

On Nanomodification of Coating Obtained by Laser Cladding of Composite Powder 12NVK-01

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Abstract. The results of an experimental study of the effect of nanomodifying additives on the structure and mechanical properties of a multilayer coating during laser surfacing of a composite powder with a strengthening phase are presented. As a surfacing material, nickel powder 12NVK-01 with a strengthening phase of tungsten carbide was used, and as a modifying additive was a mixture of nanosized refractory powders of titanium nitride and yttrium oxide clad with iron and chromium. It is established that the deposited coating represents a complex system of phases formed during the melting and interaction of the chemical elements of the substrate and the melted powder mixture. The main component of the coating is the combination of nickel with iron and chromium of the type Ni₃(Fe,Cr). In the melting process, a partial decomposition of the strengthening phase occurs, depending on the concentration of the nanomodifier. In the case considered, the optimum amount of the modifying additive providing the maximum hardness and wear resistance increase of the composite coatings of the Ni-Cr-B-Si-Fe / WC system is 0.1% by mass of the refractory TiN + Y₂O₃ nanopowder additive in the composite material.

Introduction

One of the most promising methods of applying hardening coatings is laser surfacing using alloying (modifying) elements, as indicated by a large number of scientific papers in this field [1–10]. Laser welding has several advantages, which include the ability to make multilayer (additive) composite coatings with various thermophysical and mechanical properties, the possibility of introducing any elements and compositions into the surface layer of strengthened metal that leads to formation of new structures with virtually no analogues among known materials. At that, the small size of zone of the radiation thermal impact minimizes the warping and deformation of the processed products. The most acceptable from the viewpoint of saving alloying (modifying) materials is the application of slip coatings. This also makes it possible to create an optimal concentration of the alloying (modifying) element in the coating. To increase strength, contact endurance and resistance to wear, it is necessary to increase the hardness of the surface layer, which can be achieved, in particular, by laser deposition of nanostructured composite powders containing a strengthening phase and refractory nanoparticles.

Recently, specially prepared nanopowder compositions have been increasingly used to modify welded joints, as well as castings from steel and alloys. They have demonstrated effective influence on the strength and performance properties of metals [11–13].

The purpose of this work is to study the effect of nanomodifying additives on the structure and properties of a multilayer coating at laser surfacing of a composite powder 12NVK-01.

Materials and methods of research



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Nickel powder 12NVK-01 with a hardening phase of tungsten carbide (WC, 32% by weight) was used as a surfacing material, and a mixture of nanosized powders of titanium nitride and yttrium oxide, clad with chromium and iron, was used as a modifying additive. The chemical composition of the surfacing powder 12NVK-01 is presented in Table 1.

Table 1. Chemical composition of the surfacing powder, wt. %

Brand	C	B	Si	Cr	Fe	WC	Ni
12NWC-01	0.3	1.5	2.1	8.0	>3.4	32	the rest

Nickel self-fluxing powder alloy 12NVK-01, containing tungsten carbide, is effectively used for the application of wear and corrosion-resistant coatings [14]. The presence of silicon and boron in the alloy contributes to its self-fluxing and good wettability of the product surface by the alloy, and the presence of ~32% tungsten carbide makes it possible to increase the hardness and wear resistance of the deposited coating [15]. Cladding of refractory TiN and Y₂O₃ nanoparticles was carried out by processing them in centrifugal planetary mill AGO 2 in a powder mixture with chromium and iron for 3 minutes. Then, the powder composition with a nanomodifying additive made of TiN:Y₂O₃ = 1:1 was mixed for 2 minutes in a planetary mill. Analysis of the morphology and particle size of the composite surfacing powder 12NVK-01 and nanoscale particles TiN and Y₂O₃ was carried out by scanning and transmission electron microscopy (Figs. 1–3, respectively).

The phase composition of the deposited coatings was determined on diffractometer DRON-7 in CoK α radiation at accelerating voltage of 35 kV and current of 20 mA. The presented diffractograms were preliminarily processed using a special WinPLOTR software package [16]. The wear resistance of the deposited coatings was studied on 3D-profilometer "MICRO MEASURE 3D station" of French company STIL. The measurements were carried out by scheme "rotation of the sample with a stationary counter-piece". The load on the diamond cone was 5 N, the final number of revolutions of the sample was 2500. With micrometer system Micromesure System STIL (Science et. Techniques Industrielles de la Lumere, STILS. A, France), the friction forces were measured continuously, and, then, converted to absolute values of the coefficient of friction. At the end of the cutting process, the cross-sectional profile of the cutting groove was measured by a diamond counter-piece of surface of the deposited coatings with numerical determination of the cutting depth and the cross-sectional area of the groove.

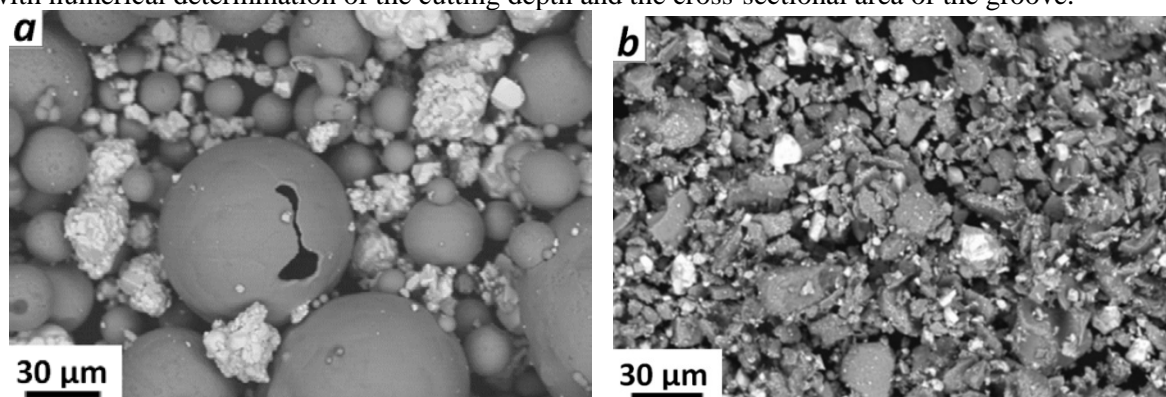


Fig. 1. Morphology of the base of the surfacing powder and aggregates of the strengthening phase before (a) and after (b) treatment in a planetary mill.

In the initial state, the shape of the nickel alloy particles is spherically symmetric, while the tungsten carbide particles have a crushed shape and are coagulated into aggregates (Fig. 1a). Processing in a planetary mill destroys the coagulated aggregates and particles of a nickel alloy, and the powder mixture gets substantially dispersed (Fig. 1b).

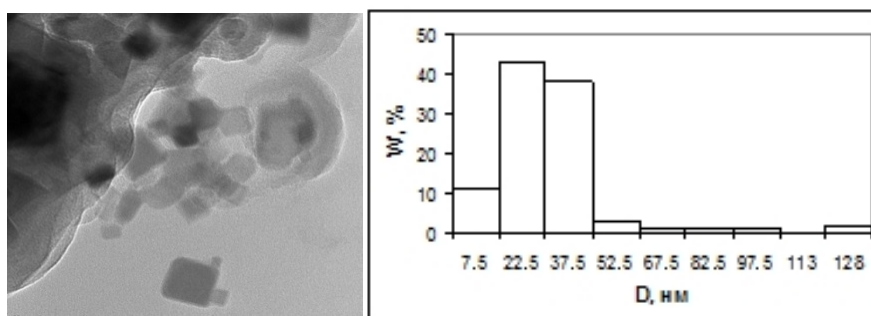


Fig. 2. General view of nanosized particles of titanium nitride TiN and their size distribution.

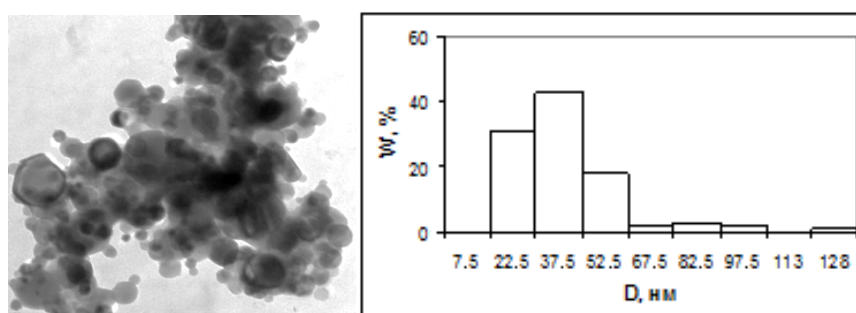


Fig.3. General view of nanosized yttrium oxide particles Y₂O₃ and their size distribution.

As can be seen from Figs. 2–3, the average size of TiN and Y₂O₃ nanoparticles is from 22.5 to 37.5 nm. The studies were carried out on plate-like samples of carbon steel. The surface of the samples was covered with a slip coating consisting of a composite surfacing powder and a mixture of TiN and Y₂O₃ nanoparticles. Zapon lacquer diluted with acetone was used as the binder. The experimental and control (without nanomodifying additive) samples were processed using a continuous CO₂ laser with power of 0.6–1.2 kW in a protective helium atmosphere at various laser beam velocities. The samples were cut in a cross-section. Then, they were subsequently ground on abrasive paper and polished using a 0.05 μm silicon oxide paste. The chromium-nickel steel was etched with a chemical solution containing HCl and HNO₃ in proportion 3:1 for 20–25 seconds. Microstructural studies were carried out using an optical (OM, Carl Zeiss Axio Observer Z1m) and a scanning electron microscope (SEM, Carl Zeiss EVO 50 XVP) equipped with a spectrometer for micro-X-ray analysis (MRSA, Oxford Instruments INCA X-ACT). Microhardness according to Vickers (Wolpert Group 420 MVD) was evaluated on metallographic samples. The load on the diamond indenter was 0.49 N, and the distance between the prints was 0.3 mm. The average value of the microhardness was evaluated over four measurements.

Results of the study

Some results of metallographic studies of the test samples are shown in Figs. 4–8. The formation of the structure and properties of the hardened coating deposited by continuous laser radiation depends on the chemical composition, thickness of the slip layer, power and speed of the laser beam. When welding a powder material containing a strengthening phase, it is important that the particles of this phase are uniformly distributed throughout the entire deposited layer.

Figure 4 shows a microphotograph of cross section of a test sample with fused layer, indicating a sufficiently uniform distribution of the hardening carbide phase over the cross section of the layer and a good (defect-free) fusion with the substrate without deep penetration and, therefore, without significant mixing of the surfacing metal with the substrate material.

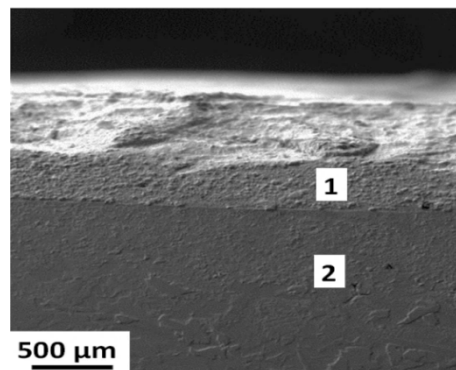


Fig. 4. General view of cross-section of a fused nickel alloy coating with hardening WC phase containing 0.1% titanium nitride and yttrium oxide nanoparticles; 1- coating, 2- substrate.

The addition of a nanomodifier has a significant effect on the evolution of the strengthening phase in the process of laser surfacing of a powder composition. This follows from analysis of microphotographs of the coatings cross-sections at various concentrations m_p of the introduced nanomodifying additives (Figure 5), fused using laser irradiation with power $W = 0.65$ kW and velocity of the laser beam movement $v = 0.3$ m/min, focal spot diameter of 2 mm and thickness of the applied slip layers of 0.2 mm (four layers).

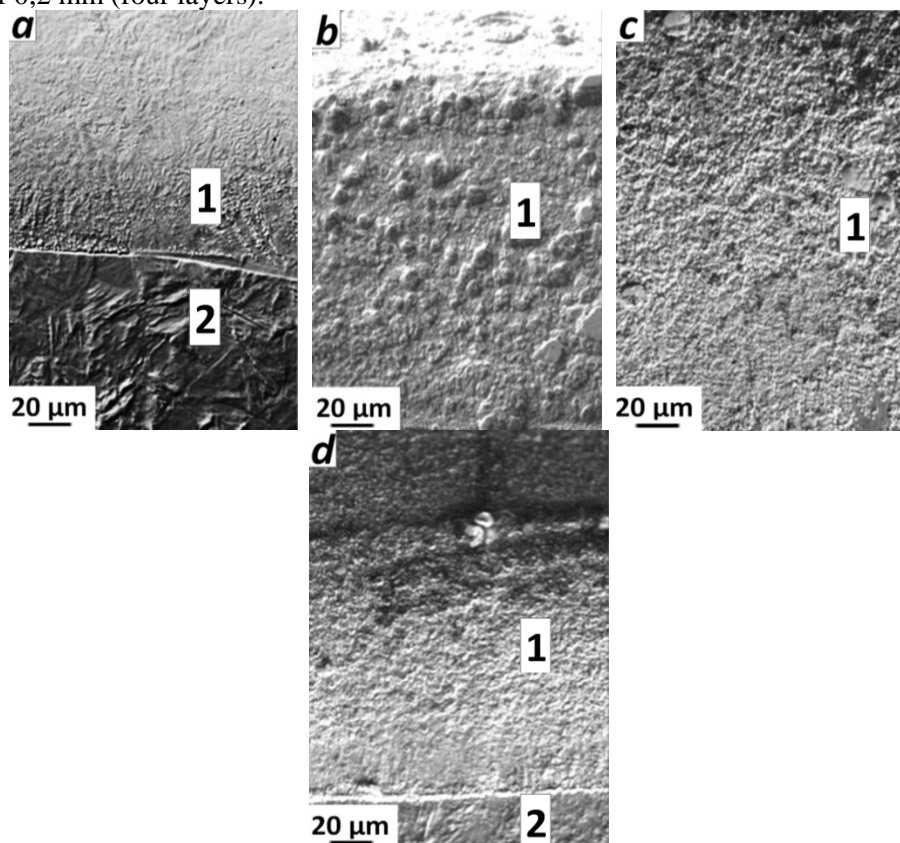


Fig. 5. Macrostructure of cross-sections of samples with deposited coatings containing different amounts of nanomodifying (NM) additives: (a) without NM, (b) 0.1% NM, (c) 0.2% NM, (d) 0.4% (% by weight); 1- coating, 2 - substrate.

The addition of a nanomodifier has a certain effect on the dispersion of the composite structure of the deposited coating (Fig. 5). The composite structure of the deposited coating without a nanomodifying additive has a dispersed structure formed in the form of cells based on individual tungsten carbide

particles in a nickel alloy matrix. The morphology of the surface of the deposited coating is characterized by a regular structure and individual spherical formations of tungsten carbide particles with a nickel alloy shell (Fig. 5a). With the introduction of nanomodifier in the amount of 0.1% by weight into the starting powder mixture, the formation of composite cells based on tungsten carbide particles with a wide range of dimensions, including the formation of large cells (Fig. 5b), results in the coating structure. The latter means either the preservation of large particles of tungsten carbide upon surfacing the coating, followed by the formation of large composite cells, or the formation of composite cells based on conglomerates of titanium carbide particles. With an increase in the content of the nano-sized modifier in the initial powder mixture to 0.2% and then to 0.4%, the average dimension of the composite cells decreases, and a composite structure of the coating is regular in size and distribution of the individual cells. In this case, the dimension of the cells exceeds the corresponding dimension in the coating without a nanomodifying additive, but is noticeably smaller in comparison with the coating containing 0.1% of the modifying additive (Fig. 5c, d). The morphology of the coating surface with 0.2 and 0.4% nanomodifier clearly reflects their cellular structure with the central part of single particles of tungsten carbide.

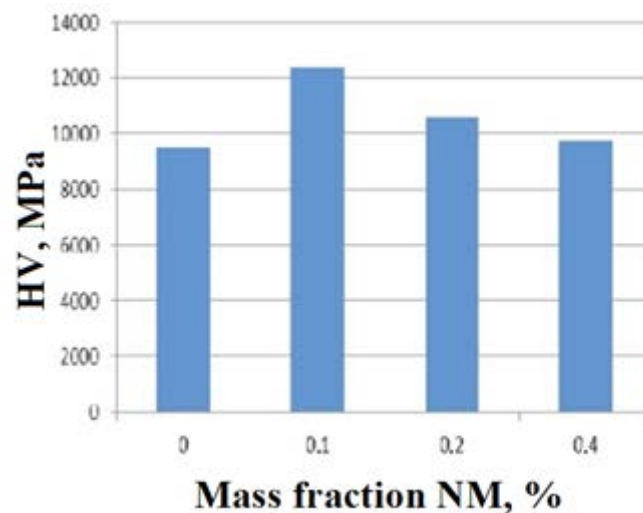


Fig.6. Diagram of the change in microhardness of the deposited coating, depending on the mass fraction of NM.

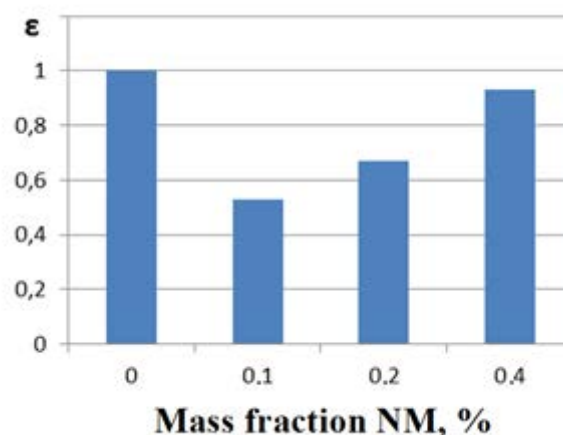


Fig. 7. Relative depth of the groove of cutting by a diamond counter-piece on surface of the coating for various contents of NM additives in the coating.

Fig. 6, Fig. 7 shows diagrams of microhardness and relative depths of the cutting groove $\varepsilon = h_i / h_0$ depending on the mass fraction of the nanomodifying additive, where h_i is the depth of the cut of modified coating, and h_0 is the depth of the coating cut without nanomodifier.

As follows from the diagram above, the minimum wear of the coating (the maximum wear resistance) is observed when the content of NM is 0.1% of the coating, exceeding the wear resistance of the coating without NM additive by almost 2 times, which agrees well with the microhardness dependence shown in Fig.6.

Modeling the profile of the diffraction curve in this program makes it possible to identify even minor peaks against the background of noise, related to the chemical compounds present in the material in low concentrations, such as TiN. In general, the nature of the diffractograms is very complicated. The welded coating is a mixture of phases formed as a result of the redistribution of chemical elements between the steel substrate and the melted.

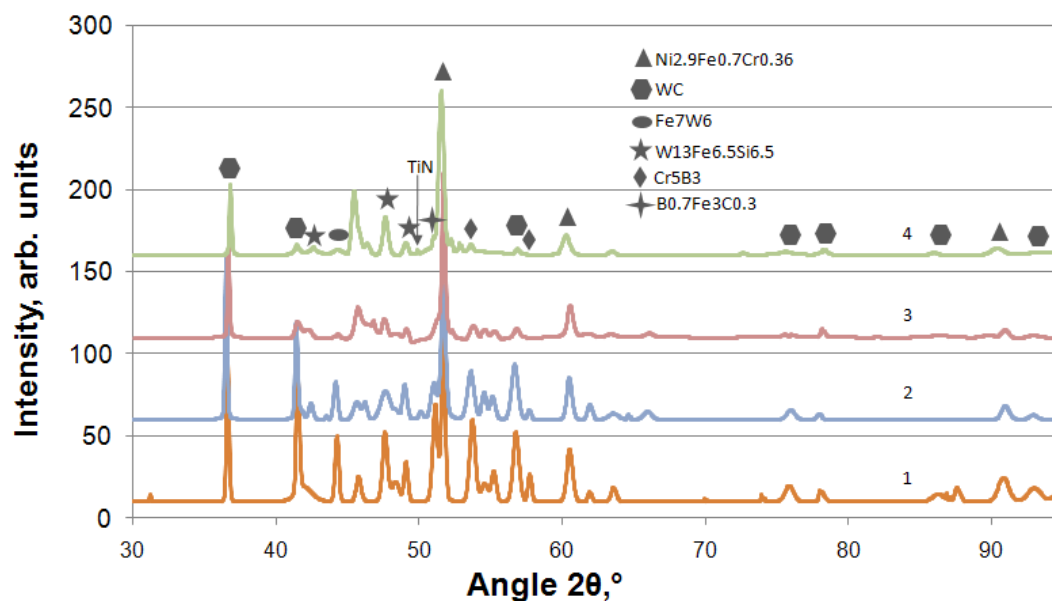


Fig. 8. Diffractograms of the deposited coatings containing different amounts of NM: (1) 0.0%, (2) 0.1%, (3) 0.2%, (4) 0.4% (% by weight)

The main component of the coating is a combination of nickel with iron and chromium of type $\text{Ni}_3(\text{Fe}, \text{Cr})$. It is not pure nichrome because of a small displacement of the peaks due to introduction of iron into the lattice simultaneously with chromium. The peaks of tungsten carbide, initially present in the deposited powder, are very well identified. However, it should be noted that the relative intensities of its X-ray peaks from diffractogram 1 to diffractogram 4 have been reduced consecutively with the exception of diffractogram 2 at $2\theta = 36.25^\circ$, where its value is the largest in comparison with the others. At the same time, the relative intensity of the peak of $\text{Ni}_3(\text{Fe}, \text{Cr})$ phase at $2\theta = 51.25^\circ$ of diffractogram 2 has the smallest value here compared with the corresponding peak in the remaining diffractograms. It should be noted here that in the reference diffraction pattern of tungsten carbide, peak $\{001\}$ at 36.72° is not the most intense, and, therefore, in this case it is necessary to take into account not only this peak but also all the other most intense peaks contributing the most to formation of the common profile of diffractograms. In particular, the most intense peaks are $\{100\}$ at 41.62° and $\{101\}$ at 56.69° . Their behavior in the experimental diffractograms is completely synchronous, which allows us to state that the tungsten carbide during coating partially dissolves in the melt of the base metal, and the intensity of the peak at $2\theta = 36.72^\circ$ can increase due to the formation of a new chemical compound, possibly containing a small amount of yttrium. This question requires more detailed analysis using the methods of electron microscopy.

The dissolution of tungsten carbide in the melt of powder surfacing releases tungsten atoms forming tungsten compounds with iron W_7Fe_6 and with silicon $W_{13}Fe_{6.5}Si_{6.5}$. The diffraction peaks of these compounds are characterized by a small intensity, which increases in direct proportion with decrease in the intensity of tungsten carbide peaks. The unidentified peak at 45.76° apparently refers to intermediate compounds based on iron with a low content of chromium and nickel. The peak of TiN is manifested in the diffractograms only when the concentration of NM in the coating is equal to 0.4%.

Conclusions

1. Introduction to the powder mixture based on 12NWK-01 for laser deposition of nanoparticle coatings ($TiN + Y_2O_3$) modifies the structure of the deposited coating, forming in the coatings a complex of composite cells consisting of tungsten carbide particles in a nickel alloy matrix, the size of which depends on amount of nanomodifier in the coating.
2. The phase state of the deposited coating modified by nanoparticles ($TiN + Y_2O_3$) is formed on the basis of a nickel-iron and chromium compound of the $Ni_3(Fe,Cr)$ type with a sufficiently uniform distribution of the basic hardening coating of the phase - WC tungsten carbide particles.
3. In accordance with the change in the dispersion of the composite structure and the phase composition of the deposited coating, when a nanosized modifier is introduced into its composition, the key properties of the coating change. Its microhardness and wear resistance reach a maximum value at a content of nanomodifier ($TiN + Y_2O_3$) in an amount of 0.1% by weight.

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