Characterisation of the TiO$_2$ coatings deposited by plasma spraying

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Abstract. Plasma spraying of materials such as ceramics and non-metals, which have high melting points, has become a well-established commercial process. Such coatings are increasingly used in aerospace, automobile, textile, medical, printing and electrical industries to impart proprieties such as corrosion resistance, thermal resistance, wear resistance, etc.

One of the most important characteristics of thermal barrier coatings is the ability to undergo fast temperature changes without failing, the so called thermal shock resistance.

The formation of residual stresses in plasma sprayed ceramic and metallic coatings is a very complex process. Several factors, such as substrate material, substrate thickness, physical properties of both the substrate and the coating material, deposition rate, relative velocity of the plasma torch, etc. determine the final residual stress state of the coating at room temperature.

Our objective is to characterize the titanium oxide and aluminium oxide coatings deposited by plasma spraying in structural terms, the resistance to thermal shock and residual stresses.

1. Introduction

Ceramic thermal barrier coatings deposited by plasma spraying are used aerospace, automobile, textile, medical, printing and electrical industries to impart proprieties such as corrosion resistance, thermal resistance, wear resistance, etc. [1], [2].

The coating is built up particle by particle and it has a lamellar structure resulting from the flattening of particles on already solidified flattened particles of the substrate. Thus the thermomechanical properties of the coatings depend strongly on the effective contacts between the lamellar and the cracks network resulting from relaxation stresses (stresses induced during spraying or in service condition) [3].

Our objective is to characterize the TiO$_2$ and Al$_2$O$_3$ coatings deposited by plasma spraying in structural terms, the resistance to thermal shock and residual stresses.
2. Experimental part

2.1. Experimental conditions at the TiO2 coatings spraying in plasma

The substrate is a martensitic stainless steel (Z12CNDV 12) whose chemical composition is presented in Table 1.

| Chemical composition | C     | Si    | Mn    | S     | P     | Cr    | Ni    | Mo    | V     | N2    |
|----------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|                      | 0.06  | ≤ 0.50 | ≤ 0.35 | 0.50  | 0.25  | 11.0  | 2.00  | 1.5   | 0.25  | 0.02  |
|                      | 0.15  | 0.35  | 0.90  | 0.025 | 0.035 | 12.5  | 3.00  | 2.0   | 0.40  | 0.04  |

The powder used is Metco 102, with 99% TiO2 and particle sizes between 7.8 and 88 μm.

The coatings have been made using the GPPR-400 plasma generator.

The work has been done using the following parameters: intensity of the current at the generator: 500 A, voltage: 70 V, spraying distance: 70 mm, plasma gas flow: 36.6 l/h, coating thickness: 0.3 mm.

2.2. Thermal shock testing

For the coats made by using the Metco 102 powder on a martensitic stainless steel substrate, the thermal shock testing consist in: fast heating to 800°C or 500°C in 10s and immediate water cooling (600°C/s) without maintaining the maximum temperature.

2.3. The model of Takeuchi for calculation of residual stresses in plasma sprayed ceramic coatings

The formation of residual strains in plasma sprayed ceramic and metallic coatings is a very complex process. Several factors, such as substrate material, substrate thickness, physical properties of both the substrate and coating material, deposition rate, relative velocity of the plasma torch, etc., determine the final residual stress state of the coating.

Several authors present models concerning the origin of residual stresses in plasma sprayed ceramic and metallic coatings. Many of the models are merely qualitative and predict only the sign of the stress in the coating, compressive or tensile [4-6].

Takeuchi [7], Elsing [8-10] and Buckley-Golder [11], [12] present quantitative models for the calculation of residual stress. The model of Takeuchi takes primary cooling into account by introducing a strain term εe, representing strains in the coating caused by primary cooling. The Takeuchi model uses a uniform substrate temperature and assumes that the entire coating is deposited in one pass.

The stress in the coating at elevated substrate temperature is describe by the following equation:

\[
\sigma_i (x, t, \text{Ts}) = E_c \left[ \left( \frac{E_c \cdot \varepsilon_c + E_s \cdot \varepsilon_s}{E_c \cdot \varepsilon_c + E_s \cdot \varepsilon_s} \right)^{\varepsilon_e} \left( 1 + \varepsilon_e \right) - 1 \right]
\]

Where:
- \( x \): position in coating [m]
- \( E_c \): Young's modulus coating [Pa]
- \( E_s \): Young's modulus substrate [Pa]
- \( t_s \): thickness of substrate [m]
- \( t_c \): thickness of coating [m]
- \( \varepsilon_c \): strain in coating due to primary cooling [-]
- \( \text{Ts} \): substrate temperature [K].

According to Takeuchi, the strain \( \varepsilon_e \), caused by primary cooling equals:

\[
\varepsilon_e = \alpha_c (T_m - T_s)
\]

Where:
- \( \alpha_c \): coefficient of thermal expansion coating
When the stress, caused by primary cooling, exceeds the yield of tensile strength of the coating material, \( \varepsilon_c \) has to be derived from the stress strain curve of that material.

After cooling down to room temperature, the stress in the coating is equal to:

\[
\sigma_c(\varepsilon_c, \xi, T_s) = \frac{E_c}{\beta + (\gamma + 1)(\varepsilon_s \cdot \xi)} \left( \frac{E_c \cdot \varepsilon_s}{E_s \cdot \varepsilon_s} + 1 \right) - 1
\]

With:

\[
\beta = \frac{1 - \alpha_c(T_s - T_r)}{1 - \alpha_s(T_s - T_r)} \quad \gamma = \frac{E_c \cdot \varepsilon_d}{E_s \cdot \varepsilon_s}
\]

\( T_s \): substrate temperature [K]
\( T_r \): room temperature [K]
\( \varepsilon_s \): coefficient of thermal expansion substrate [K\(^{-1}\)].

The determination of the crystalline structure of the covering layers was done by means of RX spectra obtained of a DRON-3 refractometer. Radiation Cu K\(_a\) was used at a voltage of 30 kV and a current of 30 mA. The detector movement rate was 1°/min.

3. Results and discussions

By comparing the RX spectra for the Metco 102 powder and for the coating obtained with this powder (Figure 1), it can be observed that the position of peaks are identical in both cases.

![Figure 1. Comparison of the RX spectra obtained with the powder and covering layer achieved with Metco 102 (TiO\(_2\))](image-url)
3.1. Thermal shock determination

Some results of the experimental determination are shown in Table 2.

| Sample ref. | The number of thermal cycles | The maximum temperature cycle [°C] | Cooling medium | Observation |
|-------------|------------------------------|------------------------------------|----------------|-------------|
| 48          | 20                           | 800                                | water          | The appearance of scorches |
| 50          | 30                           | 800                                | water          | The appearance of scorches |
| 54          | 25                           | 800                                | water          | The appearance of scorches |
| Medium      | 59                           |                                     |                |                          |
| 3           | 180                          | 500                                | water          | No cracks, No scorches   |

Figure 2 shows some images for the coatings made using Metco 102 powder, in a different moments of the determination. Samples were examined by optical microscopy using a stereo microscope.

As expected, it can be observed that TiO2 coatings has a reduced resistance to heat shock at 800°C (over 25 cycles).

The coat, in its original state, has a characteristic ceramic deposition, with a pronounced roughness without visible cracks to the naked eye or to the optical microscope at low zoom. The images in Figure 2 reveal the fact that a smooth network of cracks is formed after the first set of 22 set of cycles. The cracks enlargement is fast, showing in this way the extended cracks and the exfoliations detected on the sample number 54. The breaking of the surface is highlighted by the glossy appearance of the detachment surface limits. The observed cracks have the propagation way perpendicular to the longitudinal axis of the sample, highlighting the direction with maximum stretching tensions during the experiment. Also, the cracks orientation on the layer thickness is from the substrate towards the deposit surface determined by the tensions in the substrate during the experiment.

Because the treatment chose in the first step was considered excessively harsh for the ability of TiO2 to take thermal shocks, the experiment was resumed on a new set of samples covered in the same conditions at a maximum temperature of the thermal cycle of 500°C with a cooling speed of 6000°C/s. After 180 cycles there were no signs of exfoliation. The network of cracks appears to form at a higher number of cycles (54) and extends slowly, increasing the number of cycles. The number of cracks expand significantly over 135 cycles. At the limit of 180 cycles the apparition of the first dislocation of the covering layer on the limits of the cracks can be notified.
3.2. The determination of the strains in the coating layer using Takeuchi’s method

The constants necessary for the determination of strains in the aluminium oxide and titanium oxide coating layers were obtained from the literature. They can be found in Table 3.

| Constant | Symbol in the Matlab program | Al2O3 Z12CNDV12 | TiO2 Z12CNDV12 |
|----------|-------------------------------|-----------------|-----------------|
| $\alpha_c$ | $ac$                         | $8 \times 10^{-6}$ | $7,1 \times 10^{-6}$ |
| $\alpha_s$ | $as$                         | $1,2 \times 10^{-5}$ | $1,2 \times 10^{-5}$ |
| $e_d$ | $ed$                         | $10^2$ | $10^3$ |
| $e_s$ | $es$                         | $1,5 \times 10^{-3}$ | $1,5 \times 10^{-3}$ |
| $E_a$ | $Es$                         | $780 \times 10^6$ | $780 \times 10^6$ |
| $E_s$ | $Ec$                         | $100 \times 10^6$ | $70 \times 10^6$ |
| $T_m$ | $Tm$                         | 2323 | 2033 |
| $T_s$ | $Ts$                         | 423 | 423 |
| $T_r$ | $Tr$                         | 293 | 293 |
| $x$ | $x$                         | $0-10^{-4}$ | $0-10^{-4}$ |

Figure 2. Images for the coats made by using the Metco 102 powder at the thermal shock
For these calculations, the strain in the coating layer at high temperature described in equation (1) was noted with $\sigma$ (sc in the Matlab program) and the strain in the coating layer after cooling described in equation (2) was noted with $\sigma_{\text{max}}$ (scmax in the Matlab program).

The data obtained was processed in Matlab, the strains $\sigma$ and $\sigma_{\text{max}}$ which form in the coating layer obtained with aluminium and titanium oxide were represented in Figure 3 and Figure 4.

It can be observed that in the coating layers obtained with aluminium oxide, the strain after the primary cooling as well as the strain after cooling have higher values than in the case of the coatings obtained with titanium oxide, which can be explained by the fact that the coefficient of thermal expansion is higher for the aluminium oxide and thus closer to the one of the steel substrate.

Figure 3. The variation of the strain $\sigma$ in the aluminum and titanium oxide realized on a Z12CNDV12 stainless steel substrate

Figure 4. The variation of the maximum strain $\sigma_{\text{max}}$ in the aluminum and titanium oxide realized on a Z12CNDV12 stainless steel substrate
4. Conclusion

Using plasma to achieve coatings is a complex process because it is influenced by many factors: generator parameters, characteristics of the powders used in the powder flow, spray distance, choosing the appropriate plasma gas, ensuring the substrate surface preparation, substrate characteristics, power, and so on.

The spectra obtained from the Metco 102 powder and the coatings obtained from it, rutile characteristic peaks appear at the same values of $\theta$, but they differ in their height and width.

Conclusions that result from analysing the results of determination the resistance to thermal shock of the TiO$_2$ layers are:

- The TiO$_2$ samples have a low resistance at thermal shock at 800°C (25 cycles);
- It has already formed a network of cracks after the first set of 22 cycles performed at 800°C;
- The growth of cracks is rapid, revealing the extended cracks and the exfoliation uncovered on the sample number 54;
- The breaking surface is highlighted by the glossy limits of the detachment surface;
- The cracks that have been seen have the sense of propagation perpendicular to the longitudinal axis of the sample attempted at 800 °C, highlighting the maximum stretch tension during the experiment;
- The orientation of the cracks on the coating layer thickness tested at 800 °C is from the substrate to the surface the deposit, this is determined by the tension of substrate during the experiment;
- Particularly in the first stage of the experiment is considered over harsh for TiO$_2$’s capacity to take heat shock;
- At a maximum temperature of thermal cycle of 500 °C and a cooling of 600 ºC/s after running a number 180 cycles, no samples presented peeling;
- The network of cracks is formed from a larger number of cycles and expands slowly when increasing the number of cycles;
- The maximum temperature of thermal cycle of 500 °C, the cracks are not extending significantly at more than 135 cycles;
- The apparition of the first displacement of coverage layer on the edge of the cracks is notified at the limit of the 180 cycles with the maximum temperature of 5000 °C.

The calculation of stresses that occur in the coating layers using the method of Takeuchi, leads to the conclusion that in the coating realized using Al$_2$O$_3$ powder (Metco 101) the tensions are higher than in the deposit made with TiO$_2$ (Metco 102). This can be understood by knowing of the fact that Al$_2$O$_3$ has a thermal expansion coefficient greater than TiO$_2$ and at the same martensitic stainless steel substrate, the difference in thermal expansion coefficients between the layer and the substrate is greater in the case of the Al$_2$O$_3$ and this tensions in the coating are greater.

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