

# Structure and functional properties of TiNiZr surface layers obtained by high-velocity oxygen fuel spraying

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**Abstract.** The authors studied a complex method of surface modification of steels for materials with shape memory effect (SME) Ti-Ni-Zr with a high-velocity oxygen-fuel spraying (HVOF) of mechanically activated (MA) powder in a protective medium. We assessed the functional properties and X-ray diffraction studies, which showed that the formation of surface layers according to the developed technology ensures the manifestation of the shape memory effect.

## 1. Introduction

The intermetallide based on nickel alumina NiAl, which has a high-temperature shape memory effect (martensitic transformation temperatures for NiAl SME alloys can reach 1000 K) is widely known and differs by the formation of several martensite variations with different structures [1]. The alloy with shape memory effect of TiNiZr is less well known. Partial replacement of titanium with zirconium increases the temperatures of martensitic transformations by more than 400 K. Thus, SME alloy Ti-Ni-Zr has a high-temperature shape memory effect [2], which has higher strength properties than NiAl alloy and can be used in various industries. Functional alloys with shape memory effect have unique applications [3], but their high cost limits their use in engineering. Efficiency and economic feasibility of using shape-memory alloys in various engineering industries can be achieved both by doping with the third component and by forming multifunctional composite surface layers of multicomponent materials with shape memory effect [4–7]. One of such composition is "steel – a layer with the shape memory effect on the basis of Ti-Ni-Zr", which is formed by the high-velocity oxygen-fuel spraying of the mechanically activated powder Ni<sub>47</sub>Ti<sub>26</sub>Zr<sub>27</sub>. This composition was studied in this article.

## 2. Mechanical activation

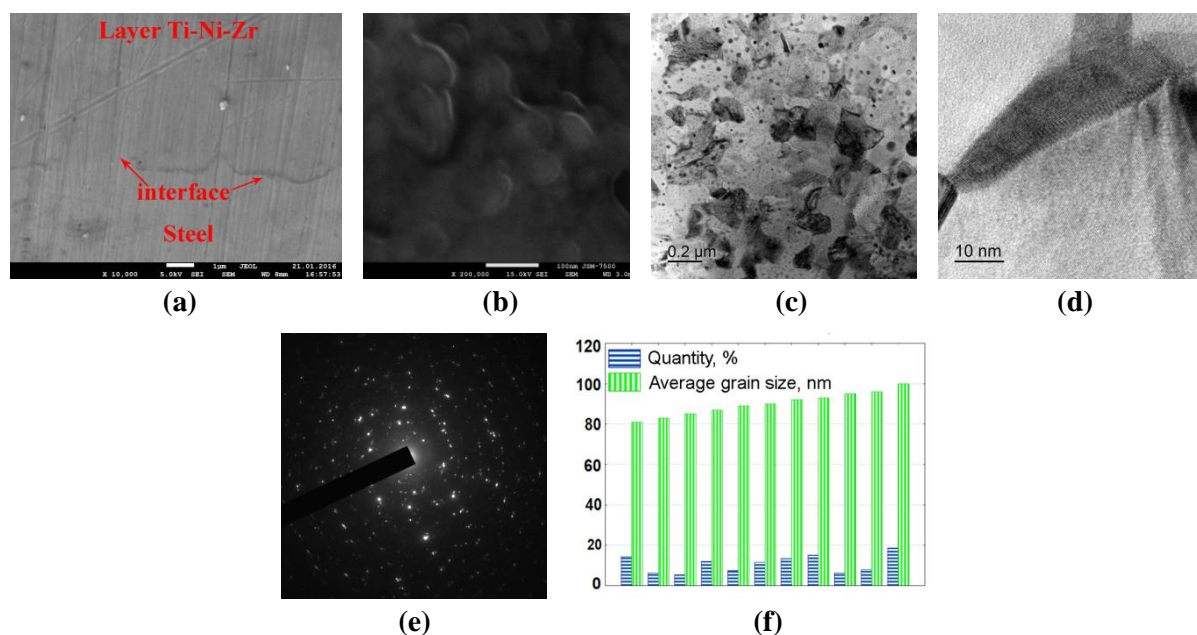
The surface layers were formed by high-velocity oxygen-fuel spraying of mechanically activated powder made of materials with shape memory effect on the basis of Ni<sub>47</sub>Ti<sub>26</sub>Zr<sub>27</sub> on the upgraded GLC-720 aggregate. The coatings were applied in argon onto steel 321. A ball mill GEFEST-2 (AGO-2U) with the following parameters was used for mechanical activation and grinding of the powder Ni<sub>47</sub>Ti<sub>26</sub>Zr<sub>27</sub>: drum rotation frequency 1200 min<sup>-1</sup>, rotational speed of the carrier 900 min<sup>-1</sup>, diameter of steel balls 6 mm, operating time 10–30 min. We used mechanically activated powder Ni<sub>47</sub>Ti<sub>26</sub>Zr<sub>27</sub> for the application of coatings. The size of the fractions was 1–10 μm, the powder was mainly in the B2 phase (~70 %).



The aim of this work is to study the structure and functional properties of the composition "steel - layer with the shape memory effect on the basis of Ti-Ni-Zr" obtained by high-velocity oxygen-fuel spraying of a mechanically activated powder in a protective medium.

### 3. Investigation of structure

Macro- and microanalysis of Ti-Ni-Zr alloy surface layers obtained by the developed technology showed that the layer structure is sufficiently dense. The boundary between the coating and the substrate has no visible defects (figure 1(a)). The Ti-Ni-Zr layer has a thickness of 1 mm. When particles of a powder pass through an oxygen-fuel jet, they heat up, melt, and, upon impact against the substrate, solidify in the form of deformed disks with a diameter of 20–35  $\mu\text{m}$ , and thickness of 5–20  $\mu\text{m}$ . The grain size in the coating obtained by high-velocity oxygen-fuel spraying in a protective medium (argon medium) is 80 to 100 nm (figure 1(b)–(d)).

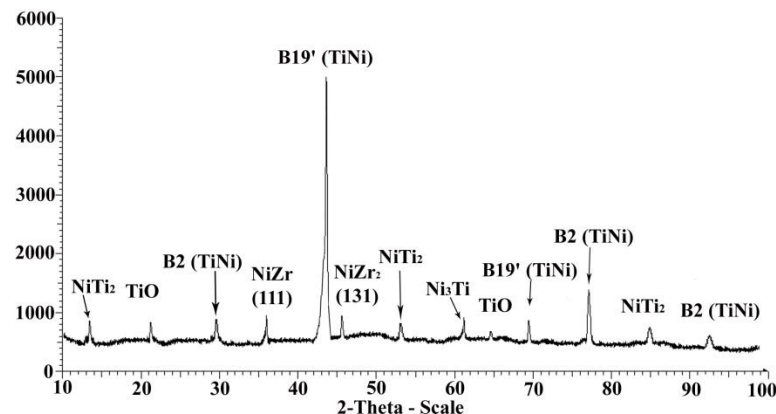


**Figure 1.** The microstructure of the Ti-Ni-Zr coating obtained by HVOF in a protective medium  $\times 10\,000$  (a); austenite structure  $\times 200\,000$  (b),  $\times 120\,000$  (c); tweed electron-microscopic contrast  $\times 150\,000$  (d); micro X-ray diffraction pattern of the coating (e); dependence of the average grain size on its percentage (f).

The dependence of the average grain size on its percentage is presented in figure 1(e). The microhardness of the Ti-Ni-Zr layer varies within  $H_{\mu} = 9.5\text{--}12.7$  GPa. The X-ray diffraction analysis showed that at room temperature the initial phase state of the Ti-Ni-Zr layer, after the HVOF of the mechanically activated powder in the protective medium (argon), is B19 martensite phases with monoclinic lattice, austenite B2 phases with a cubic lattice, intermetallic phases  $\text{Ni}_3\text{Ti}$ ,  $\text{Ti}_2\text{Ni}$ ,  $\text{NiZr}$ ,  $\text{NiZr}_2$ , with a cubic and hexagonal lattice, and a small amount of titanium oxide ( $\text{TiO}$ ), less than 2 % (figure 2).

### 4. Investigation of functional properties

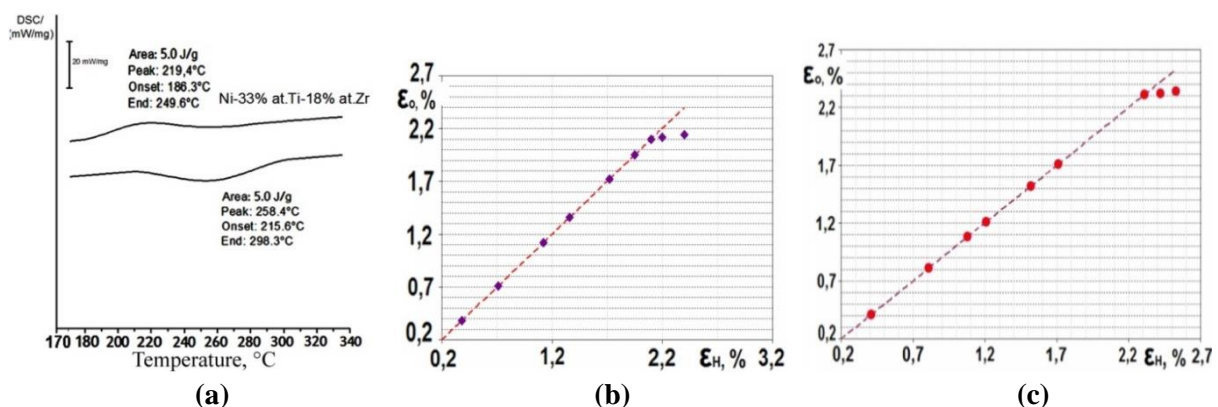
HVOF of SME coatings is a multi-stage process, at each stage of which parameters of functional-mechanical properties are improved. One of these stages is thermal operations. The necessity of heat treatment of Ti-Ni-Zr surface layers after HVOF in a protective medium, as well as the choice of temperature-time intervals for heat treatment, is dictated by the following considerations: to achieve the effect of structure stabilization with possible relaxation of residual internal stresses after deposition. It is known that with the growth of annealing temperatures for SME alloys, the processes of stress relaxation and defect elimination are activated.



**Figure 2.** X-ray phase analysis of Ti-Ni-Zr alloy, after HVOF in argon protective medium.

HVOF of mechanically activated powders with SME leads to high density of crystal lattice defects and to internal stresses (first-order stresses or residual stresses), while their magnitude and character are determined by the nature of the materials and the spraying conditions. Internal stresses, preventing the mobility of twinning boundaries, can lead to decrease in the functional and mechanical properties of the resulting layers, as well as to cracking or peeling of coatings from the substrate. In accordance with the relaxation mechanism of internal residual stresses during annealing, their partial or complete relaxation is a by-product of homogenization or recrystallization annealing. In this case, annealing is used as a means of improving the shape memory characteristics, since with the relaxation of internal stresses, martensitic twins can be mobile within free subboundaries. Homogenization (diffusion) annealing eliminates the chemical heterogeneity of the deposited layers. Homogenization annealing leads to complete dissolution of the excess phases, approximating the phase composition of the alloys to the thermodynamically balanced state and improving the properties of SME alloys. Thermal treatment also intensifies diffusion processes, which occur at the boundary "steel base – transition layer". These processes increase adhesion strength of coatings to the substrate.

In the Ti-Ni-Zr layer, after the thermal treatment and surface-plastic deformation, we observe the same sequence of martensitic transformations as after the quenching  $B2 \leftrightarrow B19'$ . This is due to the fact that the austenite structure is formed in the annealing process at 873 K, and it does not differ significantly from the structure after the alloy quenching. Figure 3 shows the calorimetric curves of Ti-Ni-Zr. It can be seen that the martensitic transformation in the Ti-Ni-Zr alloy occurs from the austenite phase to the martensitic one  $B19$ :  $B2 \leftrightarrow B19'$ .



**Figure 3.** Calorimetric curves of surface-modified TiNiZr layers, after a full annealing cycle + surface-plastic deformation (a); dependence graphs of  $\epsilon_0$  on  $\epsilon_H$  for TiNiZr after HVOF and surface-plastic deformation, annealing at: (b) – 600 °C; (c) – 800 °C.

In the Ti-Ni-Zr layer, after the thermal treatment and surface-plastic deformation, the following sequence of martensitic transformations is observed: B2  $\leftrightarrow$  B19'. Figure 3(a) shows the calorimetric curves of Ti-Ni-Zr, after a complete annealing treatment + surface-plastic deformation. Temperatures of the martensitic transformations of layers made of SME materials are:  $M_f = 459$  K,  $M_s = 522$  K,  $A_s = 488$  K,  $A_f = 571$  K. Figure 3(b), (c) shows the dependence graphs of the reversible strain magnitude  $\varepsilon_0$  on the induced deformation  $\varepsilon_H$  for TiNiZr after HVOF, heat treatment and surface-plastic deformation.

After HVOF and surface-plastic deformation, the largest amount of reversible deformation for the TiNiZr alloy is 2.1–2.3 % (figure 3(b), (c)), achieved in the annealing interval 600–800 °C.

## 5. Conclusions

After the HVOF of the mechanically activated TiNiZr powder, we obtain a nanostructured coating with a grain size of 80–100 nm. X-ray diffraction studies have shown that the formation of surface layers according to the developed technology ensures the manifestation of the shape memory effect. We also studied the functional properties of TiNiZr layer, which showed a reversible deformation of 2.1–2.3%.

## Acknowledgements

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