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Structural and technological formation of surface nanostructured Ti-Ni-Mo layers by high-speed gas-flame spraying

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Abstract. The article covers a complex method of forming surface-modified layers using materials with shape memory effect (SME) based on TiNiMo including pre-grinding and mechanical activation of the coating material, high-speed gas-flame spraying of Ni adhesive layer and subsequent TiNiMo spraying with molybdenum content up to 2%, thermal and thermomechanical processing in a single technological cycle. This allowed forming nanostructured surface layers with a high level of functional mechanical and performance properties. We defined control parameters of surface steel modification using material with shape memory effect based on TiNiMo, which monitor the structural material state, both at the stage of spraying, and during subsequent combined treatment, which allows affecting purposefully on the functional properties of the SME surface layer. Test results of samples before coating and after surface modification with TiNiMo in the seawater indicate that surface modification brings to a slower damage accumulation and to increase of steel J91171 endurance limit in seawater by 45%. Based on complex metallophysical research of surface layers we obtained new data about nano-sized composition “steel - Ni - TiNiMo”.

1 Introduction

Currently, one of the key tasks in mechanical engineering is to create new structural and functional materials and technologies for their production. The most prominent representative of both structural and functional materials are alloys with shape memory effect (SME). The urgency to use alloys with shape memory effect has been steadily increasing due to extremely broad and non-trivial features: unique effects of thermo-mechanical memory, high strength properties, thermo-mechanical and thermal cycling reliability and durability, heat resistance and corrosion resistance. The most studied and widely used in various engineering applications is TiNi alloy with shape memory effect, which is the subject of many research works and whose possibilities have almost been exhausted [1-4].

It is known that alloying TiNi with different elements of the periodic system gives possibility to regulate with the help of shape memory properties and martensitic transformation temperature, which is promising for their successful and diverse applications [5]. Among the alloys based on nickel-titanium that have been doped with the third component a special place is given to TiNiMo alloys [6-8]. TiNi alloying with molybdenum in the amount of up to 2% causes noticeable change in the nature and sequence of martensitic transformations. By varying the concentration of molybdenum up to 2 at.%, it is possible to reduce the characteristic temperatures of direct and reverse martensitic transformations or at a specific ratio of components – to reduce the temperature of the direct transformation M_s, M_f, and, on the contrary, to raise the temperature of the reverse transformation A_s, A_f. Such "change" in temperature ranges of direct and reverse martensitic transformations is of great practical importance, as it allows to create materials with predetermined intervals of forming and controllable physical and mechanical properties. Moreover, alloying with Mo greatly improves technological characteristics of TiNi based alloys, quality of rolling, drawing and extrusion. Effective influence of Mo alloying in combination with TiNi on physical and mechanical properties and parameters of forming with shape memory effect, as well as superelasticity are connected with equiprobable allocation of molybdenum atoms on titanium sublattice and nickel sublattice in B2 structure of TiNi compound [9]. For a long time it was not clear both from scientific and technological points of view if the martensitic transformation stress depends on the grain size. In recent years, the influence of nanostructuring on SME material properties is extensively discussed [10]. Certain results are achieved both in the production of massive nanomaterials, and in the formation of nanostructured surface layers [11]. Resulted effect of nanostructuring on the properties of materials with SME suggests that nanostructuring alloys with SME, and, consequently, the surface layers made of materials with SME will enhance the results with a view to their practical use [10-12].

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The aim of this work is to develop the formation technology of nanostructured surface layers using material with SME based on TiNiMo by high-speed gas-flame spraying of mechanically activated powder in a protective environment to enhance performance properties and expand functionality.

2 Materials and formation technology of the surface layers

The formation of nanostructured states both in the bulk and on the surface is achieved in various combined methods of treatment in high-energy impacts. At the same time, the principle of synergies is implemented in combined methods, which manifests itself in new high-quality effects in combination of different kinetic processes. Grinding and mechanical activation of powders for surface modification is exactly this combined process [10]. One of the effective ways to produce finely-dispersed materials in active state is processing in attritors and ball mills.

In this work, mechanical activation was carried out in an attritor with the following parameters: the working chamber with volume of 0.5L, stirrer speed 600-1200 min^{-1}, diameter of steel balls was 6 mm, and a ball mill GEFEST - 2 (AGO-2U) at drum speed of 800 - 2220 min^{-1}, the carrier speed was 600-1090 min^{-1}, steel balls with diameter of 6 mm and operating time was 2-8 min.

Powder PN52T45M3 was used as a material for mechanical activation.

To implement the technology of surface modification we used an upgraded universal vacuum system for high-speed gas-flame spraying GLC-720. The main feature of high-speed gas-flame spraying (HSGFS) in vacuum (inert environment) is the possibility to use ion cleaning in the chamber, followed by deposition. This significantly improves coating adhesion to the substrate.

The grain size of PN52T45M3 powder is 35-40 microns. The study of particles' appearance showed that they have a shape of warped perforated flakes. Thanks to these structural features, powders PN52T45M3, during bumping-down, have a bipolar structure with very small intraparticle and large interparticle pores. Studies have shown that the initial size of the particles has a significant influence on the properties of the layer formed.

The chemical composition of the powder PN52T45M3 presented in Table 1.

Table 1. Chemical composition of the powder PN52T45M3, wt. %

PN52T45M3	Ni	Ti	Mo	C	Ca	N	H
	51,88	44,91	2,92	0,07	0,09	0,07	0,06

3 Discussion of the study results

During mechanical activation the powder particles take the form of flat discs of the following sizes: powder PN52T45M3 has discs dimensions of 0,8 ÷ 8 micron (Figure 1).

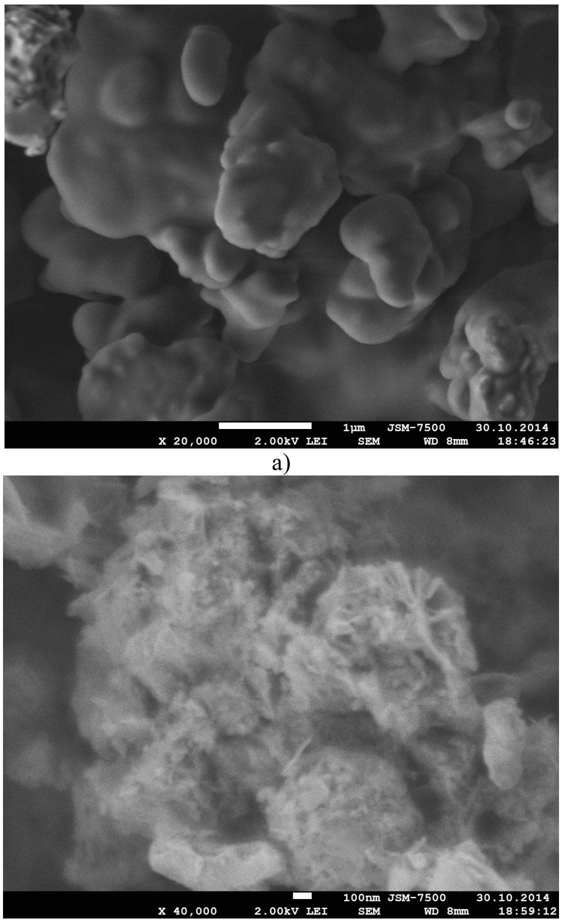


Figure 1. Powder PN52T45M3 was crushed and mechanically activated in the attritor GEFEST-2 for 25 minutes: a) × 20 000; b) × 40000

As a result of mechanical activation in local powder microvolumes we get internal stress, whose relaxation depends on the material properties and loading conditions. According to existing theories in mechanochemistry, the initiation of mechanochemical transformations is provided by heat generated by the processing of powders [13], by the energy of dislocations during plastic deformation, by release of elastic energy stored in the solid body, by presence of numerous interfaces. The analysis of TiNiMo coating structure, before and after mechanical activation has shown that preliminary mechanical activation leads to significant improvement in coating structure, decrease of porosity and increase of adhesion. This is probably due to the formation of defects in the process of mechanical activation, whose energy is released during high-speed gas-flame spraying. This leads to better melting of particles, to forming of almost monolithic structure with lower porosity and to increase of mechanical properties of the coatings.

Severe plastic deformation during mechanical activation of the powder leads to temperature increase and the formation of numerous defects, which are the centers of nanograins formation. After each contact with the working body the powder particle is soaked out (we used gasoline as inert environment, attritor camera was cooled with water). Subsequent contact with the working body brings to a further nanograins formation and lasts as long as either the whole particle acquires nanocrystalline structure or nanograins reach a critical size where the further plastic deformation is impossible. Given that the processed alloys with shape memory effect are extensively reinforcing, their sharp cooling in liquid environment results in increased brittleness and further refinement.

Figure 2 shows dependence of an average particle size of PN52T45M3 powder on mechanical activation time, which was obtained from the statistical processing of the experimental data in a medium SPSS Statistica 10.0.

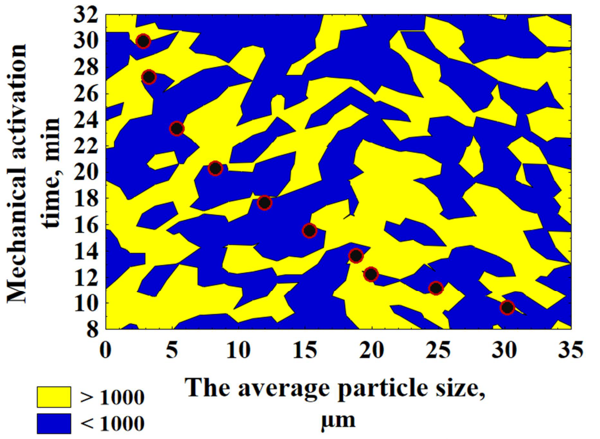


Figure 2. Influence of mechanical activation time on the particle size of PN52T45M3 powder. Activation was performed in a ball mill GEFEST 2: Drum speed was 1000 rev/min

An important step in surface modification technology is to prepare the surface. Before high-speed gas-flame spraying we cleaned the surfaces of steel samples from dirt, performed blasting followed by etching with 15-20% solution of HNO3. Then we sprayed mechanically activated nickel powder (NP-1). We obtained the intermediate Ni sublayer, with thickness of 100 microns. Ni sublayer is a binding matrix between steel and TiNiMo coating. The thickness of the modified layer is 0.6 mm TiNiMo and has three specific areas: a uniform TiNiMo layer, transition layer (~ 100um), and base metal - steel J91171.

As a result of technological process we used the algorithmic planning and statistical processing at all stages. The solution of optimization problem and experience of previous studies [14, 15] allowed to recommend the following technological modes of high-speed gas-flame spraying in protective environment: propane consumption – 60-85 l/min, oxygen consumption – 120-160 l/min, gas flow rate (argon) – 40-50 l/min, spraying distance – 200-300 mm, spraying angle – 70-90°, torch travel speed – 1-1.5 m/min, the speed of the coated parts – 800-1000 rev/min, the residual pressure of argon in the chamber – 0.8 Pa (Figure 3). These modes define such coating characteristics as adhesion and cohesive strength, level of residual stress, porosity, structure and thickness of the coated layer.

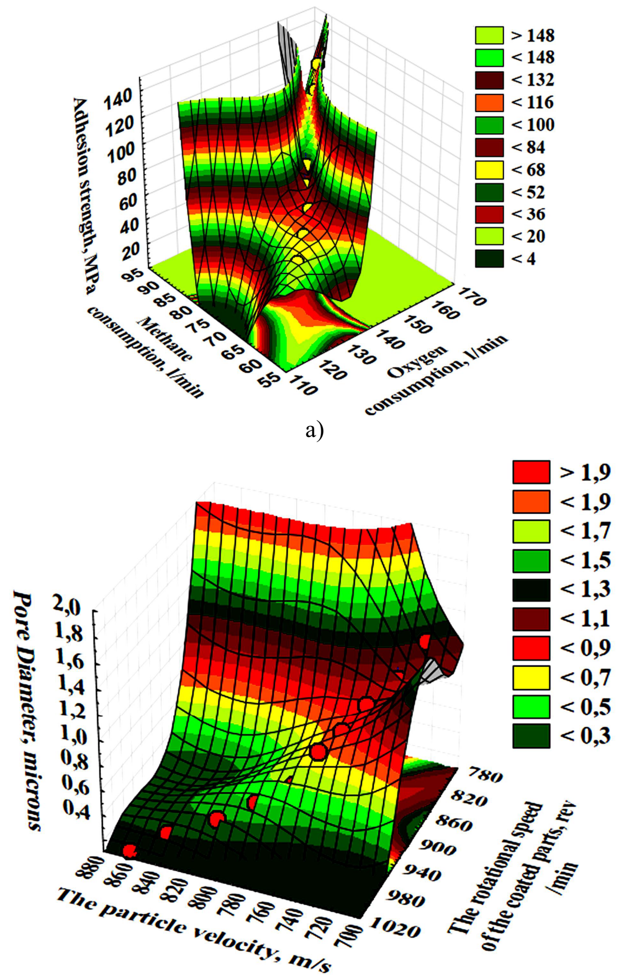


Figure 3. Influence of combustible gases composition on the adhesive strength of the TiNiMo coating to the substrate - a); impact of powder particles velocity and coated part rotation speed on pore size - b)

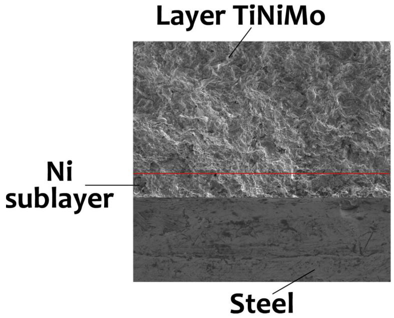
Interconnection of coating adhesion with the substrate and pore diameter with technological parameters of spraying process (oxygen consumption, methane consumption, the speed of powder particles, the rotation speed of the coated parts) is described by equations (1) and (2), which were obtained by the experimental data in the program Statistica 10.0.

$$\sigma_{adh} = 1525{,}1414 - 66{,}4563 \cdot K + 85{,}0437 \cdot M + 0{,}6724 \cdot K^2 - 1{,}6359 \cdot K \cdot M + 0{,}9741 \cdot M^2 \quad (1)$$

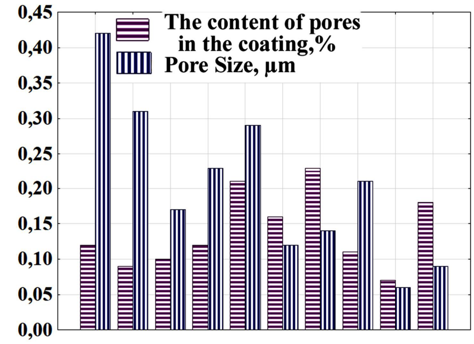
$$d = 12{,}5326 - 0{,}0509 \cdot v + 0{,}0233 \cdot n + 6{,}4774E - 5 \cdot v^2 - 5{,}6852E - 5 \cdot v \cdot n + 9{,}0721E - 6 \cdot n^2, \quad (2)$$

where K - the oxygen , l/min; M - methane consumption, l/min; v - velocity of the particles in m/s;
n - rotational speed of the coated parts rev/min.

Macroanalysis of TiNiMo surface layers, obtained according to a proven technology have shown that the coating structure is sufficiently dense with a minimum pore size (Figure 4a). Figure 4,b is a histogram of pore size distribution and their percentage in the TiNiMo coating. The interface between the coating and the substrate is without any visible cracks.



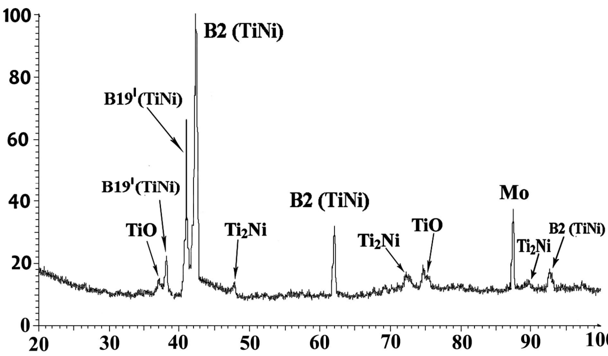
a)



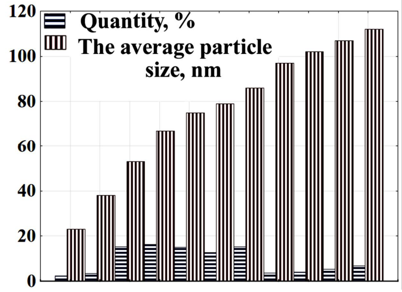
b)

Figure 4. The TiNiMo surface layers after high-speed gas-flame spraying in protective environment on steel J91171, × 300 - (a); distribution of pores in the coating and their percentage - (b)

At room temperature, the main structural component of the TiNiMo surface layer is austenitic B2-phase with cubic lattice, martensite B19' phase with monoclinic lattice, Ti_2Ni phase with a cubic lattice, Mo phase with a cubic lattice. We also found a small amount of titanium oxide – less than 1% in the coating (Figure 5a).



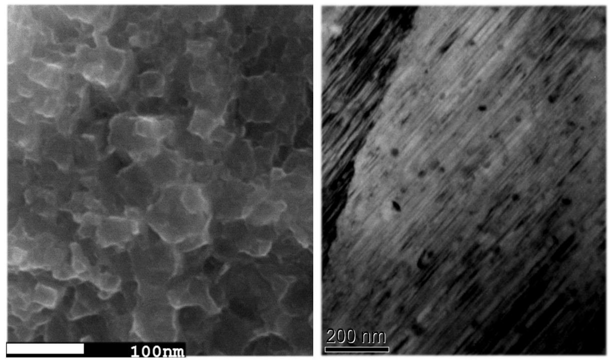
a)



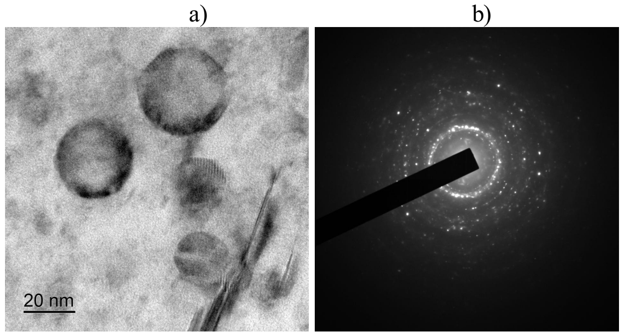
b)

Figure 5. The X-ray pattern of TiNiMo coating, obtained by high-speed gas-flame spraying in the vacuum of mechanically activated powder, δ = 1 mm a); distribution of the average grains size and their percentage in the TiNiMo coating - b)

As shown by metallographic analysis, the structure of TiNiMo mechanically activated powder formed by high-speed gas-flame spraying in a protective environment has extremely weak etchability by conventional reagents due to the strong grain refinement caused by high speed collisions of the particles with the substrate and high speed cooling. The coating structure has a grain size of 20-120 nm (Figure 6). Figure 5b shows the experimental results of the grains size and their percentage in the TiNiMo coating, the program Statistica 10.0, derived from VideoTest-Structure 4.0.



a) b)



c) d)

Figure 6. The microstructure of the TiNiMo coating, received high-speed gas-flame spraying of mechanically activated powder: B2 austenite structure (phase) layer - a) × 70 000; martensite B19 'structure (phase) layer with inclusions of Ti_2Ni phase - b) × 100 000; TiO titanium oxides - c) × 100 000; micro electron diffraction of TiNiMo layer - (d)

The study of functional and mechanical properties of J91171 steel samples with TiNiMo coating was carried out in test cycle on multi-cycle fatigue in the curve with rotation under the effect of sea water on the device MUI-6000. Test results of uncoated samples and after TiNiMo surface modification in seawater (Figure 7) show that the surface modification slows down the damage accumulation and increases the endurance limit of steel J91171 in seawater by 45%. Pseudoelasticity effect is the reason of increased durability of the surface layer containing material with shape memory effect based on TiNiMo under cyclic loading.

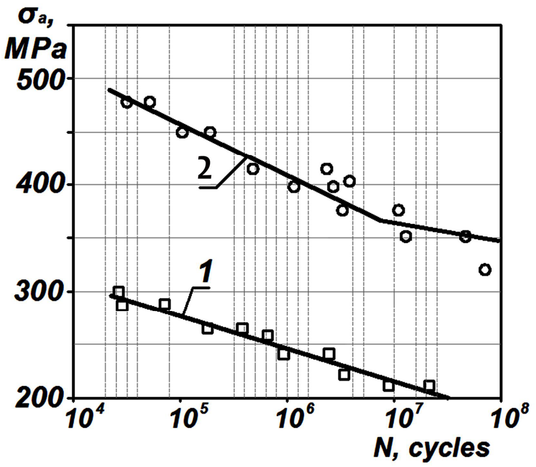


Figure 7. Cycle fatigue curves of steel J91171 in seawater: uncoated (1); after surface modification with TiNiMo - (2)

Increase in durability of steel with TiNiMo alloy surface modification is explained by the special mechanism of deformation. At comparatively low cycle stress the dominant mechanism of deformation in the surface layer is the mechanism, where at partial unloading of the sample the plastic deformation reduces significantly. Meanwhile partial "healing" of defects may take place, which is common for materials with shape memory effect. The mechanism of "healing" is the change of the stress field near microconcentrators. This causes either consistent reorientation of the martensite stress or the reverse transformation and emergence of martensite in a new place. Thus the structure adapts to external influence, preventing cracks.

In terms of the metal structure the fatigue strength is determined primarily by the energy required for crack initiation, and the speed of its spread. A high-speed gas-flame spraying in protective environment, as a means of surface layer modifying, effects, primarily, on the microcracks process. The mechanism of this effect, is probably related both to the nanostructuring of the surface layer caused by the peculiarities of the formation technological process (rapid heating 10^{-3} - 10^{-4}s and more rapid cooling on the substrate 10^{-3} - 10^{-6}s) and by the peculiarities of chemical and phase composition providing manifestation of SME. Experimental studies of the samples with TiNiMo surface layer confirmed high corrosion resistance in sea water and imitating solutions.

4 Conclusion

Experimental studies have shown the use of mechanically activated powders allows us to create an effective technology of sprayed material, which produces nanostructural three-based TiNiMo coatings by means of high-speed gas-flame spraying in a protective environment, with an average grain size of 20-120 nm. The developed high-speed gas-flame spraying technology has allowed to form TiNiMo surface layers, whose chemical and phase composition corresponds to SME. It is determined that at high-speed gas-flame spraying of mechanically activated material with shape memory effect based on TiNiMo in protective environment the nanoscale structure is formed, causing the increase of the surface layer quality: density of coating increases (of the pores, less than 1%), the strength of the coating adhesion to the substrate increases (up to 110-120 MPa). We determined the control parameters of surface modification for using steel material with shape memory effect based on TiNiMo. These parameters monitor the material structural state, both at the stage of spraying, and in subsequent combined treatment, which allows purposefully affect the functional properties of the surface layer with SME. Test results of samples before coating and after surface modification with TiNiMo in seawater indicate that surface modification brings to slower damage accumulation and to increase of steel J91171 endurance limit in seawater by 45%.

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