

UDK: 621.81:621.794.61

*Originalni naučni rad  
Original scientific paper*

## **INVESTIGATION OF MICROSTRUCTURE, ADHESION STRENGTH AND WEAR RESISTANCE OF COATINGS BEING OBTAINED WITH COMBINED METHOD**

**Yury Kuznetsov<sup>\*</sup>, Sergey Denisyev, Konstantin Kulakov**

*Orel State Agrarian University, Faculty of Agrotechnics and Energy Supply,  
Chair of Technology of Constructional Materials and Technical Service Organization,  
Orel, the Russian Federation*

**Abstract:** This paper deals with a state-of-the-art two staged coating technology involving Cold Gas Dynamic Spraying (CGDS) followed by treatment of the sprayed layer by Micro Arc Oxidation (MAO). This technology provides good physical and mechanical properties and high performance of coatings obtained. Experimental study data on the used process parameters and their impact on the performance of obtained coatings are presented. Test data relating to the properties of the coatings obtained, and general technological recommendations on practical application of the proposed technology are provided.

**Key words:** *micro arc oxidation, gas dynamic spraying, element, coating, wear resistance, microstructure, morphology, adhesion strength*

### **INTRODUCTION**

It is known that higher wear resistance of most machine parts is achieved by using coatings with required parameters. Wear of machine and equipment components is known to be 0,1 – 3,0 mm for different types of materials. Worn surfaces are industrially repaired by various methods, such as using oversize spare parts; welding and surfacing; spraying; plastic straining, various electrochemical processes, and other types of hard surfacing [1,2]. Unfortunately, these feature a lot of major disadvantages:

- they fail to always ensure the required endurance of friction pairs;

---

<sup>\*</sup> Corresponding author. E-mail: kentury@rambler.ru

- certain materials (and technologies) used are limited by strict sanitary standards, which particularly concerns surfaces coming in contact with food environment and food products;
- high complexity and high cost of the technological equipment used;
- technologies are inconsistent with ecological standards and require costly special-purpose protection.

The most promising of the current repairing technologies are certain types of thermal spraying, and fast developing micro arc oxidation. Studies of the special nature of thermal spraying and micro arc oxidation for various types of materials, including steels and valve metals have revealed a number of benefits and flaws.

Thermal spray technology does not necessarily ensure efficient coatings, which would be highly resistant to thermal cycling due to their high friability and poor adhesion. Furthermore, high porosity and roughness of coating surface require mechanical treatment of articles aimed to preserve their sizes and ensure adequate quality of surface. Cold gas dynamic spraying, which is a relatively new method of coating, has been widely used since recently [3, 4]. With CGDS, powder particles (a plastic metal powder or composite powder with less than 50  $\mu\text{m}$  particles [ ]) are accelerating up to 300-1,200 m/s by a heated Laval nozzle-generated ultrasound high-pressure gas jet. This creates a solid high-adhesive (35-40 MPa) coating of low strength metals by using relatively simple equipment [5, 6].

As regards micro arc oxidation [7, 8], it enables high-adhesive oxide-ceramic layers with adequate wear- and heat resistance properties depending on porosity and roughness of the treated material in order to maintain the initial dimensions and geometric parameters of detail and, possibly, to rule out subsequent mechanical treatment of the coated details. However, MAO is used in valve metals alone, and cannot be applied in treatment of steels used to produce most of the machine and equipment parts.

This paper deals with the results of consequent application of both of these methods (CGDS and MAO) and the development of combined repairing and hardening technology to integrate their advantages. The resulting technology is recommended for industrial use, including repairing of details made of aluminum alloys, alloys steels, carbon steels and corrosion-resistant steels. Expected increase in life cycle of reconditioned and hardened articles is about 150-200% versus brand new parts.

## MATERIAL AND METHODS

Coatings were generated on square coupons (50x50x4 mm) of aluminum UNS A91200 and steel UNS G43400.

Aluminum coating has been sprayed on samples by means of low-pressure cold gas dynamic spraying system (below 0,9 MPa), Dimet-405 (Fig. 1). Powder A80-13 (Al – base,  $\text{Al}_2\text{O}_3$ , Zn; Dimet) have been used. Compressed air was used as an actuation gas. Before spraying, the samples have been cleaned up and activated by sand blasting using 200 mesh  $\text{Al}_2\text{O}_3$  at the same equipment.

The MAO device contains a 40 kW AC power supply with a 50 Hz modulation, an electrolyte bath, a stirring and cooling system. Current density was 15-20  $\text{A}\cdot\text{dm}^2$ .

The electrolyte consisted of an aqueous solution of sodium silicate (10-12  $\text{g}\cdot\text{l}^{-1}$ ) and potassium hydroxide (1-2  $\text{g}\cdot\text{l}^{-1}$ ).



Figure 1. General view of the device "Dimet-405"

Adhesion strength of the resulting coatings was tested at PosiTest Pull-Off Adhesion Tester (DeFelsko Corporation, USA) according to ASTM D4541-95e1 [9], ASTM C 633 – 79 [10].

Metallographic tests were conducted at ZEISS Axiolab A equipped with an image review system and SEM JEOL 35CF.

Coating thicknesses (total thickness of coating and oxidized layer thickness) were measured using a digital CM-8825 (Ferrous & Non Ferrous type) coating thickness gauge, which coating thickness with an accuracy of 0,1  $\mu\text{m}$ .

Comparative coating wear-resistance tests (both for cold gas-dynamic spraying and MAO) were conducted according to ASTM G 99 – 95a [11] using «rotating disk – fixed pin» pattern at constant load and rotation speed. Non-coated aluminum alloys (UNS A04131, UNS A03561 and DIN G-AISI12) and CGDS-formed coating with no MAO hardening were used as a reference. Tests were lasting for 200 hours.

Microhardness of the resulting coating was checked at microhardness tester Buehler Micromet Microhardness 2103.

## RESULTS AND DISCUSSION

### Morphology and microstructure of coatings

The principal characteristics of coatings being obtained by means of CGDS (Cold Gas Dynamic Spraying) is that they are the composite material consisting of metal matrix and separate ceramic particle incorporated into it [11].

Fig. 2 shows typical coating formed by Gas Dynamic Spraying on steel support.

On the photo the interface between support (steel (1)) and sprayed coating (2) is clearly seen. Along the whole interface there are no clearances, cavities and foreign inclusions. The presence of the included aluminum oxide particles (position 3) are traced with definite regularities in the surface layer of the support. It is noteworthy to stress that aluminum oxide particles are rather uniformly distributed along the coating thickness.

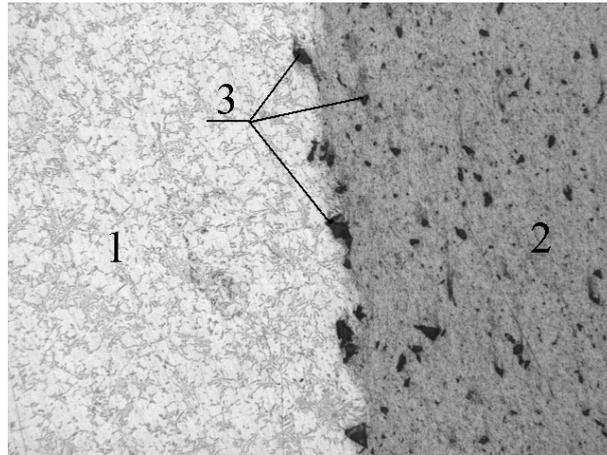


Figure 2. Microstructure of coating being obtained by Gas Dynamic Spraying from powder material of type A-80-13, 200<sup>x</sup> 1 – steel support, 2 – coating 3 – particles of aluminum oxide

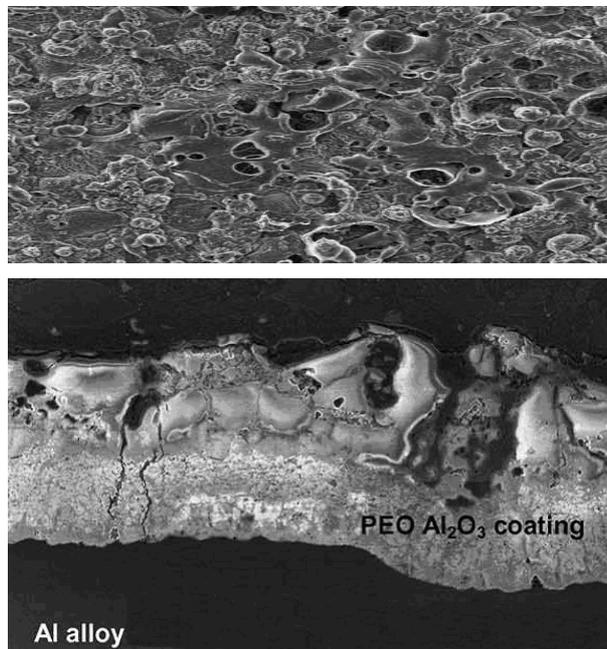


Figure 3. Morphology (up) and microstructure (down) of coatings formed by Micro Arc Oxidation Magnification 600<sup>x</sup> u 400<sup>x</sup>

It affirms their participation in creation of the main mass of the coating. Zinc particles in the coating composition are hardly differentiated probably because of their small percentage composition in a total mass of the sprayed powder material (nearly 15%). On the ground of the mentioned above it is possible to conclude that the coatings obtained by CGDS consist of tightly packed particles uniformly covering the surface.

Fig. 3 presents morphology and typical microstructure of coatings being formed with micro arc oxidation on the sprayed surfaces. Metallographic sample analysis showed that the obtained oxide ceramics layer on the sprayed surface is more consistent close to aluminum support. On the external surface it has greater porosity and consists of numerous melted areas in the form of micro craters and drop-shaped traces of melting of oxide film substance and electrolyte components. The traces of micro discharges localization in the form of melted craters can be seen in pores. It is possible to conclude that at Micro Arc Oxidation oxide ceramics layer with developed surface in aluminum support is formed.

### Adhesion Strength of Coatings

Results of adhesion studies on CGDS coatings [12, 16] on aluminum alloys and carbon alloy steels are shown in Fig. 4.

Particles of the sprayed powdered material are speeding up, as air pressure is rising in CGDS plant spraying chamber, and therefore an maximum adhesion strength of coatings is achieved (Fig. 4a). The maximum possible pressure in the spray chamber depends on design features of the plant.

As air heating temperature pressure is rising, adhesion strength of coatings reduces (Fig. 4b). This is attributed to higher activity of sprayed particles. Therefore, not only the particles with an adequate kinetic energy will adhere onto the sprayed surface, but also the particles with lower kinetic energy and higher temperature.

Adhesion strength of CGDS and gas-flame sprayed coatings is gradually rising proportionate to the increase in roughness of the sprayed surface. The maximum adhesion is achieved at  $R_z = 60-120 \mu\text{m}$ .

The experimental data obtained support our theoretical assumption that solid particle – substrate interaction associated with CGDS is not only dependent on heating temperature and air pressure in the spraying chamber, but also on sprayed particle size (Fig. 4c). There are always particles of such size which would ensure their detachment from the substrate, whatever their speed may be, even if the maximum possible number of links has been created at contact.

This evaluation of coating adhesion strength shows that under the given interaction conditions, particles with elastic energy and adhesion energy have the same order of magnitude, with elastic energy of compression gaining a major importance in solid spraying. Therefore, relatively small fractions of sprayed powder shall be used to alleviate the effect of elastic rebound of particles ( $\leq 60 \mu\text{m}$ ).

To maintain adequate strength properties of coatings created by CGDS and MAO hardening, transition area between the substrate and MAO-hardened layer shall be at least 70...100  $\mu\text{m}$  thick.

Quantitative study of adhesion strength for MAO coatings formed in KOH- $\text{Na}_2\text{SiO}_3$ -type electrolyte showed no blistering or stripping of coatings on control surfaces, regardless of the type of electrolyte, current density, and oxidation time.

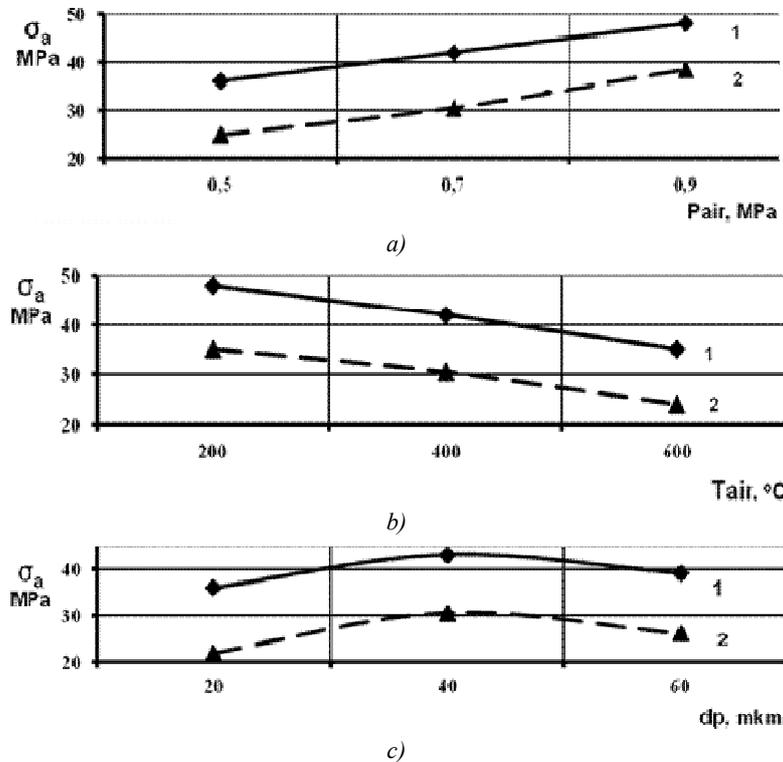


Figure 4 – Adhesion strength – CGDS mode dependence  
(1 – aluminum substrate; 2 – steel substrate):

a) dependence on air pressure in the spraying chamber  
(air heating temperature (const) – 400 °C);

b) dependence on air heating temperature in the spraying chamber  
(air pressure in the spraying chamber (const) – 0,7 MPa);

c) dependence on powdered material fraction  
(air pressure in the spraying chamber – 0,7 MPa, spraying distance – 15 mm,  
air heating temperature – 400 °C).

#### Abrasive Wear Tests

Results of wear resistance studies for proposed coatings are shown in Fig. 5. According to [13-16], wear resistance of hardened CGDS coatings is 7 – 7,8 - fold higher than of non-hardened coatings, and 5 – 6 - fold higher than of aluminum alloys.

Analysis of the data obtained shows that wear rate of friction couples with oxide-ceramic coated samples is 6-fold lower than of reference friction couples with CGDS-formed coating without hardening, and 4,1...5,2-fold lower than the wear rate of friction couples with aluminum samples (depending on the type of alloy).

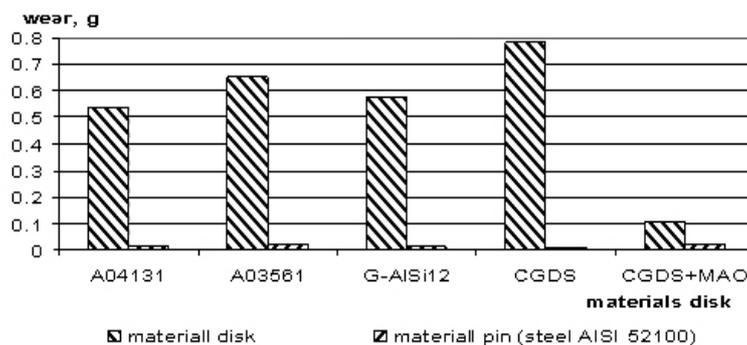


Figure 5. Wear values for "disk-pin" samples  
(CGDS – gas dynamic spraying;  
CGDS+MAO – gas dynamic spraying and micro arc oxidation)

## CONCLUSIONS

This combined technology enables to form hardened high resistant and adhesion strong layers on steel (aluminum) surfaces.

The study supports efficacy and feasibility of using combined technology that consists of creating a powdered aluminum-containing layer on metal surfaces (including non-valve metals) by means of CGDS followed by sprayed layer oxidation using MAO, with required adhesion strength obtained by treatment modes, and structural status of the working surface attributed to electrolyte composition and porosity of the interim powder sub-layer, which in its turn depends on its thickness and spraying modes.

All performance parameters obtained are conformant to standard requirements.

## BIBLIOGRAPHY

- [1] Vladimirov, V.S., Moizes, S.E. 2005. *Protective and Strengthening Coatings: Prospective Technologies and Equipment*. N.E. Bauman Moscow State Technical University, 2005, 95 pp.
- [2] Kurchatkin, V.V. 2000. *Reliability and mending of machines*. Moscow, Kolos, 2000, 776 pp.
- [3] Alkimov, A.P., Papyrin, A.N., Kosarev, V.F., Nesterovich, N.I., Shushpanov, M.M. 1994. *Gas dynamic spraying method for applying a coating*. U.S. Patent 5 302 414, April 12 (1994).
- [4] Stoltenhoff, T., Kreye, H., Richter, H.J. 2002. An analysis of the cold spray process and its coatings. *J. Therm. Spray Technol.* 11 (2002), p.p. 542–550.
- [5] Li, W.Y., Zhang, C., Guo, X.P., Zhang, G., Liao, H.L., Coddet, C. 2007. Deposition characteristics of Al–12Si alloy coating fabricated by cold spraying with relatively large powder particles. *Applied Surface Science* 253 (2007), p.p. 7124–7130.
- [6] Pattison, J., Celotto, S., Khan, A., O'Neill, W. 2008. Standoff distance and bow shock phenomena in the Cold Spray process. *Surface & Coatings Technology* 202 (2008), p.p. 1443–1454.
- [7] McNeill, W., Gruss, L.L. 1966. *Anodic spark reaction processes and articles*. U.S. Patent 3 293 158, Dec. 20 (1966).

- [8] Yerokhin, A.L., Nie, X., Leyland, A., Matthews, A., Dowey, S.J. 1999. Plasma electrolysis for surface engineering. *Surface and Coatings Technology* 122 (1999), 73-93.
- [9] ASTM D4541-95e1. "Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers". Available through: <http://www.astm.org/DATABASE.CART/HISTORICAL/D4541-95E1.htm> [Accessed date: 26.07.2013.]
- [10] ASTM C 633 – 79. "Standard Test Method for Adhesion or Cohesive Strength of Flame-Sprayed Coatings". Available through: <http://www.astm.org/DATABASE.CART/HISTORICAL/C633-79R99.htm> [Accessed date: 26.07.2013.]
- [11] ASTM G 99 – 95a. "Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus". Available through: <http://www.astm.org/DATABASE.CART/HISTORICAL/G99-95AR00E1.htm> [Accessed date: 26.07.2013.]
- [12] Kuznetsov, Y.A. 2005. Study of Adhesion Strength of Combined Coatings. *Mechanizatsia i Elektrifikatsia Selskogo Hozyaistva*, 7 (2005), 32-33.
- [13] Kuznetsov, Y.A., Kossenko, A.B., Zinigrad, M.I. 2008. Modern two stage coating technology. *Fifth International Conference on Mathematical Modeling and Computer Simulation of Material Technologies MMT-2008*. – Ariel University Center of Samaria, Ariel, Israel, September 08-12, 2008. – Volume 1 (4. Micro arc oxidation technology), p.p. 4-82 – 4-89.
- [14] Yerokhin, A.L., Voevodin, A.A., Lyubimov, V.V., Zabinski, J., Donley, M. 1998. Plasma electrolytic fabrication of oxide ceramic surface layers for tribotechnical purposes on aluminum alloys. *Surface and Coatings Technology*, 110 (1998), p.p. 140-146.
- [15] Kuznetsov, Y.A. 2005. Improved Wear Resistance of Gas-Dynamic Sprayed coatings. *Mechanizatsia i Elektrifikatsia Selskogo Hozyaistva*, 6 (2005), p.p. 27-28.
- [16] Kuznetsov, Y.A., Denisiev, S.A., Leonov, M.S. Investigation of some characteristics of coatings being obtained on the elements by means of gas dynamic spraying with their micro arc oxidation hardening. *Proceedings of the union of scientists. Fifth conference «Energy efficiency and agricultural engineering»*. Ruse, Bulgaria, 17-18 may, 2013. p.p. 554-559, ISSN 1311-9974.

## ISTRAŽIVANJE MIKROSTRUKTURE, ADHEZIJE SILE I OTPORA HABANJU PREMAZA NANETIH KOMBINOVANIM METODOM

**Yury Kuznetsov, Sergey Denisiev, Konstantin Kulakov**

*Državni Poljoprivredni Univerzitet Orel, Fakultet za poljoprivredne i pogonske mašine,  
Katedra za tehnologiju konstruktivnih materijala i organizaciju tehničkog servisa,  
Orel, Ruska Federacija*

**Sažetak:** U radu sa razmatra najsavremeniju dvostepenu tehnologiju nanošenja premaza koja uključuje dinamički sprej hladnog gasa (CGDS) praćen tretiranjem nanetog sloja spreja mikro-lučnom oksidacijom (MAO). Ova tehnologija daje dobre fizičke i mehaničke osobine i visoke performanse dobijenih premaza. Predstavljani su eksperimentalni rezultati istraživanja parametara ovih procesa i njihov uticaj na

performanse dobijenih premaza. Dati su rezultati testiranja svojstava dobijenih premaza i opšte tehnološke preporuke o praktičnoj primeni predložene tehnologije.

***Ključne reči:*** mikro-lučna oksidacija, dinamički sprej gasa, element, premaz, otpor habanju, mikrostruktura, morfologija, adheziona sila

Prijavljen: 16.07.2013.  
*Submitted:*  
Ispravljen:  
*Revised:*  
Prihvaćen: 26.09.2013.  
*Accepted:*

