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DEVELOPMENT OF TECHNOLOGICAL RECOMMENDATIONS FOR THE FORMATION OF BORIED POWDER FOR PLASMA SPRAYING OF NICKEL ALLOY

The article describes the choice of the method and medium for diffusion alloying of nickel alloy powders. One of the main and most effective ways to protect parts from high-temperature corrosion and oxidation is to create a nickel-based plasma coating system on their working surface. Their performance properties depend on the order of distribution of γ' - and β - phases in the formed γ -solid solution. In the technologies for creating heat-resistant coatings based on nickel, a whole range of alloying materials (zirconium, tungsten, molybdenum, rhenium, hafnium, niobium, tantalum, vanadium, etc.) are introduced into these systems to further improve performance properties. They affect the thermal stability of the precipitates of the strengthening γ' - phase. Carbon and boron are also introduced, promoting the formation of carbide and boride phases, increasing fracture toughness, creep time, and long-term strength period. Based on a number of advantages (simplicity, general availability, reliability of the technology, high stability of results, possibility of repeated use of the saturating medium) for diffusion saturation of powders based on nickel alloys in order to ensure high performance properties, the method of saturation in powder media of boron and silicon carbides was selected. It was found that from the point of view of ensuring the stability of the shell thickness, good fluidity and stability of the dispersion composition, the best ratio of the saturating medium to the saturated one is in the range of 4:1, the ratio in the saturating medium is B₄C-SiC (40%:60%) with approximate equality of particle sizes and their size of 40-60 μ m, and sodium fluorides in an amount of 1-1.5% are most suitable as an activator.

Keywords: nickel-based plasma coatings, method and environment for diffusion alloying of nickel alloy powders, diffusion saturation of powders, study of structure and properties, performance characteristics.

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РАЗРАБОТКА ТЕХНОЛОГИЧЕСКИХ РЕКОМЕНДАЦИЙ ПО ФОРМИРОВАНИЮ БОРИРОВАННОГО ПОРОШКА ДЛЯ ПЛАЗМЕННОГО НАПЫЛЕНИЯ НИКЕЛЕВОГО СПЛАВА

В статье описаны выбор метода и среды для диффузионного легирования порошков никелевых сплавов. Одним из основных и наиболее эффективных способов для защиты от воздействия высокотемпературных коррозии и окисления деталей является создание на их рабочей поверхности системы плазменных покрытий на никелевой основе. Их эксплуатационные свойства зависят от порядка распределения в сформированном γ -твердом растворе γ' - и β - фаз. В технологиях создания жаропрочных покрытий на базе никеля, для дальнейшего улучшения эксплуатационных свойств в данные системы вводят целый спектр легирующих материалов (цирконий, вольфрам, молибден, рений, гафний, ниобий, тантал, ванадий, и др.) Они оказывают влияние на термоустойчивость выделений упрочняющей γ' - фазы. Вводят также углерод и бор, способствующими образованию карбидных и боридных фаз, повышающие вязкость разрушения, время ползучести, период длительной прочности. Исходя из ряда преимуществ (простота, общедоступность, надежность технологии, высокая стабильность результатов, возможность многократного использования насыщающей среды) для диффузионного насыщения порошков на основе никелевых сплавов с целью обеспечения высоких эксплуатационных свойств выбран метод насыщения в порошковых средах карбидов бора и кремния. Установлено, что с точки зрения обеспечения стабильности толщины оболочки, хорошей текучести и устойчивости дисперсионного состава наилучшим является соотношение насыщающей среды к насыщаемой в интервале 4:1, соотношение в насыщающей среде B₄C-SiC (40%:60%) при примерном равенстве размеров частиц и их величине 40-60 мкм, а в качестве активатора наиболее целесообразны фтористые натрий в количестве 1-1,5%.

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Ключевые слова: плазменных покрытий на никелевой основе, метод и среда для диффузионного легирования порошков никелевых сплавов, диффузионное насыщение порошков, исследование структуры и свойств, эксплуатационные характеристики.

1. Introduction

Since the beginning of the 21st century, the use of thermal spray coatings to improve the quality of parts in various industries has become the norm. If at first thermal spraying technologies for restoration or strengthening were used for important or expensive parts due to the high cost of high-quality materials, the complexity of technological processes, the need for qualified personnel, problems with subsequent processing, then after many years of development in the technological and theoretical aspects of this area, they have become more accessible. New types of spraying have been developed - high-speed, hybrid, plasma spraying technologies in air and vacuum have been improved, methods for feeding small and submicron powder materials have been developed, processes for subsequent high-energy processing have been developed, modern spraying equipment has been automated and computerized, i.e. thermal spraying processes are becoming standard. At present, in the Republic of Belarus, restoration and strengthening technologies are used in various industries for a wide range of industrial equipment parts. The main characteristics of coatings that determine their high-quality use are operational: hardness, adhesive and cohesive strength of adhesion, porosity. However, a number of questions remain regarding the application of these technologies, especially in agriculture. As a rule, the indicators of reducing the cost of restoration and strengthening processes come first, the acquisition of high-quality powder materials is difficult, and technological equipment has a long service life. It is necessary to create materials, if possible, on a local raw material base or from inexpensive components that are available and relatively inexpensive for applying wear-resistant and corrosion-resistant coatings that operate under high-temperature conditions. One of the main and most effective methods for protecting parts from high-temperature corrosion and oxidation is the creation of a nickel-based plasma coating system on their working surface. Their operational properties depend on the order of distribution of γ' - and β - phases in the formed γ - solid solution. In the technologies of creating heat-resistant coatings based on nickel, for further improvement of operational properties, a whole range of alloying materials (zirconium, tungsten, molybdenum, rhenium, hafnium, niobium, tantalum, vanadium, etc.) are introduced into these systems. They affect the thermal stability of the precipitates of the strengthening γ' phase. Carbon and boron are also introduced, promoting the formation of carbide and boride phases, increasing the fracture toughness, creep time, and the period of long-term strength.

2. Selection of the method and environment for diffusion alloying of nickel alloy powders

Analysis of existing methods and techniques of boriding processes shows that the most common is processing in powder media [1-15] due to its manufacturability and applicability for processing powder materials [9, 10]. Boriding in liquid media is unacceptable due to the problems of extracting processed powder materials from melts and cleaning them; boriding in liquid media is unacceptable. Application in industry of processing in electrolyte solutions has not found due to its non-ecological friendliness. Due to the complexity of the equipment, low reliability and instability of the results of the technology - the explosion hazard of boriding in gaseous environments has also not found wide application. Boriding using technical boron carbide powder as a saturating medium has a number of qualitative advantages due to general availability, simplicity and reliability of the technology, high stability of the results, the possibility of repeated use of materials of the saturating medium. For the diffusion alloying meth-

od, we selected technical boron carbide powders as the main boron-containing components, and for borosilicate coating, the silicon-containing saturating component is silicon carbide in powder mixtures [8-10]. To conduct preliminary studies for borosilicate coating, the ratio of boron carbide and silicon powders was 40:60 [1, 2]. Further, it was assumed that it was necessary to optimize the compositions of the saturating medium and the conditions during diffusion processing. The important role of the ratio in the powder mixture of the saturating and saturating media is known. Their optimal ratio was established empirically at constant temperature-time values (Figure 1). From Figure 1 it is evident that the formation of a continuous boride layer on the M-roll powder material is observed when the amount of boron carbide is 4 times or more greater than the amount of metal powder in the mixture. A smaller amount does not ensure the formation of a continuous boride layer, which subsequently causes the formation of low-quality coatings. With an increase in the proportion of boron carbide from 4 to 5 parts, the power of the diffusion source increases, and the growth of the continuous borated layer is activated. At ratios of 5:1 and higher, the growth of the diffusion layer stabilizes. Based on the fact that with a further increase in the proportion of the saturating medium, the proportion of metal powder decreases and the productivity of the process for obtaining borated powder material decreases, we refused to further increase the proportion of the saturating medium. The study of the effect of the ratio of components in the powder mixture on fluidity also showed that with an increase in the proportion of metal powder over 25%, fluidity deteriorates sharply (Figure 2). This pattern occurs with an insufficient amount of boron carbide in the mixture, in which case the particles of the metal powder sinter together. The results of chemical-thermal treatment directly depend on the particle sizes of the powder media [14, 15].

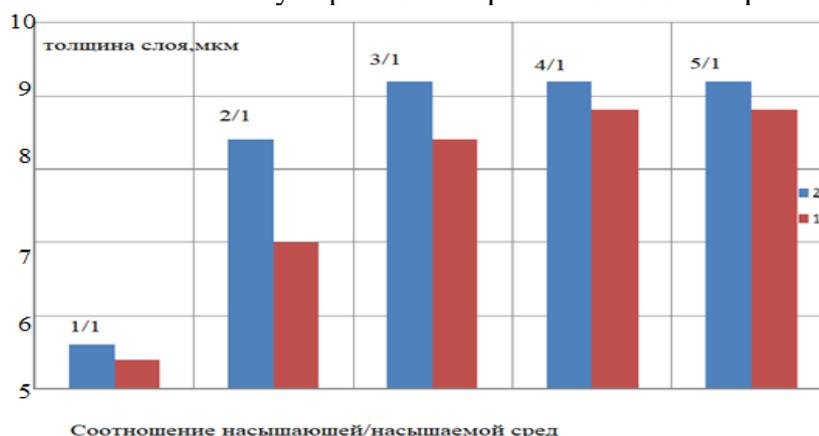


Figure 1. Effect of the ratio of the saturating and saturable media during boriding of nickel-chromium-aluminum-yttrium (1) and nickel-cobalt-chromium-aluminum-yttrium (2) powders for 2 hours at 900°C on the thickness of the continuous diffusion layer

Studies of the effect of the particle sizes of the saturating and saturable media on the thickness of the diffusion layer on spheroidized metal powder (Figure 3) have proven that the best results are obtained with equal particle sizes constituting the powder mixtures. In this case, the size of the powder particles should be within 40-60 μm. Reducing the size of the powder particles to less than 40 μm reduces the thickness of the resulting layer due to deterioration in the gas permeability of the powder mixture for moving the vapor-gas phase with boron halides. At particle sizes over 60 μm, due to the decrease in the total surface area of the powder particles of boron carbide and metal powder, the process of formation of boron halides and the amount of boron itself capable of diffusion decrease. An important characteristic of the technology is the possibility of multiple use of the saturating mixture. The study of the

frequency of use of the saturating mixture made it possible to establish the following pattern. With an increase in the frequency of use of the powder mixture, the proportion of the fine fraction of boron carbide (less than 40 μm) increases and the flowability of the powder worsens (Figure 4).

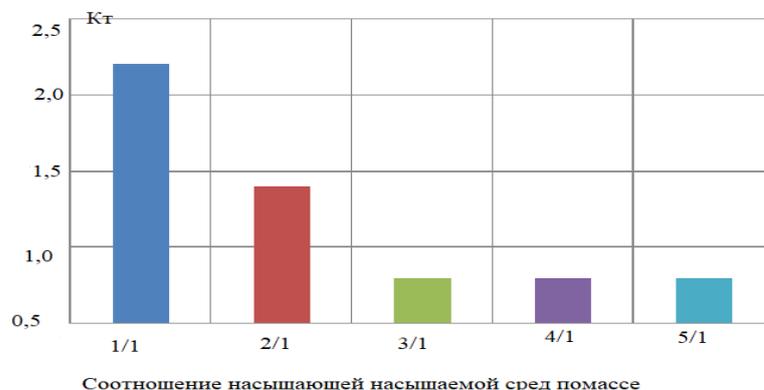
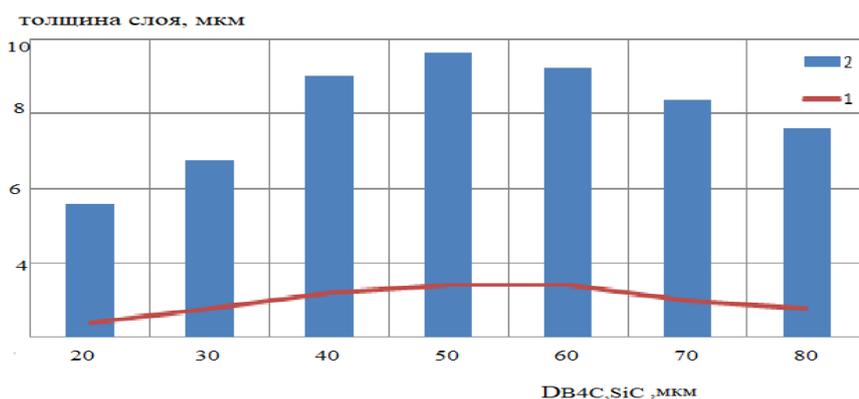
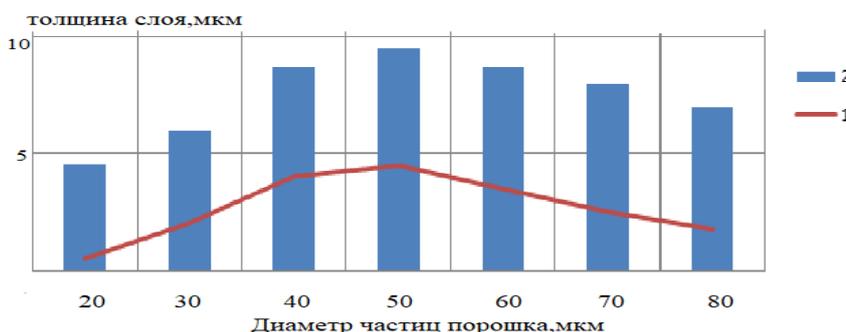


Figure 2. Effect of the mixture component ratio on the fluidity of the processed nickel-chromium-aluminum-yttrium powder (T=9000, t=2h)



a)



б)

Figure 3. Effect of the particle size of the powder medium on the thickness of the diffusion layer during boriding of nickel-chromium-aluminum-yttrium powder for 2 hours at a temperature of: 1 – 800°C; 2 – 900°C a – saturating medium; b – nickel-chromium-aluminum-yttrium powder

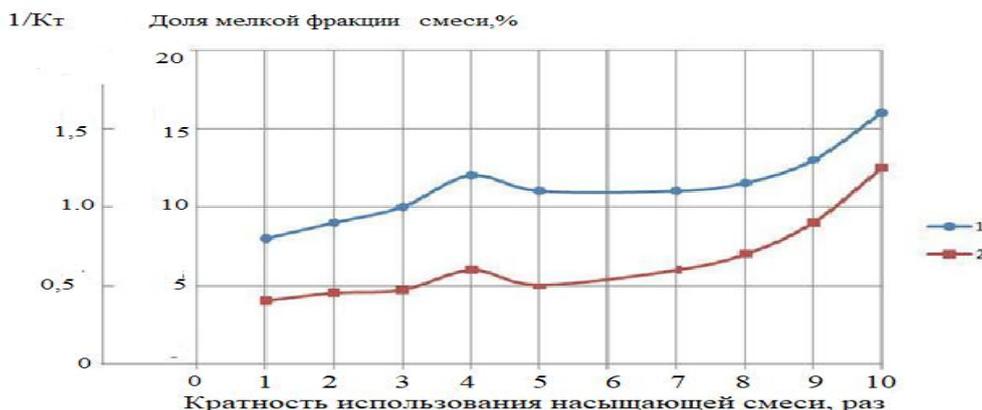


Figure 4. Effect of multiplicity when using a saturating powder mixture without regeneration on the particle size of the saturating mixture (1) and the flow properties of the processed nickel-chromium-aluminum-yttrium powder (2)

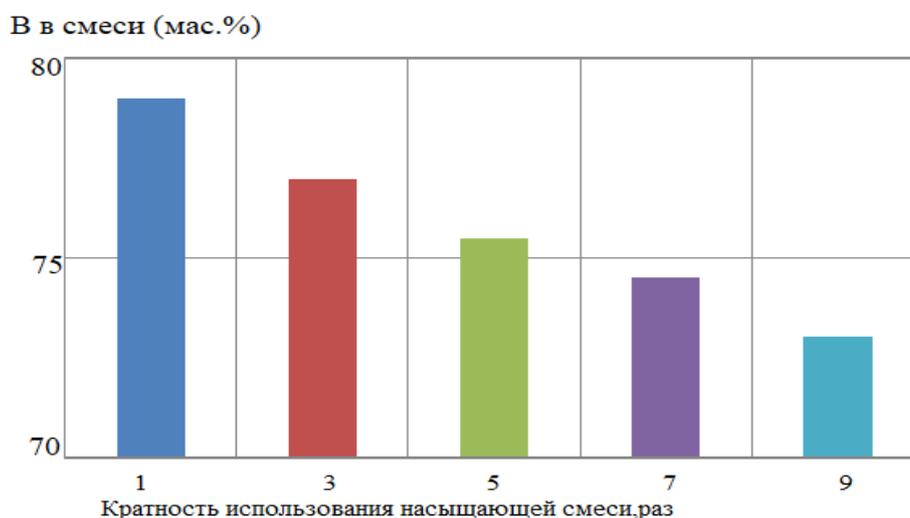


Figure 5. Effect of multiplicity when using a powder mixture on the boron content in it

The grinding of the boron carbide powder occurs due to its interaction with activating halides, with oxygen and the gradual transformation of a certain part into volatile compounds with the corresponding depletion of the powder in boron (Figure 5). A sharp increase in the proportion of fine fraction occurs after 6-7 times the mixture is used (without regeneration). The nature of the effect of multiplicity on the fluidity (see Figure 5) of the processed powder is similar; a study of the appearance of the powder material using a microscope indicates the sintering of the smallest particles of boron carbide to the metal powder of the m-croll (Figure 6, a).

This is additionally confirmed by the increase in the integral hardness of the layer sprayed from the processed powder with a decrease in the thickness of the diffusion layer on the powder and its microhardness (Figure 7). Before the six-fold use of the saturating powder mixture, there is some increase in the thickness of the diffusion layer on the powder material, caused by an increase in the reaction surface of boron carbide. Then, when using the mixture and grinding it, there is a decrease in the thickness of the diffusion layer with a decrease in the amount of boron in the saturating mixture, which is caused by a decrease in the gas permeability of the mixture. A decrease in the supply of boron halides to the processed surface of the

metal powder causes a simultaneous decrease in both the proportion of the high-boron phase in the diffusion layer itself on the powder material and the microhardness of the diffusion layer (see Figure 7). Therefore, the main factor limiting the frequency of use of boron carbide is grinding and, accordingly, deterioration of the technological and physical-mechanical properties of the processed powder. Accordingly, it is advisable to use the saturating mixture without regeneration no more than 6-7 times. After that, the resulting small fractions are screened out with further use of the mixture. The effect of the activator on the results of diffusion processing of metal powder was studied. Sodium fluoride, aluminum fluoride and ammonium chloride were taken as activators (Figure 8).

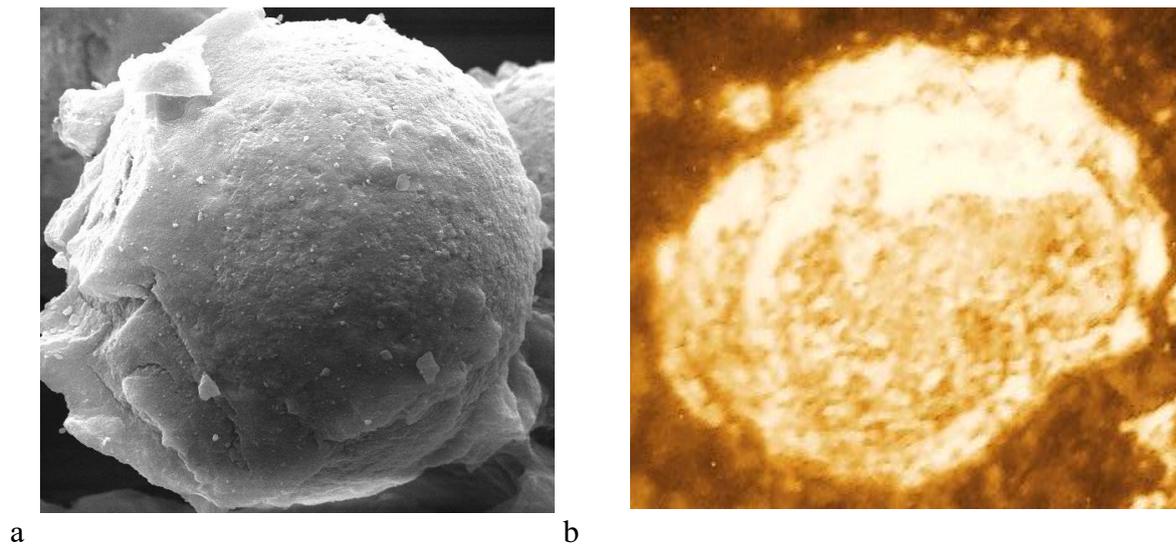


Figure 6. Appearance a) and microstructure b) of diffusion-alloyed NiCrAlY powder (x300)

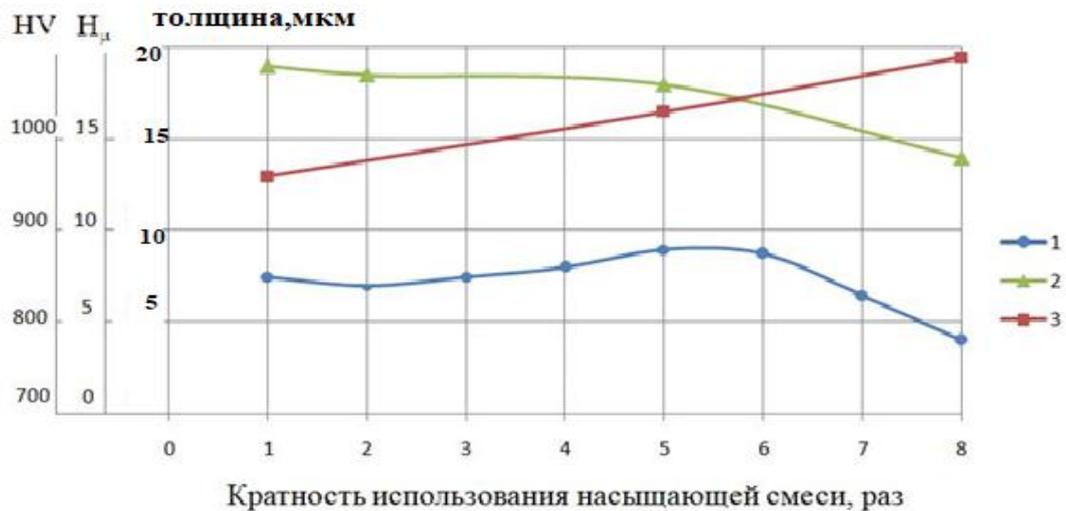


Figure 7. Effect of multiplicity when using a powder mixture on the thickness (1), microhardness of the boride layer on nickel-chromium-aluminum-yttrium powder (2) and on the hardness of the sprayed layer (3)

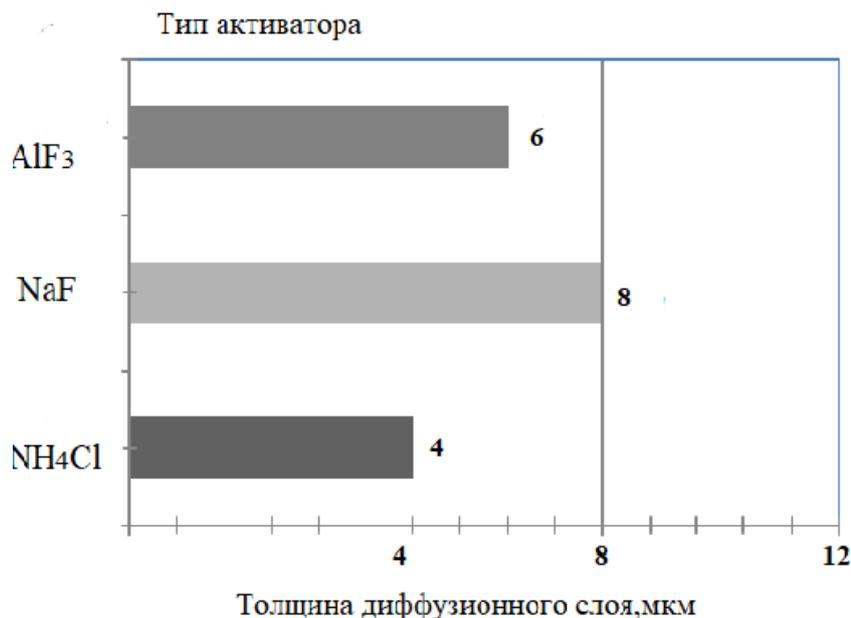


Figure 8. Effect of the type of activator on the thickness of the diffusion layer when boriding m-grain for 2 hours at a temperature of 950°C

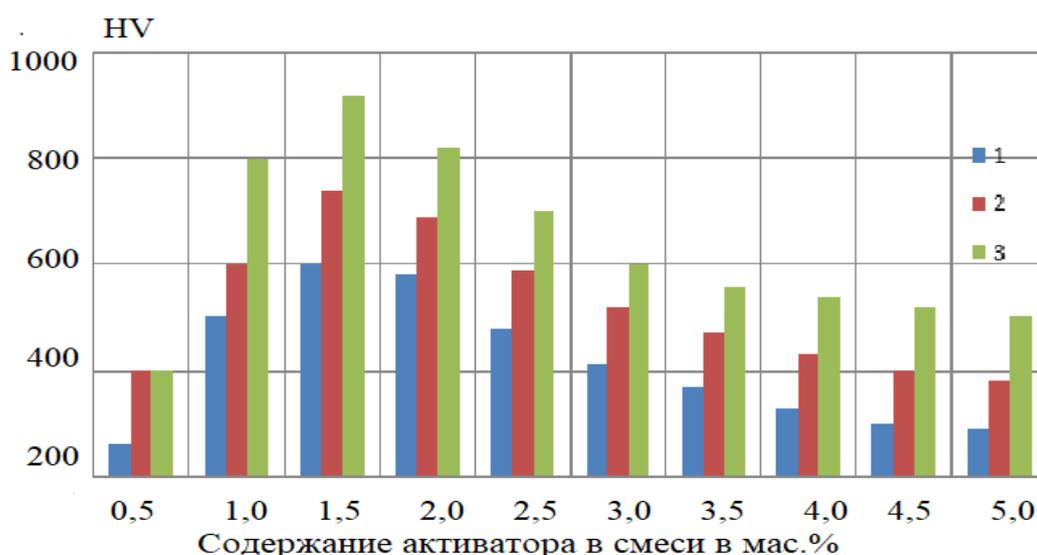


Figure 9. Effect of the activator type 1 – NH₄Cl; 2 – NaF; 3 – AlF₃, its amount in the mixture (b) on the hardness of the sprayed layer during boriding of m-roly for 2 hours at a temperature of 950°C

The best results were obtained when using sodium fluoride and aluminum fluoride as activators (Figure 9) in an amount of no more than 1-2%. The activator - ammonium chloride shows a good result in terms of layer thickness during diffusion treatment in the mixture, but has a number of significant drawbacks: the dispersion of boron carbide powder worsens and increases due to corrosion by chlorides, with repeated use of mixtures their gas permeability worsens, the surface of the metal powder is deformed, its fluidity is worse, and the tendency to corrosion increases upon contact with the atmosphere. The main reason for the increase in intensity when adding 1-2% of the activator of diffusion saturation of the powder is the pres-

ence of a sufficient amount of boron fluorates formed in the powder mixture, actively transporting boron to the saturated surface of the m-roll. In the absence of sodium fluoride in the mixture, B_2O_3 , contained in an amount of up to 3.5 wt.% in boron carbide, can play a significant role of the activator. The scheme of the installation for diffusion boriding is shown in Figure 10. In accordance with the previously conducted studies, we optimized the boriding duration, temperature conditions, the ratio of the components of the working mixture during boriding in a rotating container, and the rotation frequency of the container. Mixing of the components of the powder mixture is best carried out for 20-30 minutes in drum-type mixers at a rotation speed of 60-100 rpm. The optimal rotation frequency of the container n , ensuring maximum mixing of the working mixture during boriding of powders, was determined based on the source [13]. According to the calculation results using the dependence from the source, the value of n , consistent with the capabilities of the installation, should be 60-100 rpm. The prepared powder mixture is packed in a container. The container is sealed by backfilling with layers of boron carbide and silicon carbide. When heated at temperatures of 600-700°C, boron carbide reacts with oxidizing silicon carbide and creates a sintered layer of borosilicates sealing the container. The studies have shown that the rate of formation of diffusion layers at a temperature below 800°C is low to create the required properties in the powder (experiments were carried out in the range of 700-1000°C at 25°C and holding for 3-4 hours). Therefore, heat treatment was carried out at 850-1000 °C for 3-4 hours. Further increase in temperature is impractical, since there is a decrease in the significance for activation of cyclic deformation-recrystallization processes in the mobile working mixture during boriding. After the processing, the container was cooled, opened and the mixture was subjected to magnetic separation. The isolated diffusion-alloyed m-krol powder was used to obtain sprayed coatings, and the saturating medium was reused. The appearance of the obtained diffusion-alloyed powder material is shown in Figure 6, a. As can be seen from Figure 6, b in section, each powder particle is formed from a core and a diffusion layer of a certain thickness and phase composition. The thickness of the diffusion layer, its structure, phase, chemical composition for each type of powder material depend on the type of saturating mixture, process temperature and duration of diffusion treatment. It is clear that the technological properties of the obtained powder materials also depend on the parameters listed above.

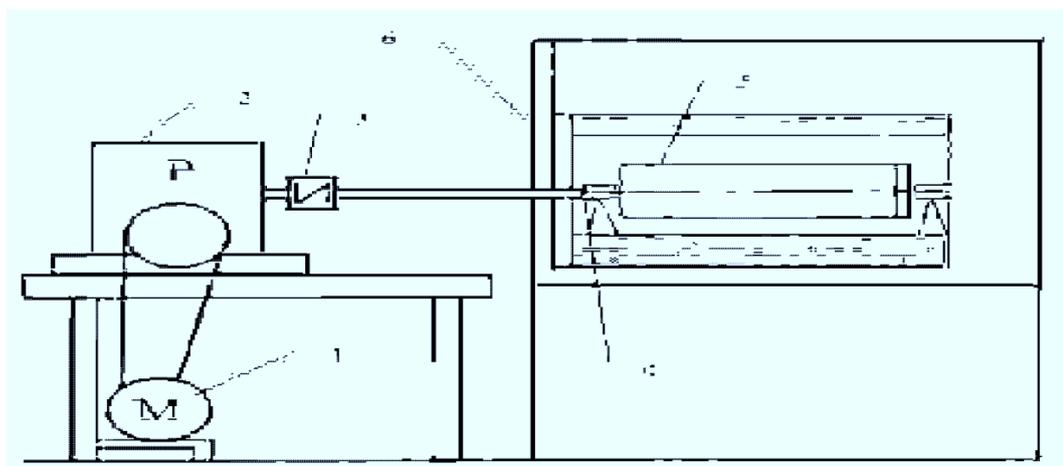


Figure 10. Scheme of the setup for diffusion borating of powders 1 – engine; 2 – reducer, variator; 3 – cardan coupling; 4 – supports; 5 – container; 6 – furnace

Concerning the ratio of components in the working mixture - to form thin-film ceramic shells with a thickness of about 8-10 μm (according to the accepted criterion) on the particles of the powder material, it is necessary to significantly reduce the proportion of the saturating medium. Experiments have shown that the ratio of the volumes of the saturated powder and the saturating medium (99% amorphous boron, 1% sodium fluoride) should be fixed at the level of 1 – 3. This composition of the working mixture was placed in a sealed container made of heat-resistant steel. The degree of filling the container with the powder mixture was selected taking into account the recommendations of the source [13] and was approximately 70%. Borating of powder materials was carried out at different durations (τ) with analytics of the change in the thickness of the diffusion shell. The results of the conducted research are presented in Table 1.

Table 1. Results of the study on the optimization of the boriding process

Composition of the powder material	Thickness of the diffusion shells, μm		
	$\tau = 2,0 \text{ h}$	$\tau = 3,0 \text{ h}$	$\tau = 4,0 \text{ h}$
Nickel-chromium-aluminum-yttrium	4,9	6,3	8,4
Note – The table provides average data on the thickness of the shells			

As can be seen from Table 1, the averaged data on the shell thickness indicate that the optimal duration of boriding is 4.0 h. With this duration, a thickness of 8.4 μm is achieved, which corresponds to the adopted optimization criterion. At the same time, metallographic analysis of the powder particle sections showed that there is an increase in the interval in which the shell thicknesses obtained in one boriding duration mode are located. For example, for a duration of 2.0 h, a change in thickness from 3.8 to 4.9 μm was observed. It should be noted that the lower limit of this interval does not correspond to the optimization criterion. Thus, a duration of 2.0 h does not ensure stable formation of a sufficient thickness of the cladding shells. Therefore, the optimal duration of boriding is finally accepted as 3-4 h.

3. Conclusions

The method and medium for diffusion alloying of M-roll powders have been selected, and technological recommendations for boriding nickel M-roll have been developed. Based on a number of advantages (simplicity, general availability, reliability of the technology, high stability of results, the possibility of repeated use of the saturating medium) for diffusion saturation of powders based on m-rolays in order to ensure high performance properties, the method of saturation in powder media of boron and silicon carbides was selected. It was found that from the point of view of ensuring the stability of the shell thickness, good fluidity and stability of the dispersion composition, the best is the ratio of the saturating medium to the saturable one in the range of 4:1, the ratio in the saturating medium B4C-SiC (40%:60%) with approximate equality of particle sizes and their size of 40-60 μm , and sodium fluoride in an amount of 1-1.5% is most appropriate as an activator. It was revealed that 6-7 times the use of the saturating mixture without regeneration ensures stable results. However, its further use leads to deterioration of the technological and physical and mechanical characteristics of the processed powder due to significant grinding of the boron carbide powder. Regeneration consists of screening out the fine fraction (smaller than 40 μm). The highest stability of results in terms of the diffusion layer thickness is provided by saturating media containing 40...80% B4C, 20...60% SiC with a content of saturable powder based on m-rabbits of 25...33%.

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