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Nanoparticles processing for fabrication of multi-functional nanostructured coatings

Zastosowanie nanocząstek do wytwarzania wielofunkcyjnych powłok nanostrukturalnych

Abstract
Development of novel technologies for nanoparticles macro-applications has recently become a very important field in materials science, because the size reduction to nanometric scale could provide significant improvement in macro material properties: hardness, toughness, wear, and corrosion resistance. Recent research results have shown that consolidated nano-materials have significantly improved operating properties: increased hardness and toughness in conjunction with low friction coefficient. To reach these advantages, preservation of the nanometer grain sizes of the initial materials should be provided with applied consolidation methods (sintering of bulk materials or coating deposition by spraying). Conventional thermal spraying techniques (Plasma Spraying, Flame Spraying and HVOF) can not solve completely this problem due to considerable particle heating in spraying jet. Detonation Spraying (DS) is based on the principle of extremely high particles acceleration at low particle temperature. The present article presents novel DS technique to deposit dense nanostructured tungsten carbide/cobalt coatings. Deposited nanostructured coating was studied by modern technique for nanostructure research (Auger nanoprobe, Tunnel Microscopy, etc.). It was shown that DS technique allows to keep initial powder nanostructure. Tribological and mechanical trials have demonstrated high coating wear resistance and fracture toughness.

Streszczenie
W ostatnim czasie rozwój nowych technologii stosujących nanocząstki do wytwarzania makroelemntów stał się bardzo ważnym obszarem inżynierii materiałowej. Zmniejszenie wymiaru cząstek do skali nanometrycznej może powodować znaczne polepszenie takich właściwości makro-materiałów jak: twardość, odporność mechaniczna, odporność na zużycie i korozję. Ostatnie wyniki badań pokazują, że skonsolidowane nanomateriały posiadają lepsze właściwości eksploatacyjne: podwyższoną twardość i odporność mechaniczną w połączeniu z niskim współczynnikiem tarcia. W celu utrzymania nanometrycznych wymiarów ziaren materiału wyjściowego ważne jest zastosowanie odpowiednich metod konsolidacji (np. spiekanie materiałów litych lub nakładanie powłok poprzez natryskiwanie). Konwencjonalne techniki natryskiwania cieplnego: natryskiwanie plazmowe, natryskiwanie płomieniowe oraz natryskiwanie naddźwiękowe (HVOF- Hhigh Velocity Oxyfuel Spray) nie rozwiązują całkowicie tego problemu ponieważ w tych procesach następuje utlenianie materiałów w podwyższonych temperaturach. Natryskiwanie detonacyjne (DS) polega na nadaniu dużego przyspieszania cząstkom przy niskiej ich temperaturze. Niniejszy artykuł przedstawia nową technikę (DS) nakładania gęstych nanostrukturalnych powłok wolframowo-węglikowych/kobaltowych. Nałożoną powłokę nanostrukturalną poddano badaniom na: skaningowym mikroskopie tunelowym (STM) i spektroskopie elektronów Augera (AES) Wykazano, że technika DS pozwala na utrzymanie wyjściowej nanostruktury proszku. Testy tribologiczne i mechaniczne wykazały wysoką odporność powłoki na zużycie.

Key words*:* nanoparticles**,** detonation spraying**,** nanostructured coating**,** wear resistance

Słowa kluczowe: *nanocząstki, natryskiwanie detonacyjne, powłoka nanostrukturalna, odporność na zużycie*

1. INTRODUCTION

Recent experiments have shown that consolidated nano-materials have improved mechanical properties, such as increased hardness of metals and increased ductility and plasticity of ceramics [1]. Tungsten carbide (WC) is well known for its exceptional hardness and wear/erosion resistance [2]. There is strong interest in nanostructured WC/Co materials, and many efforts have been made to synthesize these composites [3, 4]. Development of nanomaterials consolidation methods is a challenging requirement for their successful engineering applications. The most important task to be solved is to provide consolidation of nanostructured WC/Co powders (or nanoparticles agglomerates) with limited grain growth. Liquid Phase and Solid State Sintering were widely studied [5, 6]. On the contrary, study of consolidation of nanostructured WC/Co materials by coating deposition just has been started [7]. Conventional thermal spraying techniques (Plasma Spraying, Flame Spraying and HVOF) can not solve completely this problem due to considerable particle heating in spraying jet. Detonation Spraying (DS) is based on the principle of extremely high particles acceleration at low particle temperature. Particles kinetic energy is much higher compare to arc, plasma, flame and even HVOF processes. Its role greatly prevails over the role of thermal energy in coating formation. That is why this technique was chosen like the most promising for deposition of nanostructured WC/Co coatings. In the frame of the reported research, the following scientific and technological problems were solved:

- Basic mechanisms of coating formation from composite nanostructured powders projected with high velocity (more than 1 km/s) and low temperature (lower than melting point) were studied. Original diagnostic system capable real-time monitoring of the coating deposition process (in-flight particle velocity and temperature, particles-substrate interaction, coating growth, etc.) were developed for process research and optimisation;
- DS technology was optimised to respect the nature of the deposited nanostructure powders and to deliver nanostructured WC/Co coatings with superior tribological properties.

2. EXPERIMENTAL PROCEDURE

The powders applied in experiments were commercially available powder Amdry 9831 (WC/17Co, Particle Size: -53+11 μm) and nanostructured WC/Co powder (WC/17Co, Particle Size: -55+12 μm) specially produced by agglomeration method for the present research. Each individual macro particle (size: -55+12 μm) of nanostructured powder contains WC nanograins with typical size in the range 50-80 nm.

Flat samples (stainless steel substrate) were sprayed using Russian Detonation Spraying equipment. Spraying parameters (gas mixture, percentage of combustion chamber filling, distance to the substrate, and amount of powder for single spraying cycle) were optimised with the help of original diagnostic tool allowing real-time monitoring of individual particle velocity, temperature and size.

The characterization of coatings structure and phase composition was carried out by Auger Electron Spectroscopy (AES) and Tunnel Microscopy (TM). Cross-sectional microhardness measurements were performed by LECO tester M-400-H at load of 100 g. Fracture toughness of coatings was evaluated through conventional Vickers microindentation using a microindenter. Porosity was measured by image analysis with the help of LECO optical microscope and related software.

Tests of coatings was carried out on flat samples (disk-disk scheme) in neutral atmosphere (nitrogen) at loading 1-5 MPa and with sliding speed 0.1-1.0 m/s with the help of method described in article [8]. Test durations have been chosen within the range of: 60 minutes for definition of average wear intensity; 120 minutes for an estimation of average friction coefficient.

A scheme of the apparatus used for disk-on-disk sliding tests is presented in figure 1. The apparatus consist of: 1 - electric motor; 2 - chamber for vacuum or neutral atmosphere; 3 - magnetic coupling; 4 - spindle; 5 - punched disk; 6 - bracket; 7 - mandrel; 8 - rotation disk; 9 - ring obturator; 10 - photogauge 1; 11 - stationary disk; 12 - nut; 13 - heat exchanger; 14 - photogauge 2; 15 - electronic block; 16 - electronic tachometer; 17 - potentiometer; 18 - vacuum-gauge; 19 -converter; 20 - forvacuum pump; 21 - nitrogen trap; 22 - diffusion pump; 23 - hydraulic drive; 24 - dead weight; 25 - latch; 26 - bellows.

The first disk was fixed and the second one was rotated. The stationary disk was fixed on the basis by two pins and pressed to it by the round nut. The rotating disks had three (or one) ledges. During the tests the ledges of the rotating disk slided on a plan surface of the stationary disk. The rotating disk was installed in a self-aligning holder for uniform distribution of a load on the working surfaces. Torque was transmitted to the disk by two pins. The axial fixation of the disk in the holder was implemented by screws.

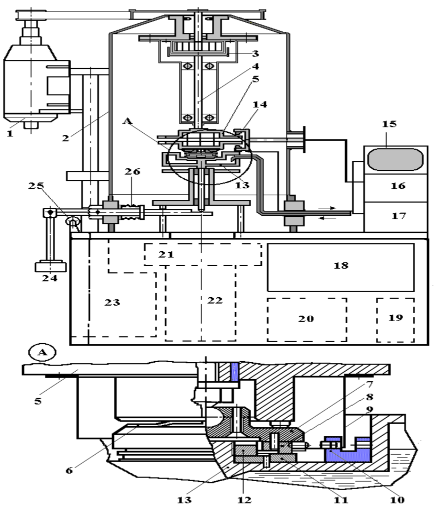

Fig. 1. Schematic diagram of sliding test apparatus
Rys. 1. Schemat urządzenia do badań tarcia ślizgowego

3. RESULTS AND DISCUSSION

The structure analysis has shown that nanostructured coating is more uniform in comparison with conventional coating (figure 2). Coating porosity is near 2% for Amdry powder and 1.5% for nanostructured coating.

At higher magnification this difference is clearly observed (figure 3). Nanocoating consists of small grains of WC. Conventional coating consists of large blocks of WC.

Analysis of nanostructured coating by tunnel microscopy (performed in height mode at constant current) has shown that correct choice of spraying parameters allow to keep initial powder nanostructure. Measured WC grain size is in the range 50-90 nm (figure 4).

Normally, for materials, when hardness is increased the toughness is decreased. It was found that for nanostructured coatings increase of hardness does not results in decrease of toughness. This phenomenon is rather important for potential application of nanostructured coatings due to their extended service-life. The table 1 shows results of microhardness test and toughness measurements (average values).

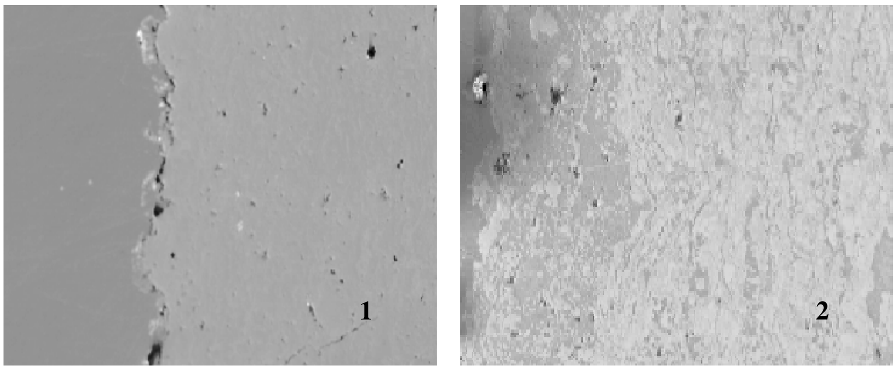

Fig. 2. The structure of WC/Co coatings: 1 - naostructured; 2 – conventional
Rys. 2. Struktura powłok WC/Co: 1 – nanostrukturalna; 2 - konwencjonalna

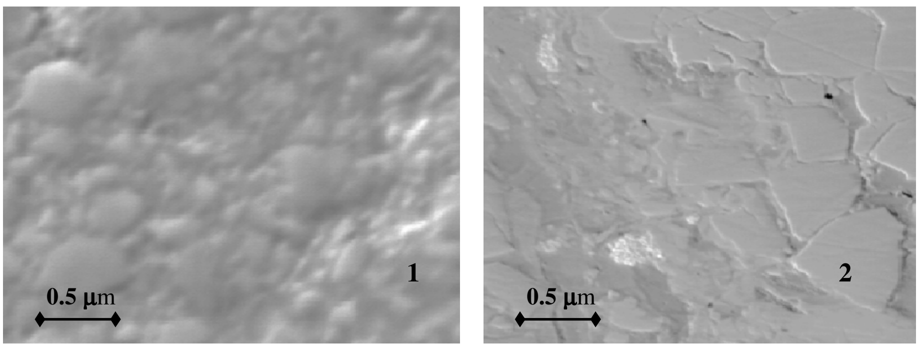

Fig. 3. Difference in fine WC/Co coatings structure: 1 - nanostructured; 2 – conventional
Rys. 3. Różnica w strukturze powłok WC/Co: 1 – nanostrukturalna; 2 - konwencjonalna

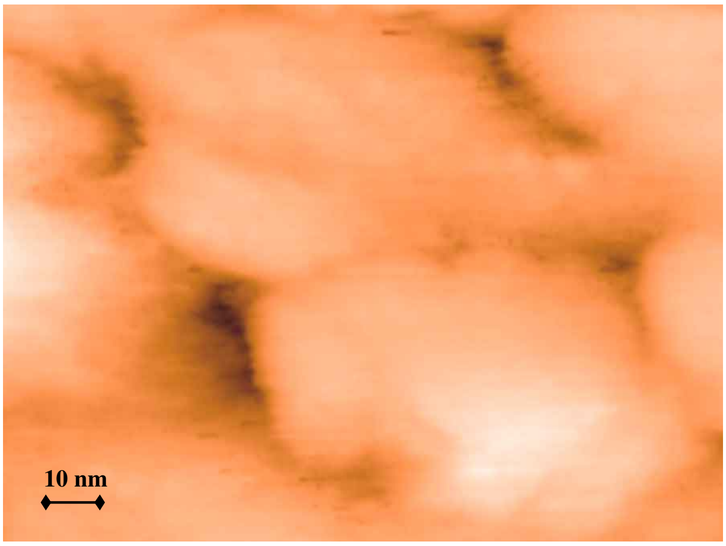

Fig. 4. Tunnel microscope image of WC/Co grains

Rys. 4. Obraz ziaren WC/Co otrzymany ze skaningowego mikroskopu tunelowego

Table 1

Tablica 1

Coating	Microhardness, Hv	Fracture Toughness (MPam1/2)
Conventional	1055	2,34
Nanostructured	1564	5,43

Wear tests have shown another specific feature of nanostructured coating: 2 times lower friction coefficient in wide range of contact pressure (figure 5). This is especially important for coating application in friction units operating under sever conditions (high temperature, high loads, abrasive media, etc.).

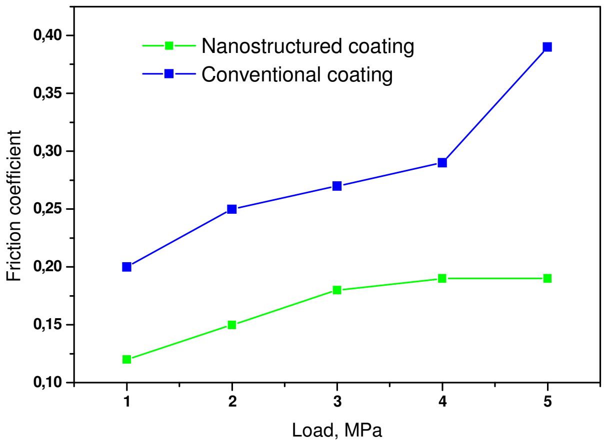

Fig. 5. Friction coefficient versus load at sliding speed 0.1 m/s

Rys. 5. Współczynnik tarcia w zależności od obciążenia przy prędkości ślizgowej 0,1 m/s

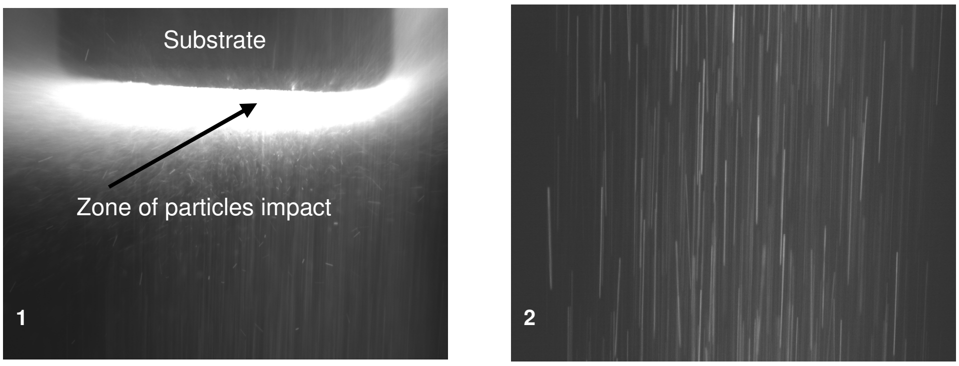

Fig. 6. Real-time monitoring of nanostructured coating spraying: 1 - image of particle impact on substrate; 2 - particle jet image allowing to measure individual particle velocity, size and temperature

Rys. 6. Monitorowanie w czasie rzeczywistym procesu natryskiwania powłoki nanostrukturalnej: 1 - obraz wpływu cząstek na podłoże; 2 - obraz cząstek w dyszy, który pozwala zmierzyć prędkość, rozmiar i temperaturę poszczególnych cząstek

The coating quality is rather sensitive for spraying parameters that is why special diagnostic instrument and related methodology were developed for optimisation of deposition process at the development stage and process control at industrial implementation stage. Figure 6 presents typical images recorded by diagnostic tool.

4. CONCLUSION

Nanostructured WC/Co coating deposited by Detonation Spraying have great industrial potential like a wear resistant material with extended resource. This coating has more homogeneous microstructure, higher hardness and toughness and lower friction coefficient in comparison with conventional coating.

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