INVESTIGATION OF RESIDUAL STRESSES IN COMPOSITE Ti+Al_2O_3 COATINGS DEPOSITED BY THERMAL SPRAYING ONTO CERAMIC SUBSTRATE

The residual stresses in thermally sprayed coatings are of great interest since they affect the reliability of the coating/substrate system. The evaluation of residual stresses in thermally sprayed composite Ti+Al_2O_3 coatings on Al_2O_3 ceramic substrates has been conducted. The purpose of the research was to measure the residual stresses generated in coatings deposited by detonation gun thermal spraying and compare the results obtained for pure titanium and Ti+30% Al_2O_3 composite coating. The stresses in deposited coatings have been obtained from the curvature measurement of the analyzed samples. A measuring system has been built for this purpose, which allowed registering of the curvature of the coated samples. The residual stresses have been calculated from the measurements using the Stoney equation and compared with the results obtained from the modified Stoney equation derived by Clyne. It was observed that tensile residual stresses are formed within the coating and grew with the coating increase. The applied stress calculation formula showed that for higher coating thicknesses, the primary Stoney equation underestimates the results comparing to the modified Stoney formula (Clyne).

Keywords: thermal spraying, residual stresses, composite coatings

BADANIE NAPRĘŻĘŚ WŁASNYCH W POWŁOKACH KOMPOZYTOWYCH Ti+Al_2O_3 NANOSZONYCH PRZEZ NATRYSKIWANIE CIEPLNE NA PODŁOŻE CERAMICZNE

Badania naprężeń własnych w natryskiwanych cieplnie powłokach metalicznych, ceramicznych czy kompozytowych należą do jednego z ważniejszych zagadnień, bowiem stan naprężeń może decydować o trwałości eksploatacyjnej nanoszonych powłok. W pracy dokonano oceny naprężeń własnych w natryskiwanych cieplnie powłokach kompozytowych Ti+Al_2O_3 na podłożu Al_2O_3. Celem badań było określenie naprężeń własnych powstających w powłokach kompozytowych (Ti+Al_2O_3) nanoszonych na podłoże ceramiczne metodą detonacyjną oraz porównanie otrzymanych wyników w stosunku do powłok nanoszonych z czystego tytanu. Naprężenia w powłokach wyznaczano w oparciu o pomiary krzywizny próbek z powłokami kompozytowymi i metalicznymi. W tym celu skonstruowano przyrząd z czujnikiem cyfrowym do rejestracji wygięcia próbek. Naprężenia własne obliczono z wykorzystaniem równania Stoneya oraz zmodyfikowanego równania Stoney’a (Clyne). Wyniki obliczeń wskazują, że w powłokach powstają rosnące naprężenia własne, których wielkość rośnie ze wzrostem grubości powłoki. Wyznaczono wielkość naprężeń własnych z użyciem równania Stoneya wykazują, że ze wzrostem grubości powłoki rośnie ich niedoszacowanie w stosunku do obliczeń dla zmodyfikowanego równania Stoneya (Clyne).

Słowa kluczowe: natryskiwanie cieplne, naprężenia własne, powłoki kompozytowe

INTRODUCTION

Thermal spraying belongs to one of the most versatile deposition methods of coatings used for the modification of substrate material. The application of this process to coat advanced ceramics (e.g. Al_2O_3, AlN) used for surface modification and regeneration can bring many economic advantages. As an example, the metallization of an advanced ceramic is an essential process used in joining ceramics to metals. Nowadays, these kinds of joints are used in many engineering applications in optoelectronics, semiconductor, nuclear or high vacuum industries [1, 2]. The thermal spraying of metals and composites onto ceramic substrates has the potential to become a cheaper and faster processing method comparing to the common but expensive and complex techniques used for ceramic metallization.

In the case of joining two materials (ceramic, metal) with highly different thermal and physical properties, high residual stresses may develop in the coating/substrate system. Their magnitude and distribution within the deposit and at the coating/substrate interface play an important role in the strength of the whole joint that often works under variable external loads. Unfavorable residual stresses formed after thermal spraying may lead to coating degradation or even failure, reduc-
ing its service life substantially [3]. Therefore, evaluation of the residual stresses in thermally sprayed metal and composite coatings is one of the most important research problems.

To estimate the residual stresses within the coatings deposited by many thermal spraying techniques, several methods have been applied which include layer removal, hole drilling, curvature measurement, X-ray diffraction and neutron methods [4]. Each of them has both advantages and disadvantages, which means that no single universal stress measuring method exists. Depending on the type of coating and substrate materials, the residual stresses may be tensile or compressive inside the coating and reach low and high stress levels that can affect the durability and stability of the coating both after the deposition as well as during its service life. Several research works devoted to residual stress estimation in coatings deposited by thermal spraying have been conducted. Most of them are related to metal (steel) substrates and metal, ceramic and composite coatings. The measurements of residual stresses in Mo, Ni+Al2O3 and NiCrAlY+YSZ composite thermal barrier coatings deposited on a steel substrate by plasma spraying have been conducted by the sample curvature, X-ray and neutron diffraction methods [5]. The residual stresses in the Mo layers obtained from curvature and X-ray measurements showed a good correlation with coating thickness increase but the stress level differed substantially which mainly resulted from the shallow X-ray penetration (around 100 MPa from curvature measurements against 40 MPa for X-ray method). The residual stress in a graded layered composite Ni+Al2O3 coating was tensile in the part containing pure Ni and changed into compressive for the pure Al2O3 layer. The residual stresses reached a neutral level at about an 80% of Al2O3 volume fraction for the curvature method and at about 30% for the neutron diffraction method. The general stress level was reported higher in the curvature measurements, which could be explained by the different specimen sizes required in each measuring technique. Using ZrO2 in the NiCrAlY+YSZ composite, we may reach lower residual stresses in a metal-ceramic composite coating due to the lower thermal expansion mismatch between the coating and steel substrate compared to the Al2O3 phase used in Ni+Al2O3 coatings. An extended comparison between the curvature measurement and X-ray diffraction method was presented in [6] for AISI 316 stainless steel and an Fe3Al-based alloy deposited onto low carbon steel by the HVOF spraying method. Good agreement has been reached for coatings sprayed at the lowest velocity, but not at greater particle velocities. The applied Stoney formula and the Tsui-Clyne progressive deposition models predicted trends corresponding to the XRD measurements, but with no quantitative agreement. Moreover, these models agreed for thin coatings where the residual stress reached about −300 MPa while the stresses in the substrate varied from compressive at the outer surface to tensile at the coating-substrate interface. The results of

in-situ measurements of residual stresses in plasma sprayed NiCrAlY and zirconia on a steel substrate were shown in [7]. The obtained through-thickness stress profiles presented tensile residual stresses within the coatings and tensile to compressive stresses inside the substrate. The residual stresses in zirconia coatings were very small (a few MPa) due to microcracks formed during the quenching of the coating. That was also confirmed by the neutron diffraction measurements. The effect of the coating thickness on the residual stresses was studied in [8] for WC-Co coatings deposited onto AISI 316L steel by the HVOF thermal spraying method. The residual stresses showed the top surface of the deposits to be in tension. The stress at the interface changed from compressive at the coating-substrate interface to tensile at the substrate side. This allowed finding a coating thickness for which the top coating stress passed through the stress-free state. The calculated residual stresses using Clyne’s analytical method were also measured using X-ray diffraction and the hole-drilling method. The differences in stress magnitude in these three methods are visible but the correlation between the methods is particularly good for higher deposit thicknesses. Nowadays, many research works include the modeling of residual stresses in thermally sprayed coatings by using the finite element method [9-13]. The developed models try to imitate the coating and substrate geometry together with initial and boundary conditions that simulate the part of the thermal spraying process that is responsible for residual stress generation in the coating-substrate system. The results of residual stress modeling need to be compared to experimental data otherwise the calculated stress state should be treated qualitatively.

In this paper, we have investigated the residual stresses in Ti and composite Ti+30%Al2O3 coatings deposited onto an Al2O3 substrate by the detonation gun (D-Gun) spraying method. The application of composite Ti+Al2O3 coatings instead of titanium coatings was applied in order to reduce the difference in material properties between the coating and substrate, which would help to reduce the residual stresses. The experimental system based on the measurement of curvature of the deposited samples has been used for this purpose. The residual stresses were calculated using the well-known formula developed by Stoney and compared to the results obtained from the modified Stoney equations (Clyne), accounting for the stress distribution across the thickness of the coating/substrate system.

THEORY

Stresses in deposited coating based on sample curvature

Residual stresses (σ) in thermally deposited coatings are the sum of the stresses coming from the quenching of melted droplets of coating material and the stresses developed during the cooling of the whole coa-
ting/substrate system. The simplest coating/substrate system may be treated as a layout of two bonded plates (Fig. 1a). As a result of the shrinkage of the coating and substrate resulting from the deposition process, a misfit strain $\Delta \varepsilon$ in the $x$-direction is imposed (Fig. 1b). The misfit strain can be replaced by the transverse opposite forces $P$ that must be in balance for the whole system (Fig. 1c). The final bending moments $M$ develop (Fig. 1d) and the curvature $\kappa$ of plates occurs, which can be measured and related to the residual stress.

Assuming the coating thickness is much smaller than that of the substrate, the average stress in a coating according to Stoney [14] can be obtained from the formula:

$$\sigma = \frac{1}{6} \frac{E_s}{(1 - \nu_s)} h_c^2 \left( \frac{1}{R_2} - \frac{1}{R_1} \right)$$  \hspace{1cm} (1)$$

where:
- $E_s$ - Young's modulus of substrate,
- $\nu_s$ - Poisson ratio of substrate,
- $h_c$ - coating thickness,
- $R_{2,1}$ - radius curvature (2 - after spraying, 1 - before spraying).

When the ratio of coating to substrate thickness does not satisfy that assumption, then the residual stresses would also be important within the substrate material. In such a case, the Stoney formula needs to be modified to account for the stresses both in the coating and in the substrate. There are several modifications of the Stoney equation that can be found in literature. One of the mostly known developed by Clyne [15] allows one to obtain the solution for the stresses in both the coating and substrate:

- stress at the top of coating surface:

$$\sigma_c \bigg|_{y=0} = \frac{P}{bh} + E_c \kappa (h - \delta)$$  \hspace{1cm} (2)$$

- stress at the bottom of coating surface:

$$\sigma_c \bigg|_{y=-h} = \frac{P}{bh} - E_c \kappa \delta$$  \hspace{1cm} (3)$$

- stress at the top of substrate surface:

$$\sigma_s \bigg|_{y=0} = \frac{P}{bh} - E_s \kappa \delta$$  \hspace{1cm} (4)$$

- stress at the bottom of substrate surface:

$$\sigma_s \bigg|_{y=-H} = \frac{P}{bh} + E_s \kappa (h + \delta)$$  \hspace{1cm} (5)$$

where:
- $\sigma_{c,s}$ - stress in coating (c), stress in substrate (s)
- $\Delta \varepsilon = (\alpha_c - \alpha_s) \Delta T$
- $\alpha_{c,s}$ - coefficient of thermal expansion for coating (c) and substrate (s)
- $\Delta T$ - temperature difference
- $h$ - thickness of coating
- $H$ - thickness of substrate
- $E_{c,s}$ - Young’s modulus of coating (c) and substrate (s)
- $\kappa$ - curvature of sample (1/R)
- $\delta$ - distance from neutral axis $y_c = 0$ to coating/substrate interface

This formula assumes an isotropic in-plane stress state ($x,y$). It needs the Young modulus to be replaced by the corrected modulus $E' = E/(1 - \nu)$, which is required for the coating/substrate system with a bi-axial stress state within the deposit.

**EXPERIMENTAL PROCEDURE**

**Scope of research**

The investigation has been conducted in order to estimate the residual stresses in composite Ti+30% Al2O3 coatings deposited by detonation thermal spraying onto an Al2O3 substrate by using sample curvature measurements and stress calculation using the Stoney equation.
Investigation of residual stresses in composite Ti+Al₂O₃ coatings deposited by thermal spraying onto ceramic substrate

and a modified formula developed by Clyne. The Ti+Al₂O₃ composite coatings were used instead of a pure titanium coating in order to analyze the effect of residual stress reduction in the produced coatings. Several coating thicknesses have been analyzed to see how they affect the residual stresses in the deposit.

Thermal spraying

The detonation gun (D-Gun) spraying method was used to deposit the coating material onto the ceramic substrate. This spraying technique was selected because it allows the generation of high kinetic energy of transporting particles, which make a strong coating adhesion to the substrate reaching up to 80 MPa [16]. It is based on the controlled detonation of a gas mixture (mostly acetylene with oxygen) started by an electric ignition between electrode sparks. Detonation of the gas generates a shock wave heating each particle of the coating material and accelerates them in a special gun up to 1200 m/s [17]. The discreet manner in which the particles are deposited in this method allows the coating/substrate system to heat up to much lower temperatures comparing to other thermal spraying methods. The D-Gun thermal spraying technique has the advantage to obtain even coatings with good adhesion and low porosity. It is possible to deposit coatings thinner than 0.1 mm while keeping the coating sealed to the substrate (Fig. 2).

Materials

For the purpose of the experiment, the coating consisted of pure titanium powder (grain size 30÷50 μm), which later was modified into a Ti+30% Al₂O₃ composite powder mixture. In both cases, the substrate material was an Al₂O₃ plate sample (30 mm length x 20 mm width) with a 0.655 mm thickness.

The spraying was conducted in four series, each one using four samples to obtain different thicknesses of coating (0.1; 0.145; 0.22, 0.35 mm by average). All of the deposited pure Ti and composite Ti+Al₂O₃ coatings adhered to the substrate over the whole deposited area. Table 1 presents the main deposition parameters.

<table>
<thead>
<tr>
<th>Coating material</th>
<th>Ti/(Ti+30% Al₂O₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detonation frequency [Hz]</td>
<td>4</td>
</tr>
<tr>
<td>Detonation gas mixture</td>
<td>C₂H₂+O₂</td>
</tr>
<tr>
<td>Acetylene pressure [MPa]</td>
<td>0.12</td>
</tr>
<tr>
<td>Oxygen pressure [bar]</td>
<td>0.12</td>
</tr>
<tr>
<td>Nitrogen pressure [MPa]</td>
<td>0.08</td>
</tr>
<tr>
<td>Distance between gun and substrate [mm]</td>
<td>160.0</td>
</tr>
<tr>
<td>Coating thickness [mm]</td>
<td>0.1÷0.35</td>
</tr>
</tbody>
</table>

Measurement of coating/substrate deflection

The deflection h of the samples was measured directly after each spraying run using a dial gauge fixed on a special stand. The measurement was conducted at the center of the sample on the substrate side (Fig. 3). The indication of the dial gauge was calibrated to zero for each ceramic substrate before the deposition.

![Fig. 3. Image of deflection measuring system (a), and scheme of sample curvature measurement (b)](image-url)

Rys. 3. Widok przyrządu do pomiaru wygięcia (a) oraz schemat pomiaru wygięcia próbki (b)

The measured deflections (averaged from four samples) are shown in Table 2 for their corresponding
thicknesses of the obtained deposits. Using geometric relations, the curvature of each sample was calculated.

### TABLE 2. Averaged deflection measured for samples of Ti and Ti+30% Al<sub>2</sub>O<sub>3</sub> coatings deposited onto Al<sub>2</sub>O<sub>3</sub> substrates

<table>
<thead>
<tr>
<th>Coating thickness [mm]</th>
<th>Coating deflection h [mm]</th>
<th>Ti</th>
<th>Ti+30% Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>0.01050</td>
<td>0.00900</td>
<td></td>
</tr>
<tr>
<td>0.145</td>
<td>0.01575</td>
<td>0.01200</td>
<td></td>
</tr>
<tr>
<td>0.220</td>
<td>0.03050</td>
<td>0.02225</td>
<td></td>
</tr>
<tr>
<td>0.350</td>
<td>0.07725</td>
<td>0.05850</td>
<td></td>
</tr>
</tbody>
</table>

### RESULTS

The mean residual stress ($\sigma$) in the coating calculated with equation (1) as a function of coating thickness is shown in Figure 4. It is apparent that the composite Ti+30% Al<sub>2</sub>O<sub>3</sub> coating has lower stresses comparing to a pure titanium coating. The increase of coating thickness led to an increase in the mean stress in both types of deposits reaching a maximum level of 53÷70 MPa. The difference in stress levels for both the Ti and composite coating is the lowest at the smallest thicknesses. The stresses reached about 29÷34 MPa in the deposit having smaller a magnitude in composite coatings.

![Fig. 4. Effect of coating thickness on mean residual stress ($\sigma$) within deposited coating calculated using Stoney equation (1)](image)

Rys. 4. Wpływ grubości powłoki na średni naprężenie własne ($\sigma$) w naniesionej powłoce obliczone za pomocą równania Stoneya (1)

To obtain the stress distribution across the coating and substrate, the modified Stoney equation has been applied. Using eq. 2-5 we received the residual stress $\sigma$ values in the metal and composite coatings and in the Al<sub>2</sub>O<sub>3</sub> substrate. The stress distribution for Ti+30% Al<sub>2</sub>O<sub>3</sub> coatings is shown in Figure 5. A similar distribution was obtained for the Ti coating but the stress level is higher. Both types of coatings show similar stress profiles characterized by the highest tensile stresses at the top of the coating, with a sudden stress drop at the coating/substrate interface and mostly compressive stresses in the substrate.

![Fig. 5. Residual stress ($\sigma$) distribution across coating and substrate for a) composite Ti+30% Al<sub>2</sub>O<sub>3</sub> deposits, b) titanium deposits calculated using Clyne formula (eq. 2-5)](image)

Rys. 5. Rozkład naprężenia własnego ($\sigma$) na grubości powłoki i podłoża dla: a) powłok kompozytowych Ti+30%Al<sub>2</sub>O<sub>3</sub>, b) dla powłok tytanowych obliczony wg formuły Clyne’a (równ. 2-5)

To compare the stresses calculated in the coatings through the Stoney equation, with the stresses calculated by the modified Clyne formula, the coating stress has been averaged over its thickness using the top and bottom coating stress values (eq. 2-3). The results are shown in a joint graph as a function of coating thickness (Fig. 6). The differences of stress level between the two calculation methods are not substantial for the smallest coating thicknesses (0.1 mm). A higher mismatch is visible for the composite coatings with an increase in coating thickness (0.35 mm). It may be the effect of the Stoney formula limit, which is mainly applicable to the low coating to substrate ratios. In this case, deposits with the highest coating ratios have not satisfied this condition, therefore calculation with the modified Stoney equation has been done.

The mean residual stresses measured in the Ti and Ti+Al<sub>2</sub>O<sub>3</sub> coatings deposited by the D-Gun method have not reached very high magnitudes. For the thinner deposits, the stresses reached 31÷36 MPa while for the thickest coatings 70÷80 MPa.
The important factor that affects such a stress level is the relatively low temperature to which the substrate is heated up during the deposition process. In the conducted calculations, it was assumed that the temperature of the substrate material increased to a maximum of 100°C based on the temperature measurement of the bottom surface of the Al$_2$O$_3$ plates during deposition.

**CONCLUSIONS**

The results of stress calculation based on sample curvature measurements of composite Ti+30% Al$_2$O$_3$ and pure titanium deposits have shown that the produced deposits exhibited tensile residual stresses that were strongly dependent on the coating thickness. For each coating thickness, the composite deposits revealed a lower stress level compared to the titanium coatings. For the highest thicknesses (0.350 mm), the maximum measured stress at the top of the coating was tensile and reached 91 MPa in the Ti+30%Al$_2$O$_3$ composite, which was 15% lower than that in the titanium coatings according to the Clyne (modified Stoney) formula. The stress results obtained from the classical Stoney equation showed these differences to be higher, reaching up to 30% between the titanium and composite coatings.

For smallest coating to substrate thickness ratios, both formulas of stress calculation (classical Stoney and modified Clyne) exhibited very close results of mean coating stresses (31±36 MPa). In each case, the composite Ti+30% Al$_2$O$_3$ coating showed lower residual stresses compared to the corresponding titanium coating which is mainly due to the effective composite material properties having a smaller mismatch comparing to the thermo-physical properties of the ceramic substrate.

The calculated residual stresses in the analyzed coatings have not reached large tensile magnitudes. There are no literature data showing the estimation of the residual stresses for composite/metal coatings thermally sprayed on ceramic substrates. The reverse system e.g. metal/composite/ceramic coatings deposited on metal substrates are mostly analyzed with the plasma spraying method. The stresses obtained by curvature, X-ray or neutron diffraction measurements have usually reached magnitudes in the range of 40±300 MPa both tensile and compressive depending on the material configuration.

The one of the main causes of the low tensile stresses in the Ti and composite Ti+30% Al$_2$O$_3$ deposits formed on the ceramic substrate seems to be the application of the detonation (D-Gun) spraying method. It introduced a much lower heat energy into the substrate material in reference to other deposition processes (flame, plasma, HVOF spraying) where the coating and substrate are heated to higher temperatures, which could be responsible for much larger residual stresses.

**Acknowledgements**

This work was supported by the National Science Centre under project No. N N519 652840

**REFERENCES**


