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# Study of the microstructure of plasma sprayed coatings obtained from $Al_2O_3$–$13TiO_2$ nanostructured and conventional powders

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ABSTRACT

The microstructure of coatings obtained from nanostructured or conventional $Al_2O_3$–$13TiO_2$ powders and deposited by plasma spraying technique on low-carbon steel was examined by transmission electron microscopy techniques. The dominating phase in both coatings was γ-$Al_2O_3$ phase. It has been observed that the grains of γ-$Al_2O_3$ grew in various shapes and sizes, that are particularly visible in the case of coating sprayed from nanostructured powder. The coatings obtained from the fully melted conventional powders exhibited a typical lamellar microstructure, into which the strips of $TiO_2$ phase were extended. The microstructure of coatings produced from agglomerates of nanostructured particles also revealed the regions consisting of partially melted α-$Al_2O_3$ powders surrounded by the net-like structure formed from fully melted oxides that improved the coating properties. Along with the observed morphology diversity some changes in the chemical composition on the cross sections of obtained coatings have been also noticed.



## 1. Introduction

Ceramic coatings composed of single or composite phases are frequently deposited using plasma spraying. Although the coatings produced by thermal spraying reveal numerous defects, such as pores and microcracks, the process efficiency is much higher and the costs are considerably lower, compared to coatings prepared by other processes. Therefore, it is possible to use this technique on an industrial scale. By combining advantages of a ceramic coating and a metal surface a material with good mechanical properties could be produced. During plasma spraying, the coating material, usually in the form of a powder, is injected into a plasma stream where it is heated and accelerated toward the substrate surface. Ceramic powders rapidly cool after impact with a substrate surface forming a coating. In the last years, a considerable progress in the fabrication of nanomaterials and the understanding of relationships between nanoscale processing, structure and macroscale properties is observed. The possibility of producing coatings with superior properties (e.g., wear resistance) compared to the conventional thermal sprayed coatings currently available, opens a wide range of research opportunities for various materials. Some researchers successfully obtained the nanostructured coatings by thermal spraying with reconstituted nanostructured powders, for example $ZrO_2$–$Y_2O_3$, $Cr_3C_2$–NiCr, WC–Co, and $Al_2O_3$–$TiO_2$ [1–4]. Although the production of nanostructured coatings is concentrated on compositions similar to currently available conventional coatings and using existing deposition equipment to fabricate them, the microstructure of the coatings changes. There are a large number of parameters that need to be selected, e.g., temperature and velocity of plasma, type and flow rate of gas used, the morphology of powder particles, distance from the gun to the substrate, position and orientation of the powder injection ports, and surface preparation of the substrate, which can affect the structure and properties of a coating. Additionally, the plasma spraying of nanostructured materials requires to form agglomerates approximately 30–100 μm in diameter, because very small particles lack a momentum necessary to penetrate into plasma [5,6]. The formation of substructures is closely related to the melting state of the feedstock powders during flying in the plasma jet and the flattening degree on impacting onto the substrate. Increase of the plasma spray power makes more powders fully molten, hence reducing the proportion of the unmelted or partially melted regions in the nanostructured coatings. The microstructure of the coatings with a retention of part of the original nanostructure is very desirable because it has beneficial effect on their mechanical properties. Plasma sprayed nanoceramic composite coatings $Al_2O_3$–$13TiO_2$ exhibited wear and corrosion resistance, bond strength and toughness unprecedented in a ceramic [5–8]. The nanostructured $Al_2O_3$–$13TiO_2$ coatings are of particular scientific interest because of their physical and mechanical properties, which are superior to those of conventional counterpart. The mechanical properties of nanostructured coatings are greatly improved as compared with those of the corresponding conventional coatings for example: hardness, bonding strength, crack growth resistance,

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**Table 1**
Parameters of the coating thermal spraying.

| Parameter | Value |
|---|---|
| Current, A | 550 |
| Voltage, V | 55 |
| Plasma gas pressure, MPa | 0.7 |
| Spraying distance, mm | 100 |
| Powder feeding rate, g/min | 90 |
| Spraying velocity, m/s | 0.3 |
| Ar flow rate, l/min | 37.2 |
| $H_2$ flow rate, l/min | 2.8 |

abrasive and sliding wear resistance, and thermal shock resistance [9–13]. They are closely connected to the microstructure of the obtained coatings, the phase composition, grain size and distribution of the existing phases.

Taking into consideration the fact that the microstructure obtained during deposition process is one of the main factors, which determine the properties of a composite coating, in this study the microstructures of the $Al_2O_3$–$13TiO_2$ coatings plasma sprayed from nanostructured and conventional powders were examined. A comparison of coatings obtained from the micro- and nanopowders was studied by researches in macroscale using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The present paper contains comprehensive analysis of the sprayed coatings carried out in micro scale using transmission electron microscopy (TEM) techniques for phase identification, chemical composition, grain shape and morphology. The similarities and differences of the obtained coatings visible on their cross sections were presented. Besides the morphology characterisation our interests are also focused on investigations whether variations of morphology observed in the examined coatings lead to significant changes of a chemical composition.

## 2. Methodology

The plasma spraying was carried out using the Plancer PN-120 gun equipped with the Thermal Miller 1264 powder feeder. The α-$Al_2O_3$ and $TiO_2$ (α-$Al_2O_3$:$TiO_2$ wt ratio = 87:13) powders were the main compositions. The coatings were plasma sprayed from the conventional (Amdry 6228) and nanostructured (Infralloy Nanox S2613S) powders designated as C and N, respectively. The coatings were deposited on substrates of flat surfaces prepared from low-carbon steel with dimensions of 30 × 30 × 3 mm. Before spraying, the substrates were degreased and grit blasted with electrocorundum EB-16 at the pressure of 0.5 MPa. The plasma generated for plasma spraying incorporated a mixture of argon (primary plasma gas) and hydrogen (secondary plasma gas), the latter constituting 7% of the mixture volume. The conventional (C) and nanostructured (N) coatings were deposited with the same parameters of plasma spraying as those presented in Table 1.

The morphology of the initial powders and produced coatings was already characterised in macroscale using XRD (crystallite phases) and SEM (morphology and microstructure examinations) techniques and presented in paper [14]. This paper contains detailed analysis of the morphology of both the top surfaces and cross sections and the chemical composition of obtained $Al_2O_3$–$13TiO_2$ coatings performed in micro/nanoscale using TEM (FEI TECNAI $G^2$). The thin foils were prepared by Focused Ion Beam (FIB) technique using FEI QUANTA 3D Dual Beam. The preparation of thin foil from the obtained coatings was very time-consuming, therefore two foils from each coating were examined.

## 3. Experimental Results

### 3.1. Characterisation of Powders

The C powder obtained in crushing manufacturing process contained only alumina and titania phases. The particles of the C powder had irregular shapes with sizes in the range of 10–100 μm. The N materials

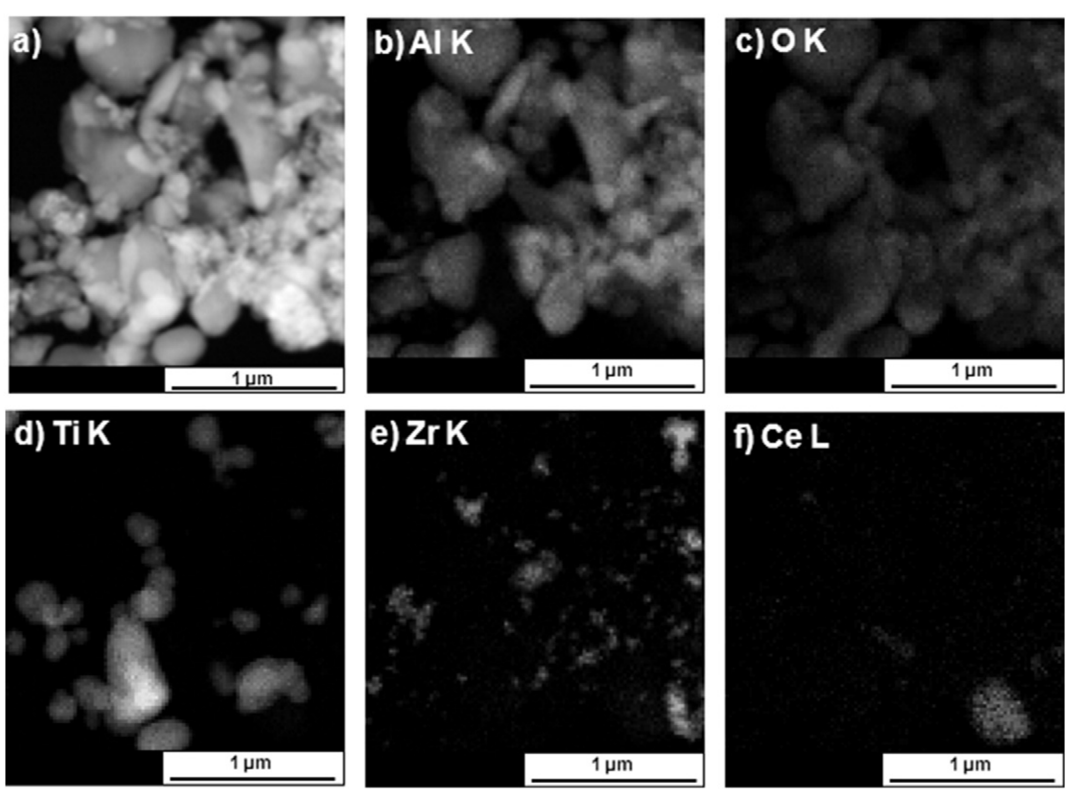


**Fig. 1.** a) STEM image of spherical particle of N powder; b–f) maps of elements distribution of Al, O, Ti, Zr, and Ce showing the internal nanostructured particles in the agglomerate.