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# Protective properties of $Al_2O_3$ + $TiO_2$ coating produced by the electrostatic spray deposition method

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A R T I C L E I N F O

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A B S T R A C T

Mechanical resistance of $Al_2O_3$ + $TiO_2$ nanocomposite ceramic coating deposited by electrostatic spray deposition method onto X10CrAlSi18 steel to thermal and slurry tests was investigated. The coating was produced from colloidal suspension of $TiO_2$ nanoparticles dispersed in 3 wt% solution of $Al_2(NO_3)_3$, as $Al_2O_3$ precursor, in ethanol. $TiO_2$ nanoparticles of two sizes, 15 nm and 32 nm, were used in the experiments. After deposition, coatings were annealed at various temperatures, 300, 1000 and 1200 °C, and next exposed to cyclic thermal and slurry tests. Regardless of annealing temperature and the size of $TiO_2$ nanoparticles, the outer layer of all coatings was porous. The first five thermal cycles caused a rapid increase of aluminum content of the surface layer to 30–37 wt%, but further increase in the number of thermal cycles did not affect the aluminum content. The oxidation rate of coating-substrate system was lower during the thermal tests than during annealing. The oxidation rate was also lower for smaller $TiO_2$ particles (15 nm) forming the coating than for the larger ones (32 nm). The protective properties of $Al_2O_3$ + $TiO_2$ coating against intense oxidation of substrate were lost at 1200 °C. Slurry tests showed that coatings annealed at 1000 °C had the best slurry resistance, but thermal tests had weakened this slurry resistance, mainly due to decreasing adhesion of the coating.

## 1. Introduction

Aluminum oxide ($Al_2O_3$) is usually used as ceramic coating for the protection of metal surface against high temperature because of high thermal stability and high resistance of this compound to thermal stress. However, pure $Al_2O_3$ coating has low fracture toughness that limits its application to thermal protection under dynamic loading. In order to improve the fracture toughness of $Al_2O_3$ coating, other compounds, for example, $TiO_2$ are added. Addition of $TiO_2$ favours the sintering of $Al_2O_3$ particles during annealing due to increased sintering rate [1]. Moreover, the sintering of titania with alumina particles promotes the reaction between them and formation of $Al_2TiO_5$ phase, which possess a good fracture toughness and wear resistance [2].

$Al_2O_3$-$TiO_2$ coating is usually produced by plasma or thermal spraying, sintering or by sol-gel method [1–9]. Due to increased demand on heat resistant coatings of improved mechanical and thermal properties, special attention has been given to $Al_2O_3$-$TiO_2$ coatings, which, however, have to be produced by cheaper and more effective method than plasma spraying or sol-gel technology. The morphology of coating, its adhesion and mechanical properties depend not only on the compounds used for the production of coating, but also on the method of its deposition [3,4,9]. Up to now, various investigations showed that wear resistance and mechanical properties (e.g. hardness) of an $Al_2O_3$-$TiO_2$ coating depend on the content of $TiO_2$ and on the size of particles used for the coating production [2–6]. Wang and Shaw [4] showed that coatings made from nanosize particles have better wear resistance than coatings made from microparticles, although other authors, for example, Luo et al. [9] have obtained opposite results. In our former paper [10], mechanical and thermal resistance of $Al_2O_3$ coating deposited by the electrostatic spray deposition method have been investigated.

In this paper, investigations of protective properties of $Al_2O_3$-$TiO_2$ coating produced by the electrostatic spray deposition method from $TiO_2$ nanoparticles and $Al_2O_3$ precursor ($Al(NO_3)_2 \cdot 9H_2O$), deposited on heat resistant steel X10CrAlSi18 and annealed at various temperatures, are presented. X10CrAlSi18 steel was chosen to these investigations in order to improve surface properties of that steel, in particular increase its working temperature. The resistance the coating to cyclic heating and its fracture under dynamic loading during slurry tests were also investigated. $TiO_2$ nanoparticles of two different sizes were used in the experiments in order to learn about the effect of the size of particles

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on the oxidation rate of coating and its resistance to dynamic loading. The annealing process was carried out at various temperatures (300, 1000 and 1200 °C) in order to investigate an influence of this temperature on coating properties (oxidation rate, resistance to dynamic loading).

The investigation of resistance of a material to dynamic loading can be performed by various methods, but slurry tests, which are used to study the coating adhesion and resistance to dynamic loading, belong to the simplest and inexpensive ones. During slurry tests, the surface of material is subjected to repetitive impingement of solid particles conveyed by flowing liquid. Investigations presented in Refs. [22–27] proved that slurry erosion rate of a material depends on its mechanical properties: hardness, fracture toughness, elastic modulus, the properties of impinging solid particles, their shape and hardness, their kinetic energy, the angle of impingement, but also on properties of conveying liquid. In the case of coating materials, slurry erosion rate depends on coating hardness, fracture toughness, elastic modulus also on coating thickness and adhesion of the coating to the substrate. Ceramic materials, to which $Al_2O_3$ belongs, are brittle and erode in the form of radial and lateral cracking, or ring cracking on the coating surface. The maximum erosion rate is reached for perpendicular impingement, i.e., at an incidence angle of 90°, and the main mechanism of material removal is brittle fracture [27,28].

Electrostatic spray deposition used to thin film deposition is a method of the formation of solid films from the aerosol phase, by which micron-sized droplets are produced via liquid atomization by electrical forces acting on the liquid jet flowing from a capillary nozzle. Electrostatic spraying of colloidal suspension of nanopowder or precursor solution allows production of thin solid film of on-demand properties after solvent evaporation [11,12,14,16–19]. The size of primary droplets produced by electrostatic spraying depends on physical properties of liquid, voltage applied to the nozzle and the liquid flow rate [13–16]. When the electric charge of a droplet (so called mother droplet) reaches the Rayleigh limit, the droplet undergoes fission into several smaller droplets (called progeny or daughter droplets) [15,20,21]. Those progeny droplets may undergo further fission, when they again attain the Rayleigh limit due to solvent evaporation, and finally they settle on a substrate forming a thin solid film from semi-dry particles. The novelty in the deposition technology used in this research is that the nanocomposite $Al_2O_3$-$TiO_2$ ceramic coating was produced in a single step by electrostatic spray deposition method from a mixture of $TiO_2$ nanoparticles dispersed as colloidal suspension in a solution of $Al_2O_3$ precursor ($Al(NO_3)_2 \cdot 9H_2O$) in ethanol.

## 2. Experimental

Nanocomposite $Al_2O_3$ + $TiO_2$ coating on ferritic X10CrAlSi18 steel was produced by the method of electrostatic spray deposition. Substrate specimens used in these investigations were 40 mm long and 10 mm wide, cut from the steel sheet of 4 mm thick. The corners of the specimens were made rounded with a radius of 5 mm, and their edges were smoothed in order to avoid unwanted electrical discharges from sharp points. Before coating, all substrates were sanded with sandpaper with grit 220, 400, 600 and 1000 SiC, washed in ultrasonic bath and weighed using an analytical balance of sensitivity of 0.1 mg. Next, all substrate specimens were thermally treated at a temperature of 800 °C for 1 h in Nabertherm L3/11 furnace, in order to obtain their optimal thermal and mechanical properties. After thermal treatment, substrates were sanded again with sandpaper with grit 800 and 1000 SiC, washed in ultrasonic bath and weighed. The roughness of surface of all substrates was measured by using SJ-301 Mitutoyo Surface Roughness Tester. After grinding, mean Ra roughness parameter of all specimens wasRa = 0.08 μm with a standard deviation of 0.04 μm, Rz = 0.65 ± 0.26 μm.

$Al_2O_3$ + $TiO_2$ coating was deposited from colloidal suspensions of

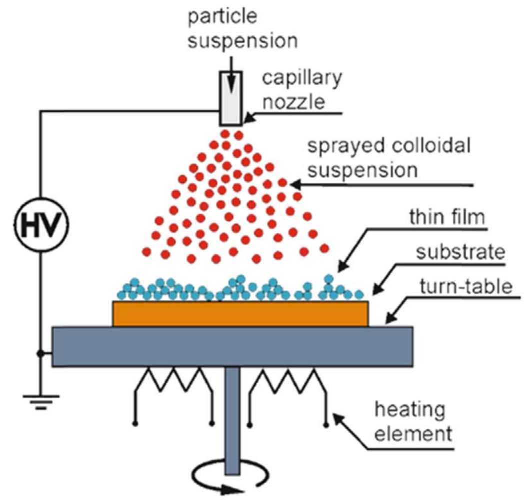


**Fig. 1.** Schematic of experimental set-up for $Al_2O_3$ + $TiO_2$ coating production by electrostatic spray deposition method.

$TiO_2$ nanoparticles, dispersed in 20 ml of 3 wt% solution of $Al(NO_3)_2 \cdot 9H_2O$ (as $Al_2O_3$ precursor) in ethanol ($C_2H_5OH$, 99.9% purity). $TiO_2$ nanoparticles were supplied by Alfa Aesar. Two kinds of suspensions, prepared from $TiO_2$ nanoparticles of two different mean sizes were used: suspension 1 prepared from 31.5 mg of 15 nm nanoparticles, dispersed in solution of $Al_2O_3$ precursor, and suspension 2 of 32 mg nanoparticles of size of 32 nm. The mixture of $TiO_2$ nanoparticles and $Al_2O_3$ precursor solution was stirred for 24 h, and the obtained colloidal suspension was sprayed for a time of 90 min.

Schematic of experimental set-up used for $Al_2O_3$ + $TiO_2$ coating production by electrostatic spray deposition method is shown in Fig. 1. A detailed description of the electrostatic spraying technology used for thin solid film deposition can be found in Ref. [10]. The system for electrostatic spraying comprised of stainless-steel capillary nozzle, connected to a high voltage supply of positive polarity set at 9.6 kV, and grounded metal collector, on which a specimen was placed. At this voltage, the multi-jet mode of electrospraying was stable that as necessary to generate monodisperse droplets, required for uniform $Al_2O_3$ + $TiO_2$ coating production. The outer and inner diameters of capillary nozzle were 0.8 mm and 0.65 mm, respectively. The distance between the nozzle tip and the substrate was 16 mm. The flow rate of suspension was 0.6 ml/h. The collector was designed as a turn-table, rotating with about 60 rpm in order to obtain more uniform deposition of droplets onto the substrate. To facilitate solvent evaporation and cause decomposition of aluminum nitrate (its melting point is 74 °C), the collector was heated to obtain the substrate temperature of about 120 °C.

Immediately after deposition, the coating was annealed at three different temperatures: at 300 °C for 1 h, at 1000 °C or 1200 °C for 3 h in furnace, and next cooled to room temperature within the furnace. A temperature of 1200 °C, much higher than typically allowed for ferritic X10CrAlSi18 steel, was chosen in order to check protective properties of the deposited coating subjected to extremely high temperatures. After annealing, all specimens were weighed in order to determine the oxidation rate during the annealing process. The oxidation rate $k_x$, has been determined from the ratio of an increase of specimen mass, $\Delta m$, during annealing time $t$ to the surface area of the specimen, $A$:

$$k_x = \frac{1}{t}\left(\frac{\Delta m}{A}\right)^n \tag{1}$$

The exponent $n$ depends on the type of oxidation mechanism. For lineal oxidation process $n$ = 1, while for parabolic oxidation process $n$ = 2. An influence of annealing temperature on coating morphology was studied using a scanning electron microscope EVO-40 (Zeiss).