Oxidation of Titanium Particles during Cold Gas Dynamic Spraying

Aleksandra Malachowska[1,2*], Marcin Winnicki[1], Lech Pawlowski[2], Bernard Pateyron[2], Andrzej Ambroziak[1], Pawel Sokolowski[1,2]
[1] Faculty of Mechanics, Wrocław University of Technology, W. St. Wyspianskiego 27, 50-370 Wroclaw, Poland
[2] SPCTS, UMR CNRS 7315, University of Limoges, 12, rue Atlantis, 87068 Limoges, France
*Corresponding author: Lukasiewicza 5, 50-371 Wroclaw, Poland, aleksandra.malachowska@pwr.wroc.pl

Abstract: This paper studies oxide forming on titanium, during cold gas dynamic spraying with air. This is a quite new spraying method, which can be used to spray material having high affinity for oxygen. The model allows for the diffusion of oxygen through the oxide layer, reaction on the oxide-titanium interface and expansion of oxide, due to difference in molar density. It was implemented in COMSOL Multiphysics through the Transport of Diluted Species and Deformed Geometry module. Simulations' results are linked to experimental oxide growth and data, available in the literature.

Keywords: Oxidation, titanium, cold spray

1. Introduction

The Cold Gas Spray Method (CGSM), called further the cold gas spraying, becomes an increasingly popular among thermal spraying methods, due to excellent properties of the coatings. In this method the powder particles are accelerated in the gas stream flowing through converging – diverging (de Laval) nozzle, and form coating upon impact onto the substrate. Because of the intensity of the impact, the oxide layer covering both particle and substrate may be broken, and their direct metallic bonding is possible [1]. It can be supposed, that the amount of oxide, in sprayed coating, is similar to the oxide amount in the powder.

The low temperature of the cold spray processes (well below the melting temperature of materials) makes it possible to deposit metal characterized by high affinity for oxygen, such as titanium. Helium and nitrogen are used as working gases, for cold spraying of titanium, due to their inert nature. The cold spray titanium coating is generally dense and its substrate adhesion parameters are salutary. Quite recently, considering the economic reasons, the researches on new gases are carried out, e.g. [2,3] the compressed air was tentatively used for titanium spraying. The quality of obtained coatings was reported as sufficient for industrial applications, although the oxide content was readily greater than in inert gases of cold sprayed coatings. Consequently, the oxidation process seems to be an important issue. The numerical simulation was chosen to determine the thickness of oxide, generated during the flight of particle in jet at processing.

2. Introduction

There are many models used for the simulation of oxide growth. Most of them assumed the O_2 diffusion through an oxide layer and reaction at the metal-oxide interface. In this study, the model proposed in [4] was used. It not only allows for study the O_2 diffusion, but also the expansion of oxide, due to the differences in the molar density between oxide and titanium. To simplify the calculation, only one dimensional model is used. The scheme of the model is presented in the Fig (1). There are three regions denoted: I - the air surrounding the sample, II – formed titanium dioxide, III - titanium respectively. During the oxidation, the air penetrates the titanium dioxide region, reaches the II/III interface, where the reaction takes place, and causes movement of II/III interface with the velocity of v_x^2, due to titanium consumption. At the same time, the I/II interface moves with the velocity of v_x^1 , due to the expansion of oxide. The following assumptions are made: Ti is initially oxygen-free; thermodynamic equilibrium is established at I–II interface; concentration of TiO_2 is constant [4].

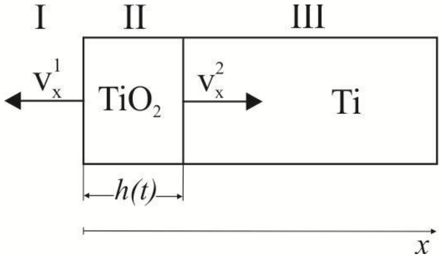

Figure 1. Scheme of 1D oxidation problem [4]

The mass balance for O_2 in oxide layer was written in form of second Fick's law:

$$\frac{\partial c_{O_2}}{\partial t} - D_{(O_2,TiO_2)} \frac{\partial^2 c_{O_2}}{\partial x^2} = 0 \quad (1)$$

Where - $D_{(O_2,TiO_2)}$ – diffusion coefficient of oxygen in titanium dioxide with following boundary conditions[4]:

$$c_{O_2} = c_0 \; at \; x = 0 \quad (2)$$

$$c_{O_2} = 0 \; at \; x = h(t) \quad (3)$$

Where: c_{O_2} is the equilibrium concentration of O_2 in titanium dioxide and h (x) indicates the oxide interface position.

The velocity of air-titanium interface (I/II) is given by equation[4]:

$$v_x^1 = -(1-\gamma)\frac{R_i}{R_0}\frac{D_{(O_2,TiO_2)}}{c_{TiO_2}}\frac{\partial c_{O_2}}{\partial x}\bigg|_{x=h(t)} \quad (4)$$

Where: R_i – the length of titanium region (III), R_0 – the length of oxidized titanium region (II), γ – the Pilling-Bedworth Ratio given by equation[4]:

$$\gamma \equiv \frac{c_{Ti}}{c_{TiO_2}} = \frac{\rho_{Ti}}{\rho_{TiO_2}}\frac{M_{(Ti)}}{M_{(TiO_2)}} \quad (5)$$

Where: ρ – density, M – molar weight.

And the velocity of the oxide-titanium interface (II/III) is denoted by equation[4]:

$$v_x^2 = -\frac{D_{(O_2,TiO_2)}}{c_{TiO_2}}\frac{\partial c_{O_2}}{\partial x}\bigg|_{x=h(t)} \quad (6)$$

The detailed description of the model can be found in [4,5].

The densities of Ti and TiO_2 are as follow 4500 kg/m^3 and 4250 kg/m^3, and respectively the molecular weights are 47.9 kg/kmole and 79.9 kg/mole [4]. Therefore the concentration of titanium (c_{Ti}) and titanium dioxide (c_{TiO_2}) are equal to 93.9 kmole/m^3 and 53.2 kmole/m^3, and hence the γ is 1.766, c_0 is 12.5 kmole/m^3[4,6].

For the one dimension oxidation problem, without an expansion of oxide, there is an analytic solution given by equation[4]:

$$h(t) = \lambda\sqrt{4tD_{(O_2,TiO_2)}} \quad (7)$$

Where: λ = 0.33

The model, described above, was implemented in COMSOL through the Transport of Diluted Species and Deformed Geometry modules and checked with analytic solution.

The particle's temperature and the residence time, in the nozzle region during the cold spraying, was calculated in MATLAB, using isentropic gas model and following equations for particle[7]:

$$m_p \cdot \frac{dv_p}{dt} = \frac{3}{4}\frac{C_D}{D_p}\frac{\rho_g}{\rho_p}\left(v_g - v_p\right)\left|v_g - v_p\right| \quad (8)$$

Where: C_D is the drag coefficient , v_p is particle velocity, v_g is gas velocity, ρ_p – density of particle material, ρ_g – density of gas:

$$\frac{dT_p}{dt} = v_p \cdot \frac{dT_p}{dx} = \left(T_g - T_p\right)\frac{6h}{c_{pp}\rho_p D_p} \quad (9)$$

where, T_p is particle temperature, T_g is gas temperature, c_{pp} is heat capacity of particle, v_p is particle velocity, C_{pg} is heat capacity, h is heat transfer coefficient related to the thermal conductivity of gas by Nusselt number (Nu),

The detailed description can be found in i.e. [7].

3. Description of simulated experiment

Air was used as accelerating gas, with the inlet temperature of T_i = 800° K and pressure of p = 2.0 MPa. The velocity of initial gas and particle was assumed to be 10 m/s. The initial particle temperature was equal to 300 K. The geometry of nozzle, used for calculation, is presented in the Fig 2 and dimensions are given in the Table 1. The particles have a diameter of 20 and 10 μm. The initial surface oxide thickness was assumed to be 6 x 10-9 m [8]

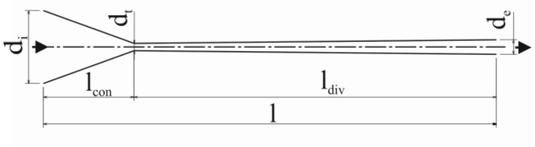

Figure 2. Nozzle geometry used for calculations

Table 1. Nozzle dimensions

Powder injection	d_i [mm]	d_t [mm]	d_e [mm]	l [mm]	l_{con} [mm]	l_{div} [mm]
axial	40	2	4	250	50	200

4. Results and discussions

The obtained particle temperature is presented in Fig 3. And the particle velocity in Fig 4.

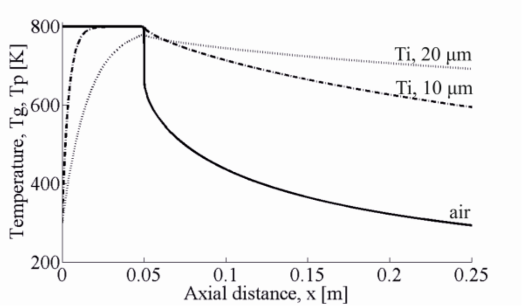

Figure 3. Titanium particles temperature during cold spraying

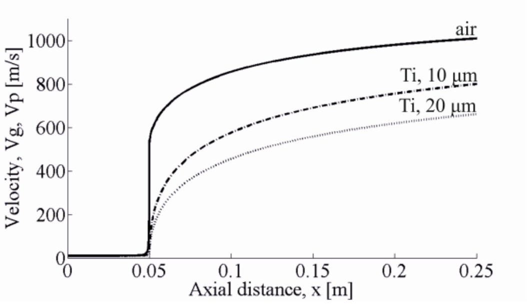

Figure 4. Titanium particle velocity during cold spraying

The results of the MATLAB calculation were implemented in COMSOL to calculate the diffusion coefficient, which was taken in form of equation from [9]:

$$D_{(O_2,TiO_2)} = 870\exp(-\frac{55535}{RT}) \qquad (10)$$

The obtained diffusion coefficients are presented in Fig. 5 and Fig. 6.

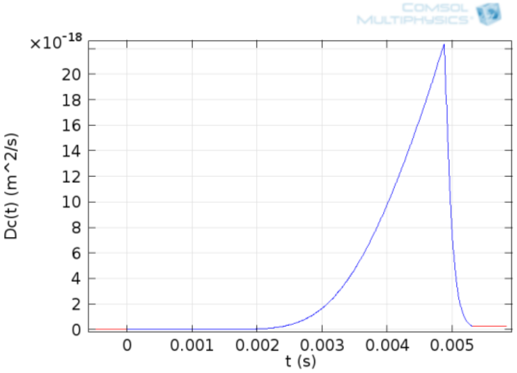

Figure 5. Calculated diffusion coefficient for particle 20 μm

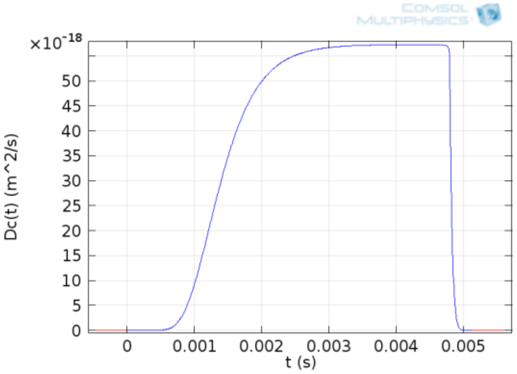

Figure 6. Calculated diffusion coefficient for particle 10 μm

The calculated oxide thickness for particle with diameter 20 μm and 10 μm is presented in Fig.7 and Fig. 8 respectively.

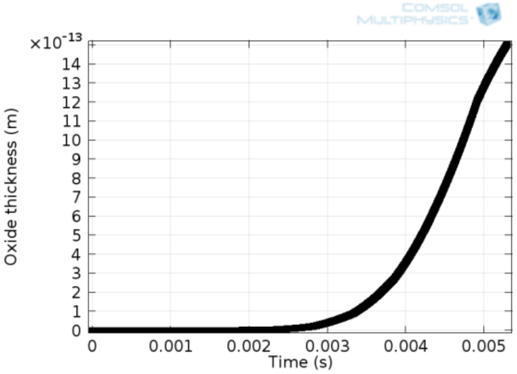

Figure 7. Oxide thickness grow during residence time in nozzle for particle 20 μm

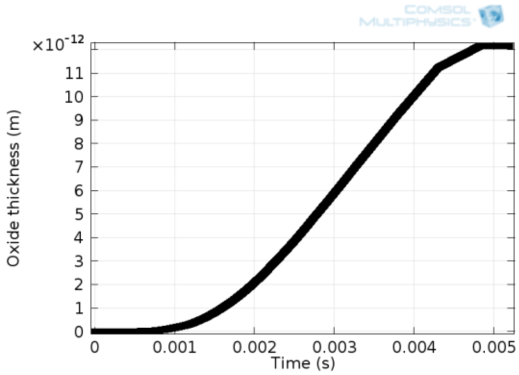

Figure 8. Oxide thickness grow during residence time in nozzle for particle 10 μm

As can be seen on the fig 7. and 8, although titanium is very reactive metal, especially in increased temperature, the oxide layer formed during spraying is very thin. This is due to the low temperature of the process and a very short residence time in the nozzle, which is about 0,0052 s. Such thin layer, in compare to naturally formed oxide, should have negligible influence on the bond formation, but the model does not allows for the phenomena of oxygen dissolution in titanium. This is very important issue, as titanium can dissolve up to about 13 wt. % [10].

It is reported that during the impact onto the surface, the oxide layer is broken and removed as a jet [7,11]. In turn in the work of Lee [3], there is reported an increase of the oxygen content in the obtained Ti-6Al-4 coating, comparing to the original feedstock powder used for the spraying process, from 0.42 wt. % to 0.57 wt. %. It may be explained due to much longer contact time between the forming coating and air issuing from the nozzle. The other issue is possibility of damage to the oxide layer during the spraying process. In that case the new layer is formed in instantly. As can be seen on fig 9 in case when the originally oxide layer is about 1e-10 μm during the same spraying conditions the formed oxide thickness is one order of magnitude grater.

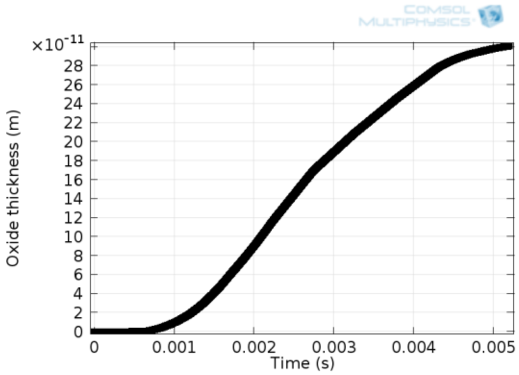

Figure 9. Oxide thickness grow during residence time in nozzle for particle 10 μm when initial oxide thickness 1e-10 μm

5. Conclusions

Due to economic benefits, several attempts have been conducted to understand the influence of using air as accelerating gas in the cold spray method. In this work, the thickness of an oxide layer, built during spraying, was investigated. The model was adopted from [4] and introduced to COMSOL. It seems that the oxygen dissolution in titanium as well as the possibility of damage to the oxide layer have an effect on the final oxidation of the sprayed coating but much more important issue is the long contact time between the air stream and forming coating. The further work is necessary for a better understanding of influence of air spraying, instead of inert gases.

6. References

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