a length of 1000 mm. The particles of the processed material are introduced into the plasma jet as a gas-dispersed flow using a carrier gas. During particle heating, melting occurs, and spherical shapes form due to surface tension forces. The particles then crystallize, deposit on the inner surface of the plasma reactor, and partially exit to the waste gas filtration system. A reactor wall cleaning system collects and accumulates the product in receiving hoppers.

During plasma processing of the precursor powder with a wide particle size distribution, a nanosized fraction may form due to the partial evaporation of small particles and the condensation of vapors. The presence of this fraction significantly degrades the physical and technological properties of the final product and increases oxygen and nitrogen impurities due to active oxidation of nanoparticles in contact with air. The nanosized fraction was removed from the spheroidized product by sedimentation in distilled water after ultra-

sonic treatment. The target product was dried under low vacuum conditions at $t = 150\text{ }^{\circ}\text{C}$ for 180 min.

The granulometric composition of the powders was measured by laser diffraction in a liquid medium using an ANALYSETTE 22 MicroTec plus device (FRITSCH, Germany) according to ASTM B822-17. Powder flowability was assessed using a Hall funnel (calibrated funnel diameter 2.5 mm) by the standard ASTM-B213 2017 test method. Bulk density was measured according to GOST 19440-94. Impurity oxygen content was determined by reductive melting using a TC-600 instrument (LECO, USA) according to the standard ASTM E1019-18 test method.

The construction and optimization of selective laser melting (SLM) modes were carried out on an SLM-260 setup (SLM Solutions, Germany) in an inert atmosphere. The scanning speed and power were varied in the ranges of 100–1000 mm/s and 50–300 W, respectively. To eliminate defects such as pores and microcracks, SLM samples were additionally subjected to hot isostatic pressing (HIP), and to modify the structure type after HIP, they were thermally treated (HIP + TT). The HIP process was performed on a HIRP10/26–200 setup (ABRA AG, Switzerland) at a temperature of $t = 1240\text{ }^{\circ}\text{C}$, argon pressure $P_{\text{Ar}} = 200\text{ atm}$, and isothermal holding time $\tau = 120\text{ min}$. Thermal treatment was conducted in a Termionik-T1 vacuum furnace (Russia) with a tungsten heater at $t = 1380\text{ }^{\circ}\text{C}$ and $\tau = 120\text{ min}$.

Phase composition was studied by X-ray phase (XRD) analysis on a D2 PHASER diffractometer (Bruker AXS GmbH, Germany) using CuK_α radiation in the 2θ angle range of $10\text{--}120^{\circ}$ with a step size of 0.02° and exposure of 0.6 s.

Microstructural investigations were carried out on an S-3400 N scanning electron microscope (Hitachi, Japan) with an energy-dispersive attachment NORAN System 7 X-ray Microanalysis System (Thermo Scientific, USA).

Thermomechanical tests under uniaxial compression were conducted in a vacuum ($\sim 10^{-3}\text{ Pa}$) on a Gleeble System 3800 instrument (Dynamic Systems Inc., USA). Hot deformation diagrams of samples under compressive stress were recorded in the temperature range of 800 to 1100 $^{\circ}\text{C}$ at a strain rate $d\varepsilon/dt \leq 0.001\text{ s}^{-1}$.

Results and discussion

Precursor powder structure

The SHS powder was characterized by the presence of irregularly shaped particles and consisted of $\gamma\text{-TiAl}$

and $\alpha_2\text{-Ti}_3\text{Al}$ phases [15]. According to the structural studies (Fig. 1, *a*, *b*), it has a homogeneous microstructure, which is an important condition for obtaining high-quality spheroidized powder.

As shown by laser diffraction analysis (Fig. 1, *c*), the powders have a unimodal distribution with a peak at $\sim 10\text{ }\mu\text{m}$. The quantile distribution of particles sizes D_{10} , D_{50} , and D_{90} of the powders was 24, 40, and 68 μm , respectively. Since separation in the air classifier is predominantly based on particle mass, some particles larger than 70 μm were included in the tar-

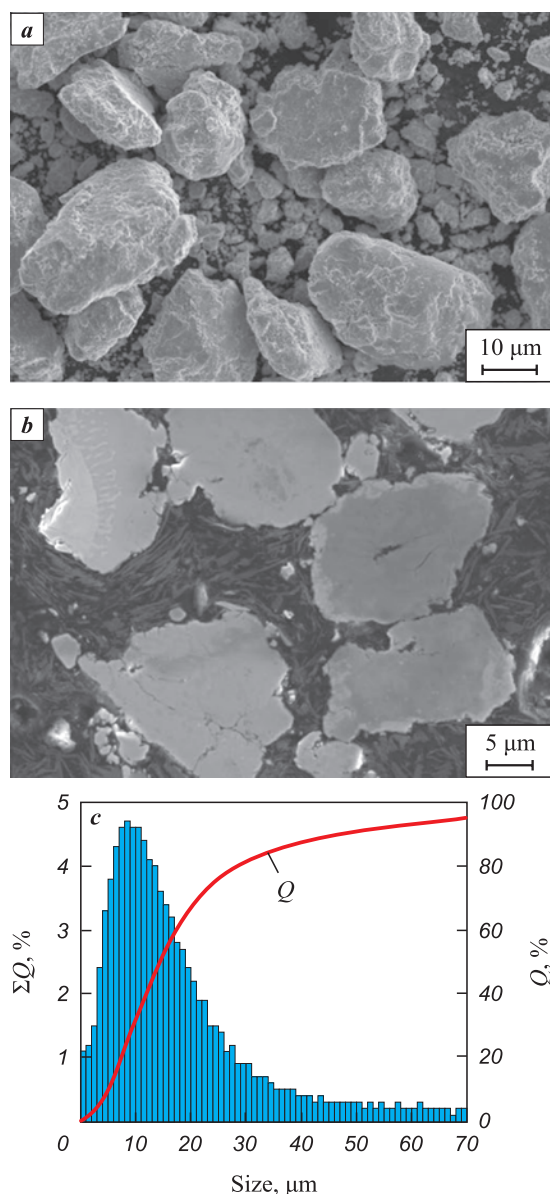


Fig. 1. Morphology (*a*), microstructure (*b*) and granulometric composition (*c*) of the TNM-B1 + 1 % Y_2O_3 powder after SHS

Рис. 1. Морфология (*a*), микроструктура (*b*) и гранулометрический состав (*c*) порошка TNM-B1 + 1 % Y_2O_3 после CBC

get fraction due to their irregular shape. The presence of a fraction smaller than 20 μm is explained by the developed surface of the particles and their mechanical interlocking. The physical and technological properties of the powders largely determine the parameters of their subsequent spheroidization in the thermal plasma stream, where a high degree (>95 %) of sphericity is required [28]. The initial SHS micropowders did not exhibit flowability, and their bulk density was 1.5 g/cm^3 .

Plasma spheroidization

Plasma spheroidization experiments were conducted with variations in the following parameters: plasma stream enthalpy, plasma-forming gas composition, and precursor powder feed rate. The main criteria for selecting the optimal plasma treatment mode for the powders were the degree of spheroidization and the minimization of the nanosized fraction in the processed powders. One significant parameter of plasma spheroidization, determining the energy contribution to the process and affecting the properties of the resulting product,

is the plasma stream enthalpy value. The properties of the spheroidized product varied depending on this parameter within the range of 2 to 3.85 $\text{kW}\cdot\text{h}/\text{m}^3$, determined by the useful power level of the DC arc plasma torch, the composition, and the flow rate of the plasma-forming gas.

At the minimum enthalpy of the argon-hydrogen plasma stream $I_{\text{pl}} = 2 \text{ kW}\cdot\text{h}/\text{m}^3$, the spheroidization degree of the product was ~73 %, which is low for powders intended for use in additive manufacturing processes (Fig. 2, *a, b*). Material evaporation with the formation of the nanosized fraction was practically absent, flowability was 57 s/50 g, and bulk density was 2.1 g/cm^3 .

Increasing $I_{\text{pl}} > 2 \text{ kW}\cdot\text{h}/\text{m}^3$ significantly raised the heat flow density to the surface of the processed powder particles, positively affecting the intensification of heating and melting particles, and consequently, increasing their spheroidization degree. However, a negative aspect of this process is the increased evaporation intensity of particles due to overheating, leading to a higher concentration of condensed

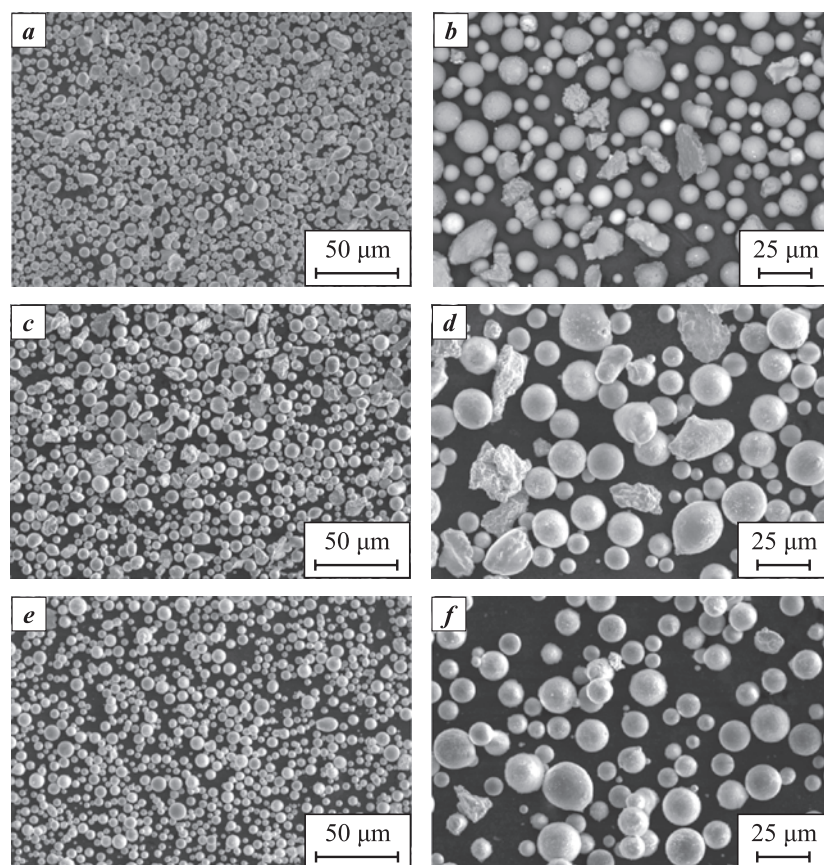


Fig. 2. Morphology of powders after spheroidization at an argon-hydrogen plasma stream enthalpy of 2 $\text{kW}\cdot\text{h}/\text{m}^3$ (*a, b*), 2.9 $\text{kW}\cdot\text{h}/\text{m}^3$ (*c, d*) and 3.85 $\text{kW}\cdot\text{h}/\text{m}^3$ (*e, f*)

Рис. 2. Морфология порошков после сфероидизации при значении энтальпии потока арговодородной плазмы 2 $\text{кВт}\cdot\text{ч}/\text{м}^3$ (*a, b*), 2,9 $\text{кВт}\cdot\text{ч}/\text{м}^3$ (*c, d*) и 3,85 $\text{кВт}\cdot\text{ч}/\text{м}^3$ (*e, f*)

nanoparticles in the spheroidized powder. Experiments showed that the maximum spheroidization degree was achieved at an argon-hydrogen plasma stream enthalpy of $I_{pl} = 3.85 \text{ kW} \cdot \text{h/m}^3$. Changing its value from 2 to $3.85 \text{ kW} \cdot \text{h/m}^3$ increased the spheroidization degree from 73 to 96 %. The nanosized fraction content increased slightly (to 2.1 wt. %), flowability reached 38 s/50 g, and bulk density increased to 2.45 g/cm^3 .

Research found that processing the precursor powder in argon plasma produced a product with a spheroidization degree of 96 %. The presence of agglomerates and particles with satellites was noted (Fig. 3, *b*). To increase the spheroidization degree at a fixed electric arc power value, the heat transfer conditions in the “hot gas-particle” system must be changed. One possible solution is to increase the thermal conductivity of the gas medium by adding hydrogen to the plasma-forming gas. Using hydrogen-containing thermal plasma intensifies heat and mass transfer processes, reducing the heating time of processed particles, resulting in a spheroidization degree of up to 99 % (Fig. 3, *a*). It was also found that hydrogen-containing plasma creates conditions for partial reduction of the precursor powder, leading to a decrease in oxygen impurity concentration in the product.

Increasing the precursor powder feed rate requires more thermal energy from the plasma stream to heat the material, reducing the spheroidization degree. Thus, increasing the precursor feed rate from 0.6 to 2.4 kg/h decreased the spheroidization degree to 88 %, while the nanosized fraction content decreased to 2.1 wt. %. The maximum spheroidization degree (96 %) at a mini-

mal nanosized fraction content was achieved with a precursor feed rate of 1.2 kg/h. As previously shown, micropowders obtained by plasma spheroidization (Fig. 4, *a, b*) contain nano- and submicron-sized particles formed by partial evaporation of the processed material and subsequent vapor condensation during cooling of the high-temperature gas-dispersed flow. Particle content varied from 3 to 10 wt. %.

A suitable spheroidized powder for SLM technology was obtained with an Ar-H₂ plasma stream enthalpy with 3.7 vol. % hydrogen, corresponding to $I_{pl} = 3.8 \text{ kW} \cdot \text{h/m}^3$. Partial evaporation of the precursor led to the appearance of a nanosized fraction $M_{nf} = 7 \text{ wt. %}$, and the spheroidization degree reached 99 % (Fig. 4, *c–e*). The spherical particles exhibited a homogeneous globular TiAl/Ti₃Al structure with Y₂O₃ nanoparticles at grain boundaries (Fig. 4, *f*). The flowability of the resulting powders was 29 s/50 g, and bulk density increased to 2.5 g/cm^3 . D_{10} , D_{50} , and D_{90} parameter values were 17, 29, and 50 μm , respectively, within a particle size range of 10 to 79 μm . It should be noted that processing the powder in argon plasma reduces oxygen impurities from 0.8 to 0.6 wt. %, while hydrogen-containing thermal plasma treatment, along with removing the nanosized fraction, reduces oxygen impurities to 0.3 wt. % (Fig. 5) and halves nitrogen impurities. Hydrogen content remained at 0.0025 wt. %.

Selective laser melting

The obtained powder was used to optimize the SLM modes on the SLM-260 setup (SLM Solutions,

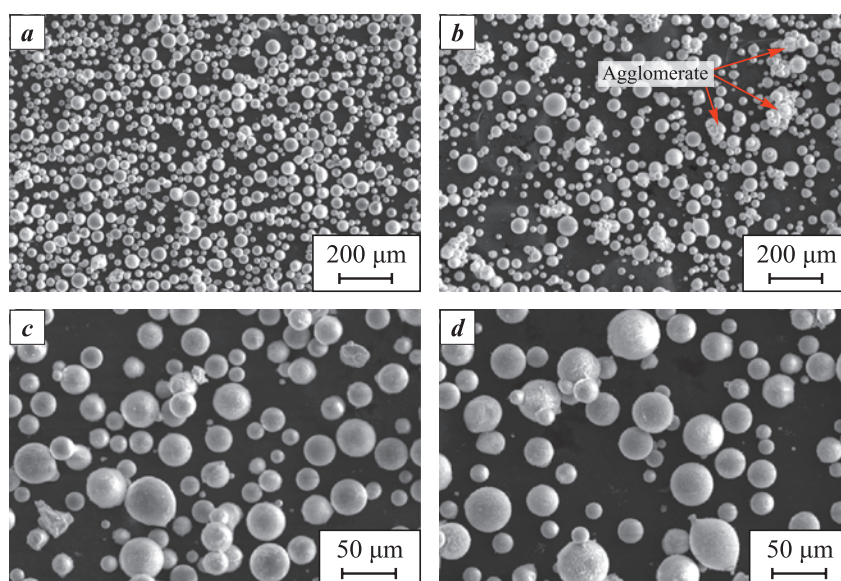


Fig. 3. Morphology of powders after spheroidization in plasma stream: Ar-H₂ (*a, c*), Ar (*b, d*)

Рис. 3. Морфология порошков после сфероидизации в плазме Ar-H₂ (*a, c*) и Ar (*b, d*)

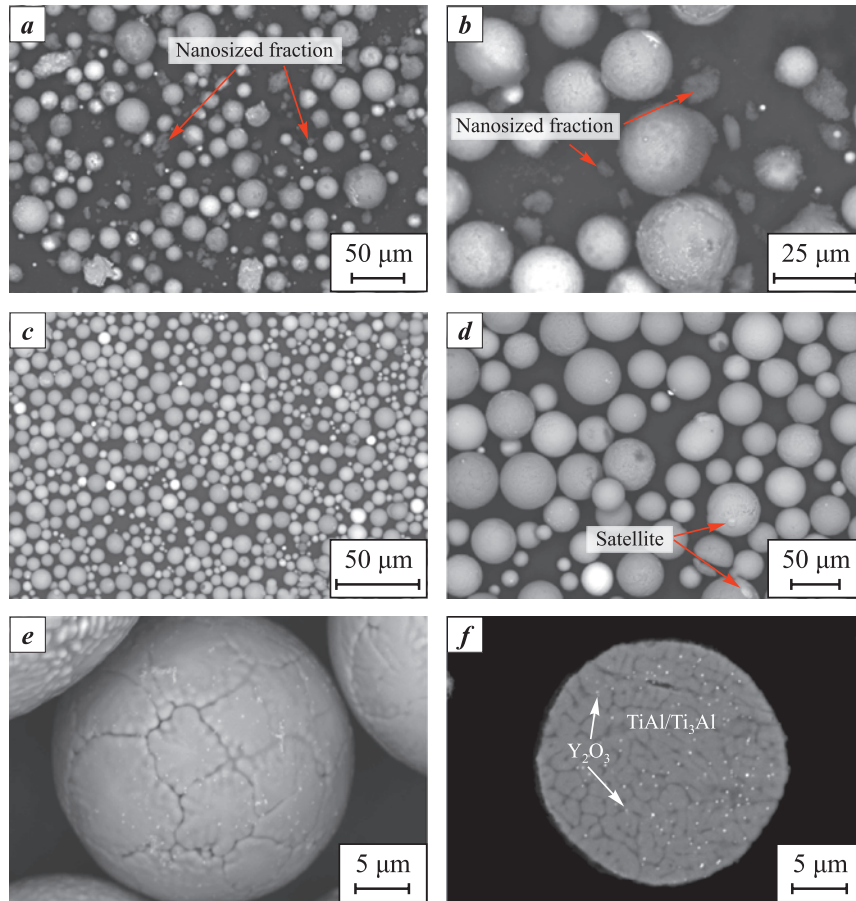


Fig. 4. Morphology of TNM-B1 + 1 % Y_2O_3 alloy powder after treatment in Ar- H_2 plasma before (a, b) and after (c, d, e) ultrasonic cleaning, and cross-section of a particle (f)

Рис. 4. Морфология порошка сплава TNM-B1 + 1 % Y_2O_3 после обработки в Ar- H_2 -плазме до (a, b) и после (c, d, e) ультразвуковой очистки и поперечный шлиф частицы (f)

Germany). The optimal ranges of the main parameters of laser synthesis were selected, considering the minimum volumetric energy density (VED) required to melt a powder layer of a given thickness, using the following formula:

$$VED = \frac{P}{vhtd},$$

where P is the laser power, W; v is the scanning speed, mm/s; h is the hatch spacing, mm; t is the powder layer thickness, mm; d is the laser beam diameter, mm.

The optimization of SLM modes using the spherical TNM-B1 + Y_2O_3 powder involved creating single tracks and evaluating the depth of melt and the presence of defects. The results of laser processing of single tracks revealed several patterns (Fig. 6). Low scanning speeds ($v < 200$ mm/s) lead to a significant increase in the depth of melt for single tracks (up to 500 μ m) regardless of the applied power, while high values of v caused significant track widening. In volumetric print-

ing, this leads to multiple remelts of adjacent tracks, and creates conditions for the formation of excessive stress and subsequent cracking of the material.

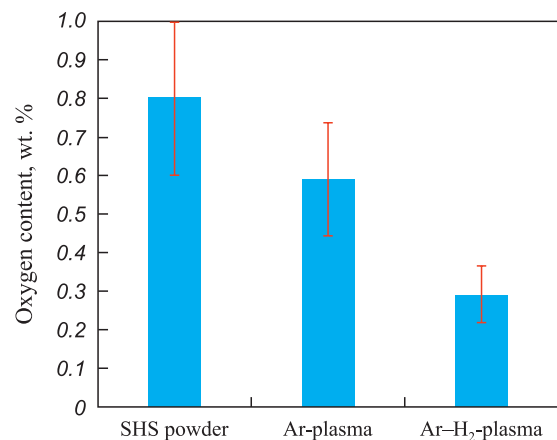


Fig. 5. Impurity oxygen content in the starting SHS powder after treatment in Ar and Ar- H_2 plasma

Рис. 5. Содержание примесного кислорода в исходном СВБ-порошке, после обработки в Ar- и Ar- H_2 -плазме

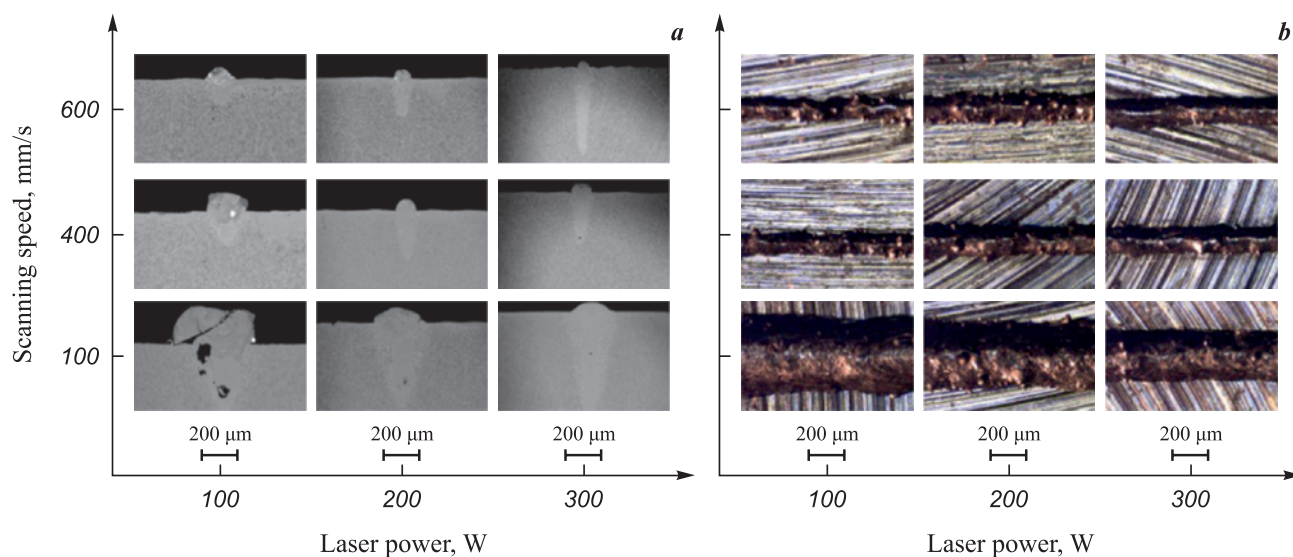


Fig. 6. SEM images of cross-section of tracks (a), and their surface images obtained by optical microscopy (b)

Рис. 6. СЭМ-изображения поперечных сечений треков (a) и снимки их поверхности, полученные методом оптической микроскопии (b)

Increasing the scanning speed from 200 to 600 mm/s reduced the number of unmelted particles on the track surface, and the track width became more uniform, ranging from 110 to 160 μm. Tracks obtained at higher scanning speeds had a smooth and uniform surface with a low number of defects. The optimal microstructure of the tracks was obtained at $v = 500 \div 600$ mm/s, and simultaneously increasing the laser power required $v > 900$ mm/s, corresponding to a volumetric energy density range of $VED = 40 \div 110$ J/mm³. Further variation of power and scanning speed for creating bulk samples was conducted within the established VED range.

Fig. 7, a shows the matrix of volumetric energy density values and a platform with bulk samples. Power variation was conducted within 70–115 W, and scan-

ning speeds in the range of 500–1000 mm/s. Samples can be divided into three groups based on characteristic defects. In Fig. 7, b, samples with warping during construction are highlighted in red, those with contour delamination in yellow, and defect-free samples in green.

For most construction modes, especially at high laser energy density (160 J/mm³), complete sample construction was not achieved. This was due to insufficient heat transfer and melt overheating, leading to warping, as well as the formation of cavities and cracks. Visual control of the SLM process for each subsequent printed layer required stopping printing for some modes due to pronounced warping of the growing samples. These modes, characterized by low laser power (70 W), ensured the formation of a dense microstructure with

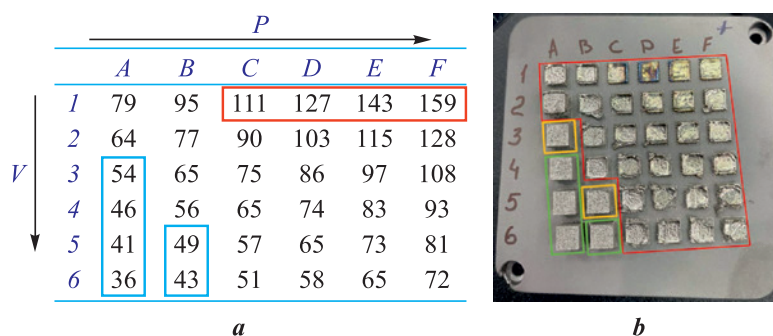


Fig. 7. SLM modes and platform with constructed samples

a – mode matrix with volumetric laser energy density values; b – image of bulk samples constructed using SLM

Рис. 7. Режимы СЛС и платформа с построенными образцами

a – матрица режимов со значениями объемной плотности энергии лазера;

b – изображение объемных образцов, построенных с помощью СЛС

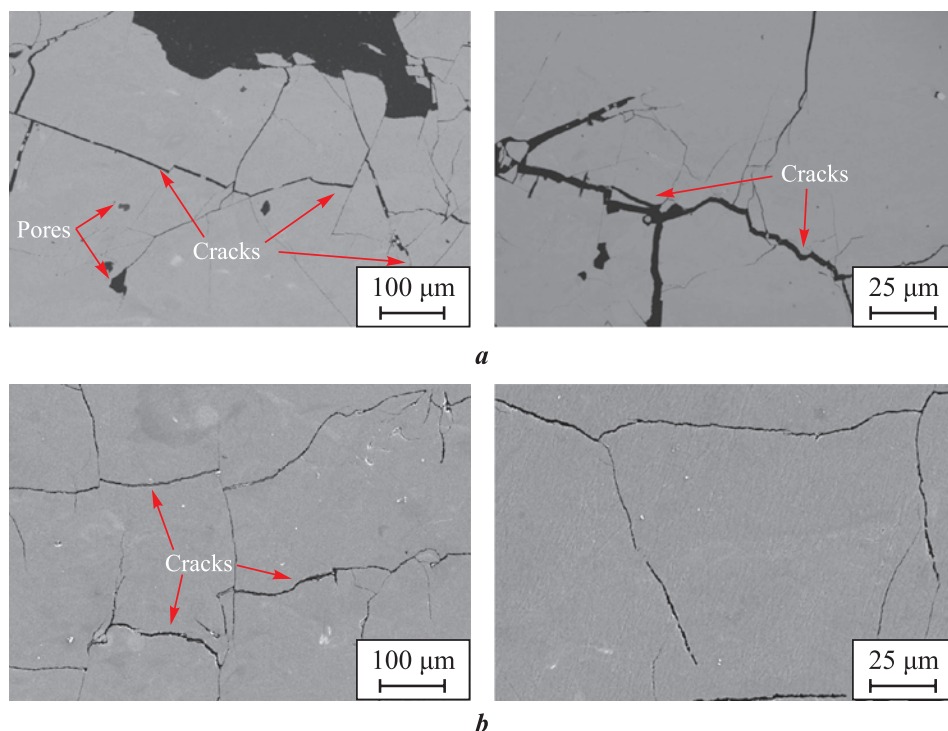


Fig. 8. Microstructures of bulk SLM samples obtained during the optimization of modes A2 (a) and A5 (b)

Рис. 8. Микроструктуры объемных СЛС-образцов, полученных при оптимизации режимов A2 (a) и A5 (b)

a uniform distribution of alloying elements. However, microcracks were present in the samples (Fig. 8, a), formed due to internal stress from strong temperature gradients.

As seen in Fig. 8, b, reducing the volumetric energy density to 50 J/mm³ and simultaneously lowering the laser power and scanning speed prevented melt pool overheating and suppressed the formation of most microcracks in the sample structures. A small number of submicron pores (<3 vol. %) were noted in these samples' structures, formed by argon entrapment in the melt pool.

Post-processing and mechanical testing

The obtained samples of the TNM-B1 + Y₂O₃ alloy with optimal structure under mode A5 (Fig. 9, a) were subjected to HIP and heat treatment. X-ray diffraction patterns were recorded after three types of treatment (SLM, SLM + HIP, and SLM + HIP + HT) and phase identification was conducted (Fig. 9, b). The TNM-B1 + Y₂O₃ alloy obtained by SLM predominantly contained the α₂-Ti₃Al phase (60 wt. %). Its concentration was 3–4 times higher than the equi-

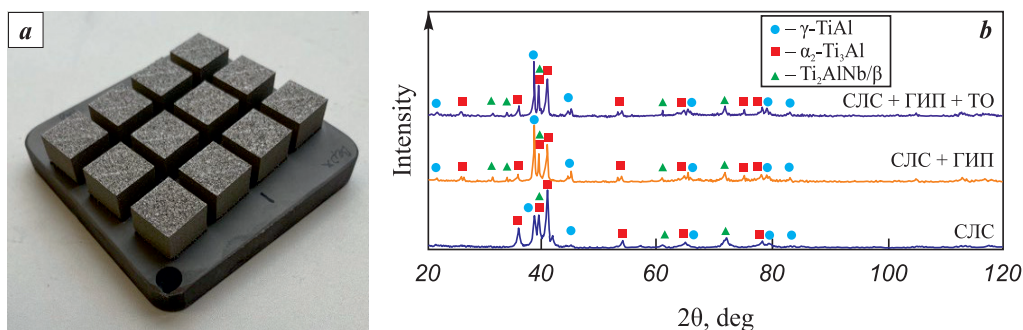


Fig. 9. Bulk samples of the TNM-B1 + Y₂O₃ alloy obtained by SLM (a) and X-ray diffraction patterns of this alloy after SLM, SLM + HIP, and SLM + HIP + HT (b)

Рис. 9. Объемные образцы из сплава TNM-B1 + Y₂O₃, полученные методом СЛС (a), и рентгенограммы этого сплава после СЛС, СЛС + ГИП и СЛС + ГИП + ТО (b)

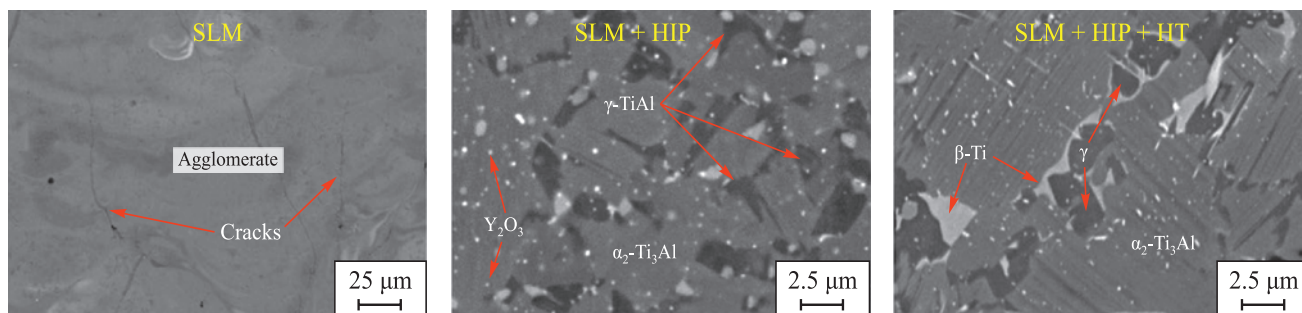


Fig. 10. Microstructures of the TNM-B1 + Y_2O_3 alloy after various types of treatment

Рис. 10. Микроструктуры сплава TNM-B1 + Y_2O_3 после различных видов обработки

librium [14]. Phase formation processes in alloys similar to TNM-B1 + Y_2O_3 are primarily controlled by the cooling rate. High cooling rates typical of SLM suppress the eutectoid reaction $\alpha \rightarrow \alpha_2 + \gamma$, resulting in an excess of the α_2-Ti_3Al [11].

HIP treatment brought the SLM TNM-B1 + Y_2O_3 alloy to an equilibrium state by transforming metastable α_2-Ti_3Al into $\gamma-TiAl$. As seen from the diffraction spectra of the SLM samples (Fig. 10), the intensity of the tetragonal $\gamma-TiAl$ phase peaks significantly increased after HIP. The $\gamma-TiAl : \alpha_2-Ti_3Al$ ratio in them was 75:20. It should be noted that both the SLM and HIP samples contained 5–7 % $\beta-Ti$ phase, which was not previously observed in this alloy obtained by HIP technology from SHS powders [15]. The SLM method for consolidation involves higher temperatures and material transition to the liquid phase, with crystallization starting with the formation of primary $\beta-Ti$ crystals according to the Ti–Al phase diagram. These $\beta-Ti$ phase grains remain in the alloy after SLM and HIP (Fig. 10).

Heat treatment (HT) did not lead to significant changes in phase composition (Fig. 9, b): the $\gamma-TiAl : \alpha_2-Ti_3Al$ ratio remained 75:20. At this stage, heating above the eutectoid transformation temperature $\alpha \rightarrow \alpha_2 + \gamma$ was carried out. As a result of slow cooling, equiaxed α -phase grains decomposed into colonies of $\gamma-TiAl : \alpha_2-Ti_3Al$ lamellae (Fig. 10).

Structural and phase changes in SLM samples occurring during HIP and HT undoubtedly affect the properties of the TNM-B1 + Y_2O_3 alloy. Fig. 11 shows deformation diagrams in the “true stress – logarithmic strain” coordinates for samples obtained under SLM mode A5, SLM + HIP, and SLM + HIP + HT. The porosity of the samples after HIP and HIP + HT did not exceed 1%. It was found that the obtained properties strongly depend on the test temperature. All deformation curves exhibit a pronounced maximum corresponding to the compressive strength and indicating the deformation hardening of the samples. All curves have a second section where deformation increases as stress decreases. This effect is explained by dynamic

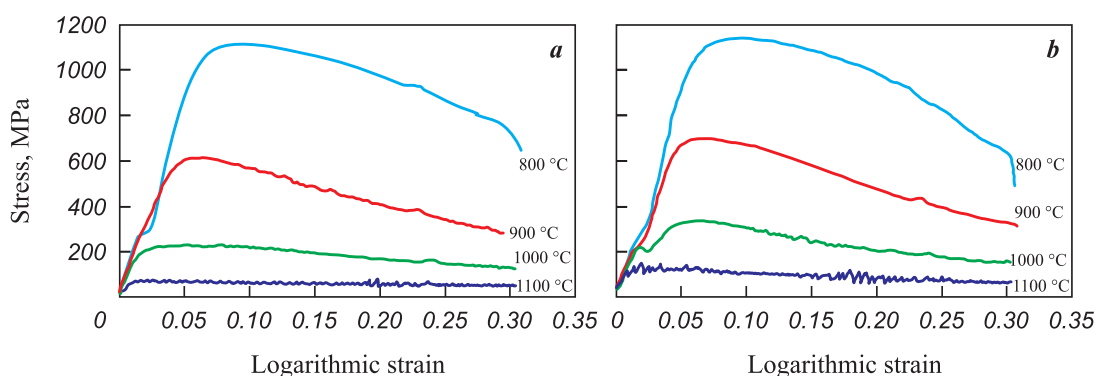


Fig. 11. Deformation diagrams under uniaxial compression in the coordinates “true stress – logarithmic strain” for SLM samples of the TNM-B1 + Y_2O_3 alloy

a – SLM + HIP; b – SLM + HIP + HT

Рис. 11. Диаграммы деформации, реализованной по схеме одноосной осадки, в координатах «истинные напряжения – логарифмическая деформация» для СЛС-образцов из сплава TNM-B1 + Y_2O_3

a – СЛС + ГИП; b – СЛС + ГИП + ТО

Mechanical properties of TNM-B1 + Y₂O₃ alloy after SLM and heat treatment (SLM mode A5)**Механические свойства сплава TNM-B1 + Y₂O₃ после СЛС и дополнительной термической обработки (режим СЛС А5)**

<i>t</i> , °C	<i>E</i> , GPa	$\sigma_{0.2}$, MPa	σ_u , MPa
Sample after SLM + HIP			
800	96.0	522	1128
900	88.0	330	622
1000	82.2	175	253
1100	73.5	94	80
Sample after SLM + HIP + HT			
800	115.2	528	1148
900	68.3	308	703
1000	54.5	181	347
1100	48.2	98	149

recrystallization or dynamic recovery and relaxation of crystal lattice defects.

Mechanical properties (elastic modulus *E*, yield strength $\sigma_{0.2}$, ultimate compressive strength σ_u) of the TNM-B1 + Y₂O₃ alloy after HIP and HIP + HT were determined using deformation diagrams (in the elastoplastic transition region). The $\sigma_{0.2}$ values of the obtained samples at 800 °C are comparable to those of cast TNM-B1 alloys ($\sigma_{0.2} = 400\div530$ MPa), and the σ_u value increased by 150–200 MPa compared to cast alloys ($\sigma_u = 880\div1000$ MPa), due to the finer grain structure [29; 30] (see Table).

HT of the TNM-B1 + Y₂O₃ alloy samples after SLM + HIP increases σ_u by 20–100 MPa due to the formation of a lamellar microstructure. The strengthening effect is more noticeable at high test temperatures (900 to 1100 °C).

Conclusions

1. Powders of the 10–65 μm fraction with a high degree of particle spheroidization (up to 99 %) were obtained from SHS powders of the TNM-B1 + Y₂O₃ alloy. The influence of particle processing parameters in thermal plasma generated by a DC plasma torch was studied. It was found that this leads to significant changes in particle morphology and the production of a product with a high degree of spheroidization ranging from 88 to 97 %, depending on plasma stream enthalpy, plasma-forming gas composition, and precursor feed rate. At the maximum spheroidization degree, partial precursor evaporation was noted, leading to the formation of up to 7 wt. % of the nanosized fraction.

2. It was established that using hydrogen-containing thermal plasma increases the spheroidization degree of the product up to 99 %. At the same time, increasing the precursor feed rate from 0.6 to 2.4 kg/h decreases the spheroidization degree from 97 to 88 %. When processing powder in hydrogen-containing thermal plasma, the impurity oxygen concentration decreases from 0.8 to 0.13 wt. %, nitrogen impurities are halved, and hydrogen concentration decreases by an order of magnitude.

3. Experiments to optimize the SLM process identified regimes that allow building preforms with minimal defects and residual porosity. The best samples were obtained at a volumetric laser energy density of 40–50 J/mm³ (laser power around 60 W) and a scanning speed above 900 mm/s.

4. The influence of post-processing (HIP and HT) on the structure, phase composition, and mechanical properties of SLM samples from the TNM-B1 + Y₂O₃ alloy was studied. After HIP, the samples had nearly zero porosity with complete healing of structural defects, and additional thermal treatment ensured the transformation of the alloy's equiaxed structure into a lamellar one.

5. Thermomechanical tests under uniaxial compression in the temperature range of 800 to 1100 °C revealed that the alloy with a lamellar structure in the SLM + HIP + HT state has increased strength values by 80–100 MPa. The best samples had the following properties at *t* = 800 °C: *E* = 115.2 GPa, $\sigma_{0.2}$ = 528 MPa, σ_u = 1148 MPa, and at 1100 °C: *E* = 48.2 GPa, $\sigma_{0.2}$ = 98 MPa, σ_u = 149 MPa.

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Information about the Authors



Сведения об авторах

Georgy M. Markov – Junior Research Scientist of the Laboratory “In situ Diagnostics of Structural Transformations” of Scientific-Educational Center of Self Propagating High Temperature Synthesis (SHS-Center) of MISIS-ISMAN, National University of Science and Technology “MISIS” (NUST MISIS)

 **ORCID:** 0000-0001-7285-7888

 **E-mail:** markov.sci@gmail.com

Andrey A. Fadeev – Cand. Sci. (Eng.), Senior Research Scientist of the Laboratory “Plasma Processes in Metallurgy and Materials Processing” of Baikov Institute of Metallurgy and Materials Science of RAS; Scientific Project Engineer of NUST MISIS

 **ORCID:** 0000-0003-2147-1787

 **E-mail:** fadeev@imet.ac.ru

Anastasia A. Skirpichnikova – Research Assistant of SHS-Center of MISIS-ISMAN

 **ORCID:** 0009-0002-1664-7039

 **E-mail:** skirpichnikova@internet.ru

Pavel A. Loginov – Cand. Sci. (Eng.), Senior Lecturer of the Department of Powder Metallurgy and Functional Coatings (PM&FC) of NUST MISIS; Senior Research Scientist of the Laboratory “In situ Diagnostics of Structural Transformations” of SHS-Center of MISIS-ISMAN

 **ORCID:** 0000-0003-2505-2918

 **E-mail:** pavel.loginov.misis@list.ru

Maxim G. Khomutov – Cand. Sci. (Eng.), Senior Research Scientist of the Laboratory of hybrid additive technologies NUST MISIS

 **ORCID:** 0000-0002-7701-1600

 **E-mail:** khomutov@isis.ru

Andrey V. Samokhin – Cand. Sci. (Eng.), Lead Research Scientist, Head of the Laboratory “Plasma Processes in Metallurgy and Materials Processing” of Baikov Institute of Metallurgy and Materials Science of RAS

 **ORCID:** 0000-0002-1708-5501

 **E-mail:** samokhin@imet.ac.ru

Evgeny A. Levashov – Dr. Sci. (Eng.), Prof., Academic of the Russian Academy of Natural Science, Head of the Department of PM&FC of NUST MISIS; Head of SHS-Center of MISIS-ISMAN

 **ORCID:** 0000-0002-0623-0013

 **E-mail:** levashov@shs.misis.ru

Георгий Михайлович Марков – мл. науч. сотрудник лаборатории «In situ диагностика структурных превращений» Научно-учебного центра (НУЦ) СВС МИСИС-ИСМАН, Национальный исследовательский технологический университет «МИСИС» (ННТУ МИСИС)

 **ORCID:** 0000-0001-7285-7888

 **E-mail:** markov.sci@gmail.com

Андрей Андреевич Фадеев – к.т.н., ст. науч. сотрудник лаборатории «Плазменные процессы в металлургии и обработке материалов» Института металлургии и материаловедения им. А.А. Байкова Российской академии наук (ИМЕТ РАН); инженер научного проекта ННТУ МИСИС

 **ORCID:** 0000-0003-2147-1787

 **E-mail:** fadeev@imet.ac.ru

Анастасия Алексеевна Скупичникова – лаборант-исследователь НУЦ СВС МИСИС-ИСМАН

 **ORCID:** 0009-0002-1664-7039

 **E-mail:** skirpichnikova@internet.ru

Павел Александрович Логинов – к.т.н., ст. преподаватель кафедры «Порошковая металлургия и функциональные покрытия» (ПМиФП) ННТУ МИСИС; ст. науч. сотрудник лаборатории «In situ диагностика структурных превращений» НУЦ СВС МИСИС-ИСМАН

 **ORCID:** 0000-0003-2505-2918

 **E-mail:** pavel.loginov.misis@list.ru

Максим Геннадьевич Хомутов – к.т.н., ст. науч. сотрудник лаборатории гибридных аддитивных технологий ННТУ МИСИС

 **ORCID:** 0000-0002-7701-1600

 **E-mail:** khomutov@isis.ru

Андрей Владимирович Самохин – к.т.н., вед. науч. сотрудник, зав. лабораторией «Плазменные процессы в металлургии и обработке материалов» ИМЕТ РАН

 **ORCID:** 0000-0002-1708-5501

 **E-mail:** samokhin@imet.ac.ru

Евгений Александрович Левашов – д.т.н., акад. РАЕН, профессор, зав. кафедрой ПМиФП ННТУ МИСИС; директор НУЦ СВС МИСИС-ИСМАН

 **ORCID:** 0000-0002-0623-0013

 **E-mail:** levashov@shs.misis.ru

Contribution of the Authors



Вклад авторов

G. M. Markov – defined the research objectives, prepared the starting materials, conducted experiments, and wrote the article.

A. A. Fadeev – conducted experiments on plasma spheroidization, participated in result discussions, and edited the article.

A. A. Skirpichnikova – participated in obtaining the starting materials.

P. A. Loginov – defined the research objectives, participated in result discussions, and revised the article.

M. G. Khomutov – conducted thermomechanical testing and participated in result discussions.

A. V. Samokhin – conceptualized and reviewed the article, participated in result discussions.

E. A. Levashov – conceptualized the research, edited the article text, and participated in result discussions.

Г. М. Марков – определение цели работы, подготовка исходных материалов, проведение экспериментов, написание текста статьи.

А. А. Фадеев – проведение экспериментов по плазменной сфероидизации, участие в обсуждении результатов, редактирование статьи.

А. А. Скирпичникова – участие в получении исходных материалов.

П. А. Логинов – определение цели работы, участие в обсуждении результатов, корректировка статьи.

М. Г. Хомутов – проведение термомеханических испытаний, участие в обсуждении результатов.

А. В. Самохин – концептуализация и проверка статьи, участие в обсуждении результатов.

Е. А. Левашов – концептуализация проводимых исследований, редактирование текста статьи, участие в обсуждении результатов.

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Научная статья

Surface modification of steels used in valve manufacturing

I. S. Sokolova^{1, 2}✉, A. V. Oborin², S. E. Porozova¹¹ Perm National Research Polytechnic University

29 Komsomolskiy Prosp., Perm 614990, Russia

² Ion Technologies LLC

47A Bld. 5 Shosseynaya Str., Krasnokamsk 617064, Russia

✉ seporozova@pstu.ru

Abstract. Shut-off and control valves are essential components in liquid and gas transportation systems; therefore, their reliable operation depends on the quality and properties of their surface parts. One method to enhance these properties is ion nitriding, which is actively used in Russia, Israel, Bulgaria, Belarus, Austria, and other countries. This method is easy to manage and control, is universal for all types of steels and alloys, is environmentally safe, ensures dimensional and surface finish accuracy, and improves the operational properties of parts. This paper presents summarized results of studies on the formation of modified layers on steels used in valve manufacturing. The steels of grades AISI 420, AISI 301, AISI 431, and AISI 321 were strengthened by ion nitriding. For the first time, comparative data obtained on equipment from different manufacturers are presented. A comprehensive metallographic analysis, durometric analysis, and hardness distribution assessment across the depth of the modified layer were conducted during the study. It was found that steels with more than 12 % Cr form a clearly defined diffusion layer, which appears dark after etching with a 4 % nitric acid solution. However, the overall depth of the layer, as assessed by the distribution of microhardness into the depth of the part, is 20–40 % greater than revealed by the microstructure. The surface microhardness after ion-plasma nitriding increased fivefold in the AISI 301 steel. Thus, strengthening parts of shut-off and control valves using this method addresses the issue of rapid surface wear. By modifying the surface, the operational properties of parts can be enhanced, ensuring the uninterrupted operation of the pipeline system.

Keywords: ion-plasma nitriding (IPN), steel, AISI 420, AISI 301, AISI 431, AISI 321, modified layer, nitride zone, Bulgarian equipment, Russian equipment, shut-off and control valves

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Модифицирование поверхности сталей, применяемых в арматуростроении

И. С. Соколова^{1, 2}✉, А. В. Оборин², С. Е. Порозова¹¹ Пермский национальный исследовательский политехнический университет

Россия, 614990, г. Пермь, Комсомольский пр-т, 29

² ООО «Ионные технологии»

Россия, 617064, г. Краснокамск, Шоссейная ул., 47А, корп. 5

✉ seporozova@pstu.ru

Аннотация. Запорно-регулирующая аппаратура является важной частью системы транспортировки жидкости и газов, поэтому ее бесперебойная работа зависит от качества и свойств поверхности деталей. Один из способов улучшения ее свойств – это ионное азотирование, которое активно применяется в России, Израиле, Болгарии, Беларуси, Австрии и других странах. Этот метод прост в управлении и контроле, универсален для всех видов сталей и сплавов, экологически безопасен, обеспечивает размерную и чистовую точность, повышает эксплуатационные свойства деталей. В настоящей работе приведены обобщенные результаты исследований формирования модифицированных слоев на сталях, применяемых в арматуро-

строении. Стали марок 20X13, 07X16H6, 14X17H2, 12X18H10T упрочняли методом ионного азотирования. Впервые представлены сравнительные данные, получаемые на оборудовании разных производителей. В ходе работы проведены комплекс металлографических исследований, дюрометрический анализ, а также рассмотрено распределение твердости по глубине модифицированного слоя. Установлено, что на сталях с содержанием более 12 % Cr образуется четко выраженный диффузионный слой, который выявляется темным цветом после травления 4 %-ным раствором азотной кислоты. Однако общая глубина слоя, которая оценивается по распределению микротвердости в глубь детали, больше на 20–40 %, чем выявляется по микроструктуре. Микротвердость поверхности после ионно-плазменного азотирования увеличилась в 5 раз на стали 07X16H6. Таким образом, упрочнение с использованием этого метода деталей запорно-регулирующей арматуры решит проблему быстрого износа поверхности. За счет ее модифицирования можно повысить эксплуатационные свойства деталей и обеспечить бесперебойную работу трубопроводной системы.

Ключевые слова: ионно-плазменное азотирование (ИПА), сталь, 20X13, 07X16H6, 14X17H2, 12X18H10T, модифицированный слой, нитридная зона, болгарское оборудование, российское оборудование, запорно-регулирующая аппаратура (ЗРА)

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Introduction

In many industrial sectors, the quality of pipes and especially shut-off and control valves (SCV) is critical not only for the uninterrupted transportation of liquids and gases but also for the overall accident-free operation of production facilities [1–4]. Protective coatings on the surface of metal and alloy products, obtained through ion chemical-thermal treatment (ICTT) methods, significantly improve their performance characteristics. One of the most promising variants of ICTT is ion nitriding [5–9]. The literature refers to this process by several names: ion-vacuum, ion-plasma, and ion nitriding [10–13]. This universal method of surface modification in a glow discharge plasma in a vacuum [14–16] is relatively simple to apply, allows for the strengthening of all types of steels and alloys, and is considered a “white metallurgy” process [17].

Engineers from the Israeli company “HABONIM” were among the first to apply low-temperature ion-plasma nitriding (IPN) to enhance the wear resistance of valve components [18]. Today, the technology of low-temperature plasma carbonitriding for ball valves is specified in all catalogs of the Israeli manufacturer [19].

Currently, the Austrians are recognized leaders in the field of ion nitriding. They have developed and patented technologies such as PLASNIT, PLASOX, and PLAPOL, which are also used to strengthen valve components [20].

Although research on the ICTT process has been conducted in Russia since the 1970s, the active use of ion nitriding in industry began relatively recently [21–24]. The production of equipment in Russia also started much later than in other countries, but today there are domestic IPN units available. Automated software based on technological know-how, the use of micro-processor and high-precision equipment, as well as

technologies for high-speed transmission of large amounts of information and modular robotic systems, allows them to compete with foreign counterparts [21].

As of 2020, the share of imports in the consumption structure of industrial SCV in Russia was 53 % [3]. In 2023, it is still necessary to import the missing product positions [25], so domestic enterprises are independently mastering new types of products and seeking new technologies to improve the reliability and quality of valve products. In this regard, comparing results obtained on units from different manufacturers, as well as conducting research and summarizing data on the strengthening of steels by ICTT, are currently pressing tasks.

The aim of this work is to study the modified layers obtained by ion-plasma nitriding on steels used in valve construction and to compare the data obtained on Bulgarian and Russian production units.

Research methodology

The ion-plasma nitriding (IPN) process was conducted using equipment from IONITECH (Bulgaria) and Ion Technologies LLC (Russia). The IPN temperatures ranged from 550 to 580 °C, the pressure was 4 mbar, and the gas mixture consisted of 25 % N₂ and 75 % H₂. The isothermal holding time (5–12 h) was determined based on the four different steel grades selected for the study. The holding duration was the same for identical samples on both setups. Fig. 1 shows images of parts during the nitriding process.

The study was conducted on steels of grades AISI 431, AISI 420, AISI 301 and AISI 321, which are used for manufacturing SCV parts such as gates, seats, stems, separators, pistons, spindles, wedges, etc. The general characteristics of the steels are provided in Table 1. For destructive testing, witness samples were placed in the working chamber along with the parts.

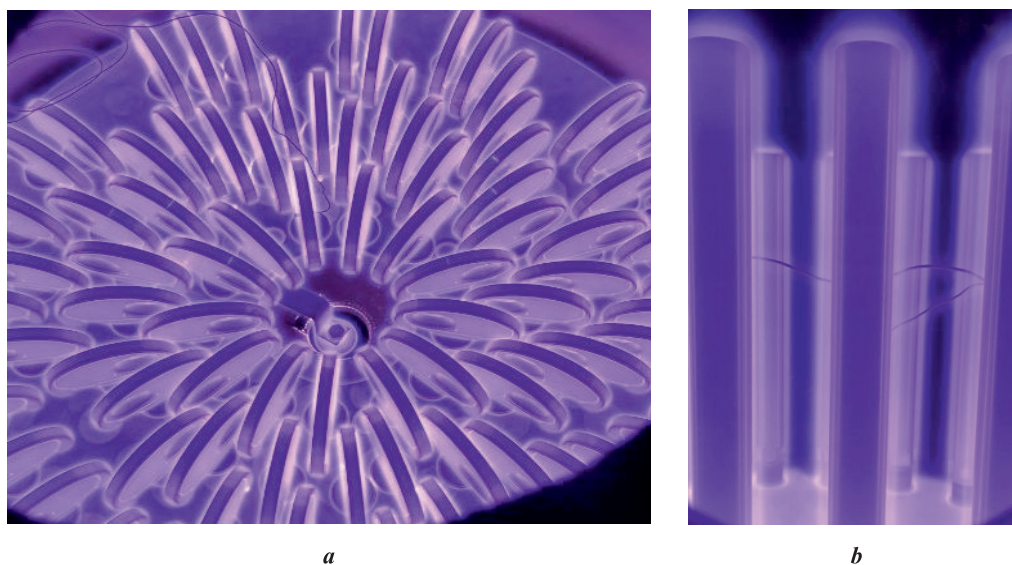


Fig. 1. View of parts “gate” (a) and “stem” (b) in plasma during the strengthening process

Рис. 1. Вид деталей «шибер» (a) и «шток» (b) в плазме во время процесса упрочнения

After IPN, the entire surface of the samples was visually inspected for external defects. The nitrided surface was checked for color uniformity, and the absence of peeling and chipping, especially along sharp edges, at a magnification of 15–30 times. The brittleness of the nitrided layer was controlled by examining the diamond pyramid indentation according to the VIAM brittleness scale (STo INTI S.70.2-2022).

One of the key indicators of strengthening is surface hardness. This value represents the hardness of the thin

modified layer, so it is important to select a load that ensures the indenter does not penetrate through the surface layer (STo INTI S.70.2-2022). Preparation for measuring this indicator involved smoothing the surface with P2500 grinding paper, after which the surface hardness of the layer was determined using the Vickers method according to GOST 2999-75 under a load of 49.03 N. Surface microhardness [26] was assessed under a load of 0.98 N according to GOST 9450-76 using a PMT-3 device (Russia).

Table 1. General characteristics of the investigated steels¹

Таблица 1. Общие характеристики исследованных сталей¹

Steel grade	Composition, %	Structure	SCV application
AISI 420	0.16–0.25 C 12–14 Cr Up to 0.6 Ni Balance – Fe	Martensitic	In atmospheric corrosion conditions and mildly aggressive environments
AISI 301	0.05–0.09 C 15.5–17.5 Cr 5–8 Ni Balance – Fe	Austenitic-Martensitic	In atmospheric conditions, saline environments, and for cryogenic equipment
AISI 431	0.11–0.17 C 16–18 Cr 1.5–2.5 Ni 0.2 Ti Balance – Fe	Martensitic-Ferritic	In mildly aggressive environments requiring increased strength and hardness
AISI 321	Up to 0.12 C 17–19 Cr 9–11 Ni 0.4–1.0 Ti Balance – Fe	Austenitic	For welded valve assemblies operating in aggressive environments

¹ GOST 33260-2015, GOST 5632-14

Samples for microstructural analysis were embedded in Bakelite powder and prepared into slides according to the standard methodology (STo INTI S.70.2-2022). Microstructural examination was carried out using a BiOptic microscope (Russia) with a universal etchant (4 % nitric acid) to reveal the nitrated layer. According to standards, the total depth

of the layer (h_h) is determined by measuring microhardness from the surface in a direction perpendicular to it until the microhardness matches the core microhardness value. The layer depth was controlled by the durometric method on a PMT-3 microhardness tester under a load of 0.98 N with a hold time of 10 s (STo INTI S.70.2-2022).

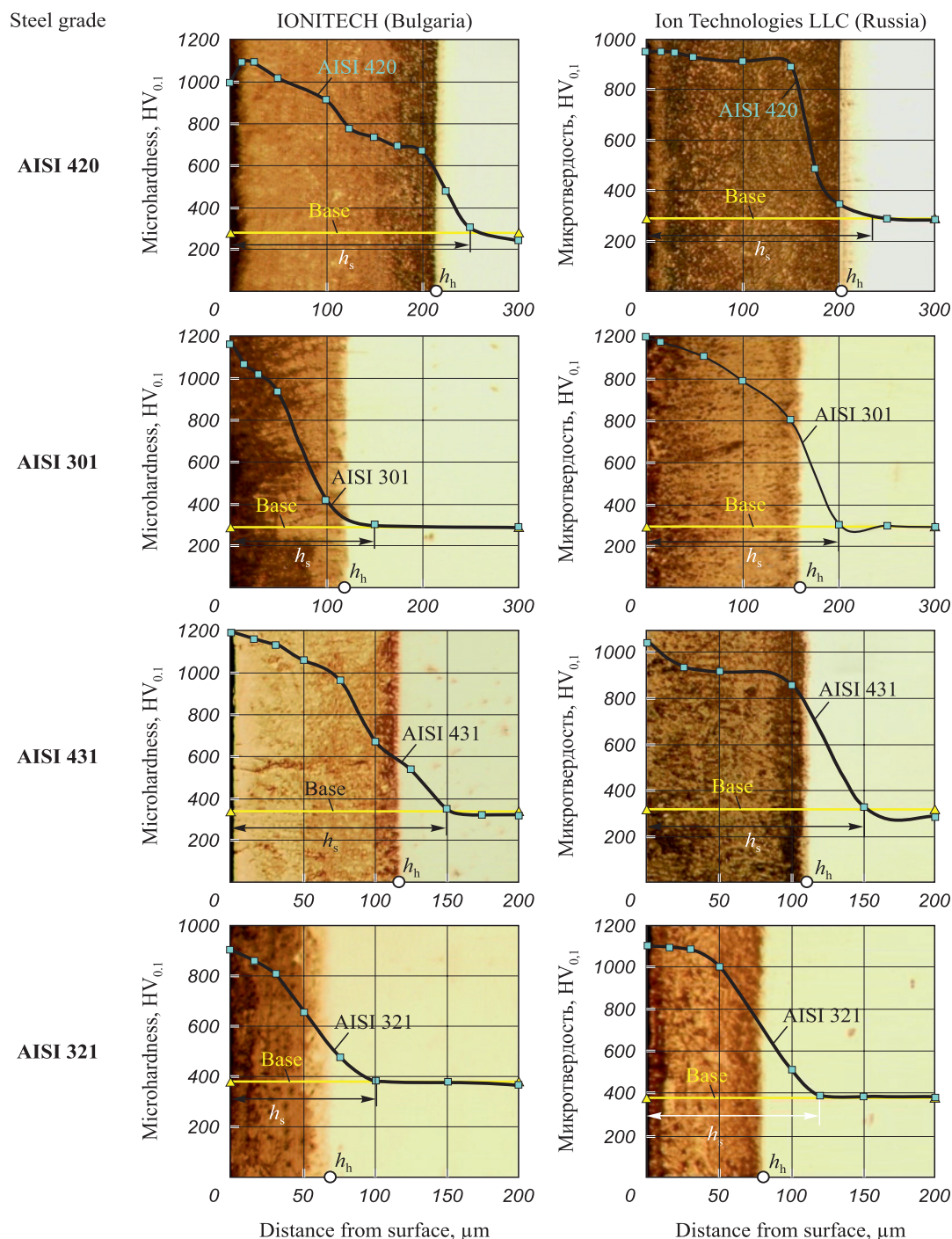


Fig. 2. Microstructures and microhardness distribution graphs by depth of nitrated layer on steels of different compositions
 h_s – depth of layers by microstructure, h_h – by microhardness distribution

Рис. 2. Микроструктуры и графики распределения микротвердости по глубине азотированного слоя на сталях различного состава
 h_c – глубина слоев по микроструктуре, $h_{тв}$ – по распределению микротвердости

Table 2. Surface hardness and microhardness of nitride layers on the investigated steels

Таблица 2. Поверхностные твердость и микротвердость азотированных слоев исследуемых сталей

Steel grade	IONITECH (Bulgaria)			Ion Technologies LLC (Russia)		
	Initial hardness HV _{0.1}	HV ₅	HV _{0.1}	Initial hardness HV _{0.1}	HV ₅	HV _{0.1}
AISI 420	260–280	840–930	980–1005	280–300	1000–1050	1080–1100
AISI 301	260–290	1070–1145	1145–1200	250–280	1080–1130	1165–1235
AISI 431	320–340	900–1050	1085–1105	250–300	970–1030	1010–1060
AISI 321	340–380	840–930	990–1150	380–400	950–1000	1100–1145

Results and discussion

The results of the study on nitrided layers on steels of different compositions (see Table 1), obtained using ion-plasma equipment from Bulgarian and domestic manufacturers, are presented in Fig. 2.

Ion-plasma nitriding (IPN) resulted in a uniformly developed, non-brittle nitrided layer on the parts. Visual inspection showed that the parts and samples had a uniform matte gray color without any surface defects. Studies of steel sections with more than 12 % Cr content revealed a modified zone that is easily etched, with clear boundaries. The depth of the nitrided layers, as determined by microstructure, reaches $h_s = 0.08 \div 0.22$ mm (Fig. 3), while the depth determined by microhardness distribution is $h_h = 0.10 \div 0.25$ mm. In all cases, the depth h_h of the nitrided layer obtained on the domestic equipment is greater.

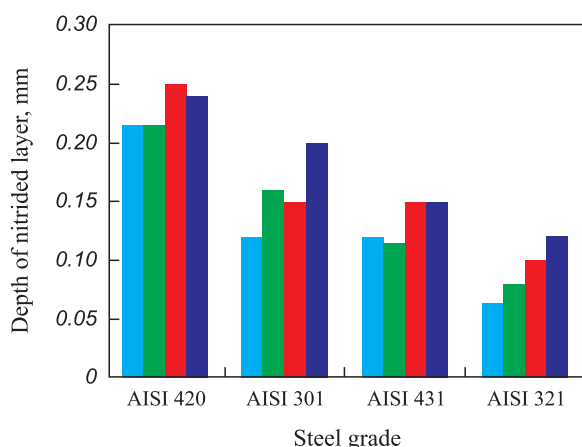


Fig. 3. Histogram of the depth distribution of nitride layers by microstructure (h_s) and microhardness (h_h)

■ and ■ – results obtained on equipment from IONITECH (Bulgaria);
■ and ■ – results obtained on equipment from Ion Technologies LLC (Russia)

Рис. 3. Гистограмма распределения глубины азотированных слоев по микроструктуре (h_c) и микротвердости ($h_{тв}$)

■ и ■ – результаты, полученные на установке производства IONITECH (Болгария);
■ и ■ – ООО «Ионные технологии» (Россия)

For steels with martensitic and martensitic-ferritic structures (see Table 1), there are minimal differences in the depth of the nitrided layer between the microstructure and microhardness for layers obtained in both cases (Fig. 3), although the results using domestic equipment are higher. For austenitic-martensitic and austenitic steels (see Table 1), the differences in the depth of the nitrided layers are significant (Fig. 3), indicating that part of the nitrided layer (the transition zone) is not revealed by etching with the reagents used. Based on the obtained data, it can be concluded that the method of determining the depth of the nitrided layer by microhardness is more informative and accurate.

Table 2 presents the results of measuring the surface hardness and microhardness of the nitrided layers, which are the main criteria for the wear resistance of shut-off and control valves.

Modifying the metal surface led to an increase in the surface hardness of all the investigated steels. During the process of diffusion saturation of the surface with nitrogen, the formation of iron nitrides and alloying elements occurred, resulting in the increased hardness of the nitrided layer. The maximum result was observed in AISI 301 steel: its surface microhardness increased fivefold from ~ 260 HV_{0.1} to ~ 1200 HV_{0.1}. The minimum increase in microhardness (2.8 times) was noted in AISI 321 steel.

Thus, the surface hardening technology allowed for the preservation of the dimensional and surface finish accuracy of the parts [27]. Three of the largest Russian SCV manufacturers [3] are already using ion nitriding to improve the quality of their products and are incorporating it into their production cycles [28].

Conclusions

The commonly used steels in valve construction, AISI 420, AISI 301, AISI 431 and AISI 321, show an increase in surface hardness by 2.8 to 5 times after ion-plasma nitriding under the conditions of the conducted studies.

The method of assessing the depth of the nitrided layer by microhardness is more accurate than determining it by microstructure. This is because, during the nitriding of austenitic-martensitic and austenitic steels (see Table 1, Fig. 3), part of this layer (the transition zone) is not revealed by etching.

A comparative analysis of the microhardness of the modified layers established that the Russian equipment produced by Ion Technologies LLC performs on par with foreign equipment under identical operating conditions. It demonstrates comparable surface hardening results for parts to those achieved with well-known global market equipment from IONITECH (Bulgaria).

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Information about the Authors

Irina S. Sokolova – Postgraduate student at the Department of “Mechanics of Composite Materials and Structures” (MCMS), Perm National Research Polytechnic University (PNRPU), Head of Laboratory at Ion Technologies LLC
 **ORCID:** 0009-0004-2603-1785
 **E-mail:** sokolova@procion.ru

Aleksei V. Oborin – Director of Ion Technologies LLC
 **E-mail:** oborin@procion.ru

Svetlana E. Porozova – Dr. Sci. (Eng.), Professor at the Department of MCMS, PNRPU
 **ORCID:** 0000-0001-5835-9727
 **E-mail:** seporozova@pstu.ru

Сведения об авторах

Ирина Сергеевна Соколова – аспирант кафедры «Механика композиционных материалов и конструкций» (МКМК), Пермский национальный исследовательский политехнический университет (ПНИПУ), зав. лабораторией ООО «Ионные технологии»
 **ORCID:** 0009-0004-2603-1785
 **E-mail:** sokolova@procion.ru

Алексей Владимирович Оборин – директор ООО «Ионные технологии»
 **E-mail:** oborin@procion.ru

Светлана Евгеньевна Порозова – д.т.н., профессор кафедры МКМК, ПНИПУ
 **ORCID:** 0000-0001-5835-9727
 **E-mail:** seporozova@pstu.ru

Contribution of the Authors**Вклад авторов**

I. S. Sokolova – conducted metallographic studies, summarized the obtained data, and wrote the article.

A. V. Oborin – prepared and conducted ion nitriding processes, and revised the article text.

S. E. Porozova – provided scientific supervision, processed the obtained results, and prepared and revised the article text for publication.

И. С. Соколова – проведение металлографических исследований, обобщение полученных данных, написание текста статьи.

А. В. Оборин – подготовка и проведение процессов ионного азотирования, корректировка текста статьи.

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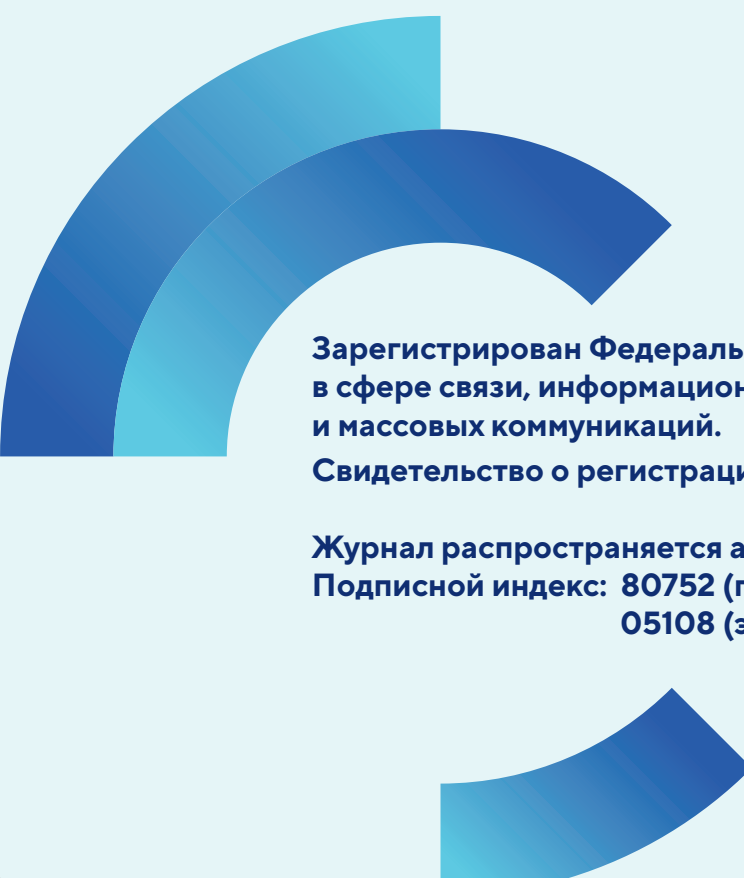
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