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Formation of Multi-functional TiNi Surface Layers via High-speed Flame Spraying

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This paper examines the formation of multi-surface layers of a material with shape memory effect characteristics, using high-speed flame spraying of TiNi. The control parameters of the process were analysed and optimized spraying regimes applied in order to ensure the formation of a structure with grain size 30 - 170 nm and adhesion strength greater than 60 MPa.

Keywords: Shape memory effect materials, High-speed flame spraying, Surface activation, Nanostructure, Technological parameters.

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1. INTRODUCTION

Functional coating materials for various purposes are today widely used in both the microelectronics and engineering tool industries. Analysis of existing processes of creating such functional coatings has shown that, particularly in engineering, an increasingly prominent role is being played by high deposition processes and surfacing, combining the advantages of using concentrated sources of energy and the ability to surface alloying material of a given composition [1]. Significant interest regarding surface alloying is currently focused on materials possessing a shape memory effect (SME); because of their versatility and unique combination of strength properties, wear and corrosion resistance, and high damping capacity, these materials are already widely employed in medicine [2] and the aerospace industry [3].

Surface layers made of SME materials are prepared via a high-impact method involving TIG and laser welding, plasma spray deposition and melting of the fusible metal along a temperature gradient [4]. Recent research has led to the development of more efficient high-speed spraying technology which can ensure the strength of adhesion of the coating to the substrate at more than 100 MPa and a porosity of 0.5% [1,5,6]. A comparison of existing high-speed coating techniques, such as cold gas dynamics, detonation, plasma and gas flame, has indicated that although coating quality in terms of adhesion, porosity and degree of oxidation is of approximately the same level, high-speed flame spraying coating is more manufacturable, has a higher performance and reduced unit costs [5-7]. However, very little is currently known about the process of forming high-speed flame-spraying coatings. Although the method of forming surface layers of TiNi has been analysed, the functional properties of the applied coating were not studied. [8]

The purpose of the present work was therefore to study the possibilities of forming surface layers composed of nickel-titanium alloys possessing the shape memory effect using the high-speed flame spraying method, as well as to study the structural features of these layers.

2. APPARATUS AND METHODS

The experiments were conducted on structural steels (steels 45, 40X), with high-speed flame spraying of TiNi manufactured via GLC applied to cylindrical samples. In order to improve coating adhesion to the substrate, provisional blasting of the steel surface was carried out followed by the application of 15% nitric acid etching solution. The combustible gas mixture used was comprised of methane and oxygen, with argon employed as the powder carrier gas. High-speed flame spraying was carried out using a burner angle of inclination of 40-90 °. The experimental setup for the coating process is shown in Fig. 1.

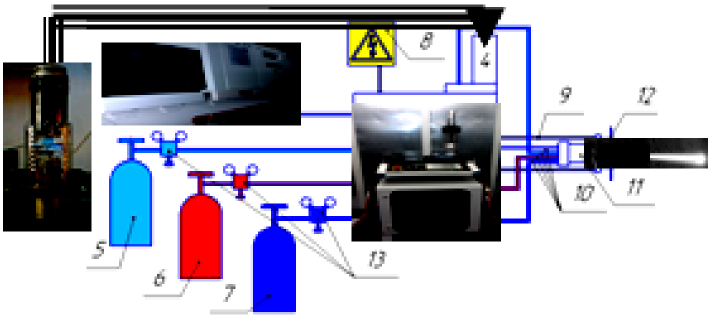

Fig. 1 – Installation scheme for the high strength coating process: 1 - compressor, 2 – receiver, 3 - Governors device TSZP-GLC-720, 4 - feeder, 5 - carrier gas cylinder (argon), 6 - fuel gas cylinder (methane), 7 - oxidant cylinder (oxygen) 8 - electric shield, 9 - electrical cable, 10 - hose, 11-gun, 12 - electrodes, 13 - gearbox, 14 - attritor

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The material selected for surface modification was the PN55T45 TiNi powder, with the following chemical composition (wt.%): 44% Ni, 56% Ti, 0.01% Fe, 0.06% C, 0.10% Ca, 0.06% N and 0.06% H. Diffraction analysis of the PN55T45 powder (Fig. 2) revealed its structure to consist primarily of an austenite phase (~ 95%), with small amounts of a martensitic phase (~ 5%).

A number of studies [9,10] have shown that the initial size of the powder particles has a significant influence on the structure and properties of the formed layer. Analysis of the particle size of the PN55T45 powder revealed that the particles have a warped form of perforated scales (Fig. 2a) which is most pronounced in larger particles (Fig. 2b). As a result of these features, the TiNi powder possesses a bipolar structure characterised by very small intra-particle and large inter-particle pores (Fig. 2c). To optimise both the size distribution of the TiNi powder and its mechanical activation, the powder was pre-processed in a Hephaestus - 2 ball mill (AGO-2U) prior to spraying, before being dried in a vacuum oven for 3-6 hours at 120-180ºC.

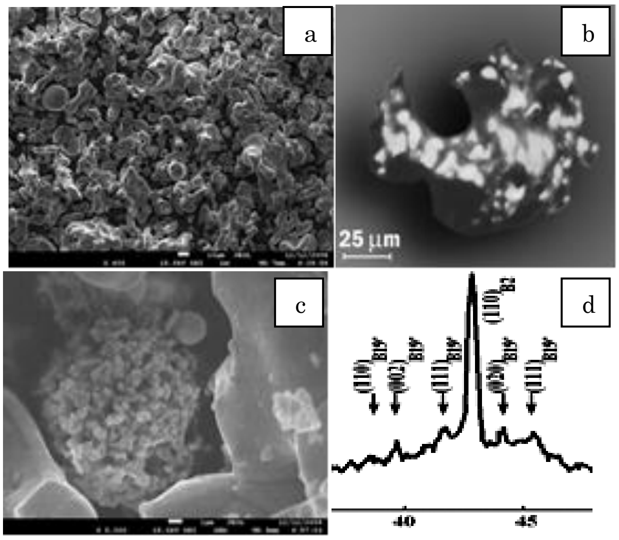

Fig. 2 – The morphology of the PN55T45 powder particles: × 100 (a); × 300 (b); × 1000 (c); powder diffraction PN55T45 (d)

Investigation of the microstructure formed by the surface layers was carried out under a JSM-7500F high-resolution scanning electron microscope, an MZI 100 measuring microscope, an MIM-8 optical microscope and an NU-2E (Carl Zeiss Jena) with planochromatic lenses. X-ray analysis was performed on a Shimadzu XRD - 7000 with Cu-K$_\alpha$ radiation, while microhardness was analysed in a PMT-3 device with an indenter load of 100g.

3. TECHNOLOGY OF NANOSTRUCTURED TINI SURFACE LAYERS

The main properties of functional coating materials possessing shape memory, in addition to their strength, hardness and porosity, are their chemical and phase compositions which determine specific shape memory properties, such as pseudoelasticity and shape memory damping. Improved multi-functional coatings can be produced by controlling the speed, temperature and enthalpy of the particles and substrate at the moment of contact and interaction, which is in turn is determined by the composition of the powder foundation, the activation energy of the sprayed material, surface preparation, as well as the carrier composition of the process gas and technological features of the equipment. Accounting for the variety of factors that affect the performance and operational characteristics of the surface layers is therefore a complex task.

One method of producing high-quality coatings involves surface preparation. In conducting this research, several activation techniques were compared, including sandblasting, cutting, 'torn' thread sublayer deposition of pure nickel (a component of the applied coating and with an unlimited solubility of substrate), plasma activation and chemical etching. Although all of these methods produce a positive effect, for reasons of quality (adhesion to the substrate of more than 60 MPa) and economic expediency, a combined method comprising sandblasting followed by chemical etching was selected as optimal.

Preliminary analysis indicated that the main high-speed flame spraying parameters affecting coating structure and quality were the selected combustible fuel gas (methane, oxygen), the powder and carrier gas (argon) spraying distance, spray angle, moving speed, feed burner flame and the speed of the covered parts. In developing the flame-spraying technology, certain parameters were taken from the literature (angle of the nozzle, spraying distance), depending on the main technological parameters of the test such as the combustible gas and the speed of the powder particles in the gas stream.

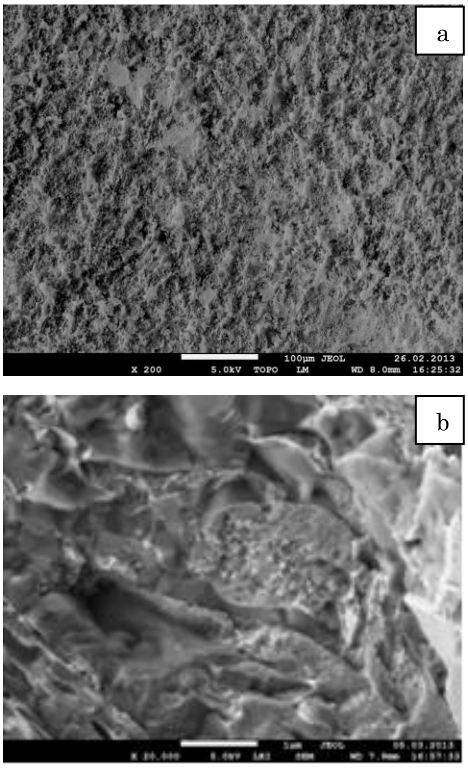

Fig. 3 – Specimen surface after high-speed flame spraying of TiNi (a) × 200; coating microstructure (b) × 20 000

The high-speed flame spraying of material in a dispersed state took place at a certain velocity, with the surface produced after the material's subsequent collision with the coated surface-forming layer shown in Fig. 3a. Metallographic analysis of the coatings revealed that after the particles are heated by passing through the flame jet, they strike the substrate as solidified deformed discs with diameter 5-10 microns and thickness 0.5-1 microns. The resulting coating was found to be laminate in form (Fig. 3b), consisting of highly deformed particles interconnected by contact surfaces.

The ultimate structure and properties of the produced coating is determined by a range of factors, including delivery process shock, deformation hardening, cooling and the interaction of the particles in motion in the gas stream. Since the formation of coatings in the present study involved a consistent stacking of the deformed particles, pores were also formed on the boundaries of the compounds. Obviously, the structure of such a coating depends on the particle size distribution of the deposited material; the finer the powder sprayed, the less likely the formation of pores. Although a size of around 40-70 microns is typically recommended for spraying powders, in recent years an increasing number of studies have utilized finer powders of around 10-20 nm [5]. Experience has shown that the use of such fine powders for spraying may cause certain technical difficulties, associated with individual components in the burnout material sprayed in the gas stream. Therefore, optimization of the powder particle size distribution represents a crucial stage in the development of coating formation technology. Research carried out using statistical analysis has revealed that for high-quality coatings produced via flame spraying of TiNi, the optimum particle size distribution of the powder is a mechanically activated 0.9-7.5 microns (Fig. 4a). When employing a finer powder fraction (less than 0.9 microns), adhesion occurs between the particles, resulting in clumping and process interruption (due to powder sticking in the dispenser channel).

The main functional parameters characterizing the properties of gas-flame coatings are adhesion, porosity, structure and phase composition. Studies have shown that for surface layers comprised of shape memory Ti-Ni, optimum coating quality is achieved using a combustible gas flow rate of 70-75 l / min for methane and 150-160 l / min for oxygen (Figure 4 b, c).

Statistical analysis of the experimental data was carried out in order to estimate the influence of the particle size distribution of the sprayed powder and the subsequent pore size of the produced coating on the latter's adhesion strength, as follows: (1)

$$D_c = 345{,}4843 + 116{,}6433 \cdot s_p - 855{,}9937 \cdot d_t + 15{,}4867 \cdot s_p^2 - 218{,}1472 \cdot s_p \cdot d_t + 769{,}7443 \cdot d_t^2 \qquad (1)$$

where d_t - pore diameter in microns; s_p - powder particle size in microns; D_c - adhesion strength in MPa.

In order to improve the adhesion strength and physical-mechanical properties of the sprayed coatings, a variety of different heat treatment methods are employed [3,9]. For the specific functional properties of surface layers composed of shape memory TiNi alloys, thermomechanical processing techniques are typically

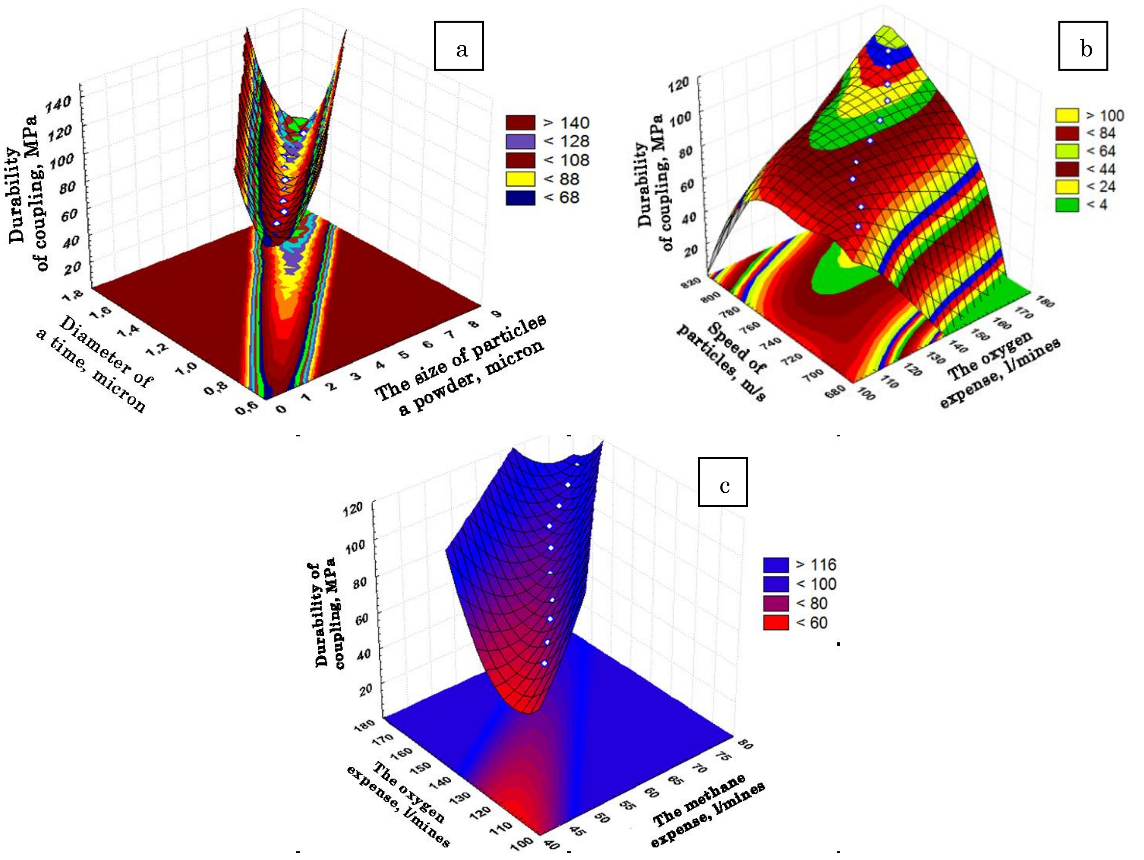

Fig. 4 – The influence of technological factors on the strength of coating adhesion to the TiNi substrate (a), (b), (c)

used, including vacuum annealing and plastic deformation of the surface [9,10]. A complete cycle of TiNi coating formation thus comprises the following steps: high-speed flame spraying using the optimum mode; annealing at 1223K in a protective atmosphere; surface plastic deformation (PPD) of a TiNi layer (initially formed at room temperature) at 293 K [10]. Run-cylindrical steel 45 specimens with TiNi coatings were here passed through three roller devices at a temperature of M_s-M_f ($M_s = 302K$; $M_f = 285K$, $A_s = 321K$, $A_f = 336K$), with the following running parameters employed: roller load F = 5.5-5.7 kN; roll diameter d = 50 mm; roller width b = 8 mm; running speed V = 110-120 rev / min; traverse S = 0.055-0.06 mm/rev. Such treatment reduces coating porosity, increases adhesion and improves corrosion resistance[10].

4. DISCUSSION

Macroanalysis of the TiNi alloy surface layers revealed the coating to have both a sufficiently dense structure and the minimum pore size (Fig. 5), while the interface between the coating and the TiNi substrate exhibited an absence of cracks. At room temperature, the major constituents of the surface layer of the TiNi were a B2 austenitic phase with a cubic lattice, a B19' martensitic phase with a monoclinic lattice and a Ni_3Ti intermetallic phase in the presence of a small amount of TiO.

As shown by metallographic analysis, the structure formed by high-speed flame spraying of TiNi alloy layers was weakly etched by conventional reagents due to the strong grinding grain, which exhibited high corrosion resistance. Examination of the microstructure of the TiNi surface layer under a high-resolution scanning electron microscope revealed the TiNi coating to be 60-70% nano-sized in structure, with a grain size of 30-170 nm (Fig. 5). In contrast, the grain size of the intermetallic Ni_3Ti phase was 20-60 nm. In many ways, the formation of the coating reflects the characteristics of high-speed flame spraying (i.e. high-speed collision of particles with the substrate, high rate of cooling and rapid quenching of the alloy). The milling of the grains in turn led to a decrease in pore volume concentration of 18-24%, with the formation of more dense grain boundaries (Fig.6).

For all samples, the micro-hardness of the sprayed NiTi layer was higher than that of the base metal, with values for the former ranging at around $H_\mu = 8.5$-12.1 GPa. Such an increase in micro-hardness reflects the formation of a high-strength, meta-stable structure due to high cooling rate and rapid quenching of the alloy.

5. CONCLUSIONS

The present study investigated the main control parameters in the surface modification of steel material using shape memory TiNi alloy, including the structural state of the material. Analysis of the structural formation of the TiNi surface layers in terms of the optimisation of deposition conditions enabled the production of nanoscale structures with a grain size of 30-170 nm;

After analysis of existing technologies, the surface layers of the shape memory materials were processed using surface activation, based on the quality of the produced surface layer and the economic feasibility of

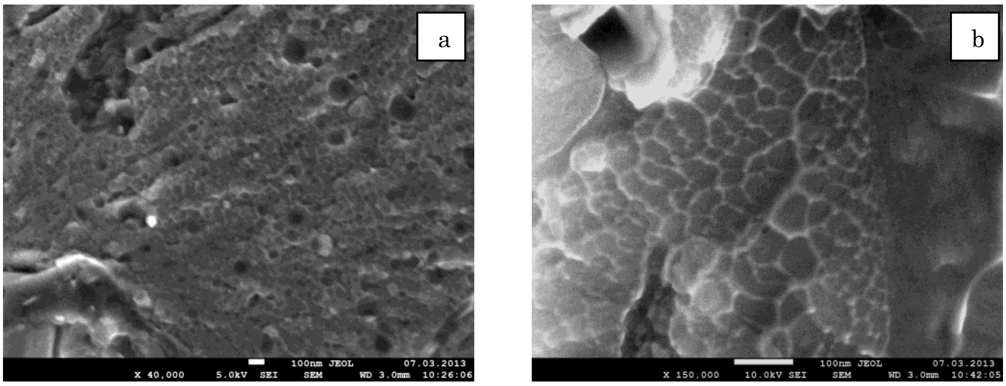

Fig. 5 – Nano-sized TiNi coating obtained via high flame spraying: × 40 000 (a), × 150000 (b)

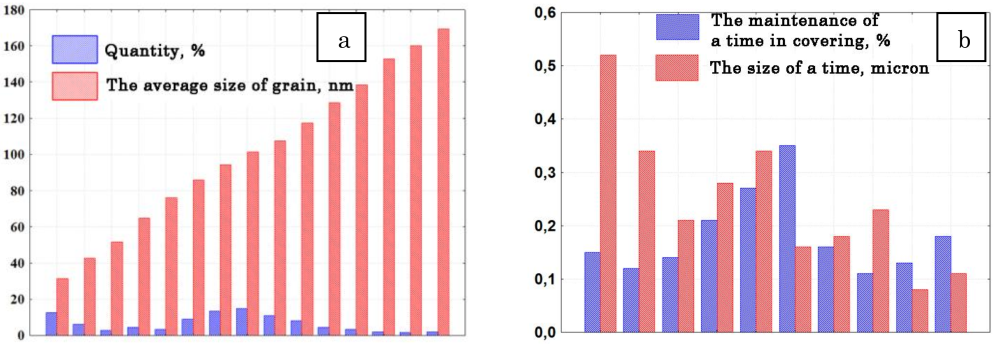

Fig. 6 – Quantitative grain size distribution and percentage of the TiNi coating (a); percentage of pore size to size (b)

the process. An increase in TiNi coating adhesion to the substrate to above 60 MPa was observed following the application of surface activation shot treatment followed by chemical etching;

Experimental examination of the effect of thermomechanical processing (comprised of heat-treating in a protective environment and plastic deformation of the surface) on the functional properties of the surface layers obtained via high-speed flame spraying revealed an installation effect of increasing microhardness and a reduction in the average pore content of 20%.

ACKNOWLEDGEMENTS

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