Parameter study on the electrical resistivity of plasma sprayed TiO$_2$/Cr$_2$O$_3$ coatings

K Bobzin, W Wietheger, H Heinemann and A Schacht*

Surface Engineering Institute (IOT), RWTH Aachen University
Kackertstraße 15, 52072, Aachen, Germany

*e-mail: schacht@iot.rwth-aachen.de

Abstract. Thermally sprayed coatings based on TiO$_2$/Cr$_2$O$_3$ gain increased attention for the application as resistive heating elements. The higher resistivity of ceramic compared to metallic coatings improves the geometric flexibility of the coating as no long or complex conductor paths are required to achieve sufficient resistances. The main objective of this work is to understand the influence of the process parameters on plasma sprayed TiO$_2$/Cr$_2$O$_3$ coatings. Therefore, a design of experiment method is conducted to investigate the effects on the coatings' resistivity. Initially, the feedstock of TiO$_2$ with a weight proportion of 20% Cr$_2$O$_3$ is characterized. A three cathode-plasma spray gun with an Ar/H$_2$ plasma gas mixture is used to apply the coatings. The current, the amount of H$_2$ in the plasma gas mixture as well as the stand-off distance of the spray gun are varied according to a circumscribed central composite (CCC) design. These three factors are found to be significant in terms of influencing the coatings' resistivity and a corresponding regression model is established. Furthermore, a significant phase change of the powder due to the spraying process is detected by means of XRD.

1. Introduction
Thermally sprayed electrically conductive coatings are gaining in importance especially for the use as surface heating elements. Possible areas of application include in particular production processes such as injection molding and die-casting. Ceramic coatings intrinsically exhibit a higher electrical resistivity than metallic coatings. This property improves the geometric flexibility since no long or complex conductor paths are required to achieve the necessary resistance values. As a result, planar heating elements can be applied in the conventional coating thickness range for thermal spraying. Furthermore, the application of these planar heating elements leads to homogeneous temperature distribution on the surface [1]. Titanium suboxides have proved to be suitable materials [2], as even a slight oxygen deficiency decreases the electrical resistivity of the initially insulating TiO$_2$ by several orders of magnitude [3]. TiO$_2$ may form a homologous series of Magnéli phases with the formula Ti$_{2n}$O$_{3n-1}$ [4]. These phases exhibit an increased stability at elevated temperatures when Cr$_2$O$_3$ is added [2]. TiO$_2$ and Cr$_2$O$_3$ are able to form another homologous series of Andersson phases with the formula Cr$_2$Ti$_{2n-2}$O$_{3n-1}$ [4]. The influence of thermal spraying processes on the electrical resistivity of TiO$_2$ was investigated by Floristán et al. [5] and Colmenares-Angulo et al. [6]. Floristán et al. observed a correlation of the electrical conductivity of TiO$_2$ coatings with residual stress-induced cracking. They further state that the H$_2$ content in the plasma gas mixture results in a reduction of titanium dioxide, while air cooling and high spray distances lead to increased oxidation. Colmenares-Angulo et al. report an anisotropic behaviour of the electrical properties of plasma sprayed TiO$_2$ coatings. Similar investigations with a mixture of TiO$_2$ and Cr$_2$O$_3$ in the feedstock were conducted by Trache et al. [7]. However, the electrical
resistivity of these coatings was determined perpendicular to the coatings’ surface instead of in-plane. In case of a planar heating elements, the electrical current is applied in-plane, thus these properties are relevant.

This study takes a systematic approach to reveal correlations between the plasma spraying parameters and the resulting electrical resistivity of coatings based on titanium suboxides within a regression model. Therefore, the electrical resistance of the deposited coatings was measured by four-terminal sensing. Together with the coatings’ thickness, the electrical resistivity was calculated. In addition, the phase composition of the powder feedstock as well as the deposited coatings was analyzed by means of X-ray diffraction.

2. Experimental and materials
In this study, coatings of TiO$_x$/Cr$_2$O$_3$ were applied on Al$_2$O$_3$ coated mild steel C45W (1.1730) substrates (WERTZ GmbH, Aachen, Germany). The TiO$_x$/Cr$_2$O$_3$ feedstock (Ceram, Albruck-Birndorf, Germany) as well as the Al$_2$O$_3$ feedstock Amdry™ 6062 (Oerlikon Metco, Pfäffikon, Switzerland) were jointly fused and crushed. The nominal grain size distribution alongside the weight composition according to the manufacturer certificates are given in Table 1. Both powders were applied using the three-cathode plasma torch TriplexPro™-210 (Oerlikon Metco). The Al$_2$O$_3$ coating’s sole purpose is to electrically insulate the TiO$_x$/Cr$_2$O$_3$ heater coating from the steel substrate.

Table 1. Nominal grain size distribution and weight composition according to the manufacturer certificates of used feedstocks.

| feedstock       | grain size distribution [µm] | Al$_2$O$_3$ [%] | TiO$_2$ [%] | Cr$_2$O$_3$ [%] | SiO$_2$ [%] | Fe$_2$O$_3$ [%] | CaO [%] | MgO [%] | Na$_2$O [%] |
|-----------------|-----------------------------|-----------------|-------------|-----------------|------------|----------------|--------|--------|-------------|
| Amdry™ 6062     | -45 +22                     | Bal. 0.02       | -           | 0.02            | 0.01       | 0.03           | 0.02   | 0.14   |
| TiO$_x$/Cr$_2$O$_3$ | -25 +5                     | 0.08 Bal. 19.95 | 0.04        | 0.08            | 0.03       | 0.06           | -      |

The current, the gas flow of H$_2$ within the plasma gas mixture as well as the stand-off distance between torch nozzle and substrate were varied within five levels each. The parameter variations were conducted according to a circumscribed central composite (CCC) design [8] and are listed in Table 2. Specimens S15-1 through S15-6 conform to the center point of the applied CCC design, which was set following earlier findings [1]. The CCC design was chosen to cover a wide range of these three spray parameters in a systematic approach.

The phase composition of the TiO$_x$/Cr$_2$O$_3$ feedstock as well as the TiO$_x$/Cr$_2$O$_3$ coatings were determined by means of x-ray diffraction (XRD 3000, GE Inspection Technologies, Hürth, Germany) with a Cu-K$_\alpha$ x-ray tube source. All patterns were recorded using a current of $I = 40$ mA, voltage of $U = 40$ kV, step width of $s = 0.05^\circ$ and scanning time per step of $t = 25$ s. Post-processing was abandoned to ensure distortion-free results.
Table 2. Overview of spray parameters and their spray order within the conducted design of experiment.

| specimen | spray order | current [A] | gas flow H₂ [SLPM] | stand-off distance [mm] |
|----------|-------------|-------------|-------------------|-----------------------|
| S1       | 7           | 400         | 3,6               | 105                   |
| S2       | 14          | 500         | 3,6               | 105                   |
| S3       | 17          | 400         | 8,4               | 105                   |
| S4       | 3           | 500         | 8,4               | 105                   |
| S5       | 2           | 400         | 3,6               | 135                   |
| S6       | 10          | 500         | 3,6               | 135                   |
| S7       | 13          | 400         | 8,4               | 135                   |
| S8       | 5           | 500         | 8,4               | 135                   |
| S9       | 1           | 366         | 6                 | 120                   |
| S10      | 9           | 534         | 6                 | 120                   |
| S11      | 6           | 450         | 2                 | 120                   |
| S12      | 16          | 450         | 10                | 120                   |
| S13      | 20          | 450         | 6                 | 95                    |
| S14      | 12          | 450         | 6                 | 145                   |
| S15-1    | 19          | 450         | 6                 | 120                   |
| S15-2    | 4           | 450         | 6                 | 120                   |
| S15-3    | 8           | 450         | 6                 | 120                   |
| S15-4    | 11          | 450         | 6                 | 120                   |
| S15-5    | 15          | 450         | 6                 | 120                   |
| S15-6    | 18          | 450         | 6                 | 120                   |

The thickness of the non-magnetic Al₂O₃ and TiO₂/Cr₂O₃ coatings was determined by the magnetic induction principle according to ISO 2178 using the Dualscope® MP 40 (Helmut Fischer GmbH, Sindelfingen, Germany) with a measuring probe of the type EGABW1.3. For each specimen, ten individual spots were measured to calculate a mean thickness value. As the specimens were sprayed with ten passes each and a constant powder feed rate, the resulting coating thickness is an indicator for the deposition efficiency. The electrical resistance R was measured by means of four-terminal sensing (TM-508A, Isothermal Technology, Southport, United Kingdom) parallel to the surface. The distance between the measuring probes was l = 75 mm. Using the coating’s thickness d as well as its width of w = 40 mm the electrical resistivity \( \rho \) was calculated according to equation (1). Since the resistivity is an intrinsic property, it allows for an appropriate comparison between the different coatings.

\[
\rho = R \cdot \frac{d \cdot w}{l} \tag{1}
\]

To visualize the correlation between the three spray parameters current, flow rate of H₂ as well as stand-off distance and the coatings’ resistivity the software MATLAB R2017b (MathWorks, Natick, Massachusetts, USA) and its evaluation tools for design of experiments was employed. The CCC design was evaluated with the response surface method (RSM) to comply with the quadratic equation (2), whereby Y resembles the coatings’ resistivity, \( \beta_i \) resemble estimates and Xᵢ resemble the factors current,
flow rate of H\textsubscript{2} and stand-off distance. Multiplications of X\textsubscript{i} equal interactions of these factors. Since the numeric values of the factors in this study significantly differ from each other, all values were normalized between 0 and 1 for their respective minimum and maximum values in Table 2 at the start of the evaluation. For visualization, however, the normalized values were reverted again. The quality of the estimates is described with an adjusted R\textsuperscript{2}. The fitting of the estimates depends on the sequence, in which they are added to the fitting equation. Thus, multiple sequences, which started the fit with different estimates, were tested. An included analysis of variance determined the significance of influence of each individual factor and its interactions. The threshold value for the significance level was set to \( p = 0.05 \).

\[
Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2
\]

(2)

Y: response  \( X_\cdot \): factor – linear effect  \( X_\cdot^2 \): factor – quadratic effect  \( \beta_\cdot \): estimates  \( X_\cdot X_\cdot \): factor – interaction

3. Results and discussion

A summarized overview of the measured values in this study is available online at [9]. Exemplary micrographs of S5 and S8 with an electrical resistivity of \( \rho_5 = 1.592 \, \Omega \text{mm} \) and \( \rho_8 = 0.312 \, \Omega \text{mm} \) are depicted in Figure 1. The TiO\textsubscript{x}/Cr\textsubscript{2}O\textsubscript{3} coating of S5 shows a more porous structure than S8. While both coatings were deposited at the same stand-off distance of 135 mm, the difference originates from the lower energy input into S5 by the plasma due to a lower current and proportion of H\textsubscript{2} as secondary plasma gas.

![Figure 1. Micrographs of S5 with the highest electrical resistivity and S8 with the lowest electrical resistivity.](image)

The XRD patterns of the TiO\textsubscript{x}/Cr\textsubscript{2}O\textsubscript{3} feedstock and the coatings with the lowest and highest resistivity, S8 and S5 respectively, are depicted in Figure 2, while the used JCPDS numbers are summarized in Table 3. Within the feedstock, clear signs of the existence of the Magnéli phase Ti\textsubscript{4}O\textsubscript{7} and CrTi\textsubscript{2}O\textsubscript{5} are detected besides a variety of additional Magnéli and Andersson phases and small amounts of Cr\textsubscript{2}O\textsubscript{3}. However, reduction and oxidation of these substoichiometric phases during plasma spraying result in a multitude of different oxygen levels and thus, a varying range of values of \( n \) in the homologous series of Andersson and Magnéli phases. It is observed that TiO\textsubscript{2} is not present in the coating. The different degrees of reduction and oxidation may occur due to a combination of the various values of factors like actual particle diameter, grain size, melt degree of the particles, energy distribution and particle trajectory within the plasma flame. As the XRD patterns within these homologous series are close to each other and partially overlapping as reported by Somiya et al. [10], those phases are given in areas to give a clearer view of the XRD patterns.
Table 3. Summary of the used JCPDS numbers.

| Phase             | JCPDS number |
|-------------------|--------------|
| Ti₄O₇             | 01-072-1724  |
| Ti₆O₉₋₁           | 00-050-0787, 00-051-0641, 00-050-0788, 00-050-0789, 00-050-0790, 00-050-0791 |
| Cr₃TiO₅            | 01-079-0302  |
| Cr₂Ti₉₋₂O₁₀₋₁      | 00-035-0098, 00-035-0099, 00-035-0100, 00-030-0420 |
| TiO₂               | 01-076-1938  |
| Cr₂O₃              | 01-084-0313  |

Figure 2. XRD patterns of TiOₓ/Cr₂O₃ feedstock as well as the coating S8 with the lowest resistivity and S5 with the highest resistivity. Andersson and Magnéli phases are displayed as areas as the peaks shift slightly in relation to values of n.

The coatings show minor proportions of rutile and eskolaite, while the amount of rutile is almost negligible in the feedstock. Among the coatings, no major difference is noticeable. The peak heights of various overlapping Andersson phases and Magnéli phases have slightly different values, however, no specific phase stands out. This corresponds with earlier findings by the authors shown in Figure 3, where heating cycles were conducted with TiOₓ/Cr₂O₃ coatings [1]. This is particularly remarkable, since the phase composition of the TiOₓ/Cr₂O₃ powder in the current study differs from the one observed in the previous study, when a different batch of the same powder was used. Since the TiOₓ/Cr₂O₃ powder consists of suboxides, which form during its production, the proportion of the different suboxides may vary according to slight changes or maybe disturbances in the process. This may result in the observed difference of phase composition within different powder batches. The phase composition of the coatings remained the same regardless of the actual phase composition of the TiOₓ/Cr₂O₃ feedstock. This leads to the assumption that the reduction and oxidation of the feedstock reach a rather stable equilibrium during plasma spraying.
Figure 3. XRD patterns of TiO\textsubscript{x}/Cr\textsubscript{2}O\textsubscript{3} powder and plasma sprayed coating according to [1].

Table 4 lists the fitted values for equation (2) as well as the respective significance levels for each estimate. Since all p values are lower than the chosen threshold of \( p = 0.05 \), all three varied parameters \( X_i \), their interactions \( X_iX_j \) and the quadratic terms \( X_i^2 \) exhibit a significant influence on the resistivity of the plasma sprayed TiO\textsubscript{x}/Cr\textsubscript{2}O\textsubscript{3} coatings. The stand-off distance certainly exhibits the least significant influence out of these three parameters. The adjusted R squared of the fitted equation results to \( R^2_{\text{adj}} = 0.95008 \), showing a rather good conformity of the chosen model with the experimental results.

| estimate \( \beta_i \) | significance level p |
|------------------------|----------------------|
| intercept              | 0.930                | 3.040E-05              |
| \( X_1 \) (current)    | -1.413               | 2.088E-04              |
| \( X_2 \) (gas flow H\textsubscript{2}) | -2.062               | 8.570E-06              |
| \( X_3 \) (stand-off distance) | 0.971               | 3.016E-03              |
| \( X_1X_2 \)           | 1.652                | 3.670E-05              |
| \( X_1X_3 \)           | -1.269               | 3.298E-04              |
| \( X_2X_3 \)           | -1.058               | 1.160E-03              |
| \( X_1^2 \)            | 0.736                | 1.965E-03              |
| \( X_2^2 \)            | 1.177                | 5.570E-05              |
| \( X_3^2 \)            | 0.396                | 4.949E-02              |

In Figure 4, the contour plot of the resistivity is shown in dependence of the current and the gas flow of H\textsubscript{2}. The stand-off distance is kept constant at 120 mm as its influence on the resistivity is the smallest of the three. A rather wide valley with an almost constant resistivity forms in the response surface. The resistivity increases at the edges of the investigated parameter field. This is especially noticeable at a low level of current and gas flow of H\textsubscript{2}. In this case, the particles experience less energy input from the plasma, which may result in a higher porosity of the coating. A higher porosity yields a higher resistivity. High particle temperatures at high levels of current and gas flow of H\textsubscript{2} may result in increased re-oxidation and hence increase the resistivity of the coating as well. The reduction and oxidation of the coatings within the observed room of spray parameter is not detectable by XRD. Nonetheless, the electrical properties of titanium suboxide are highly susceptible to changes of the substoichiometry. Liu and West made a similar observation in their study on electrical properties of sintered titanium suboxides.
The model predicts a minimum resistivity of $\rho_{\text{min}} = 0.312 \, \Omega \, \text{mm}$ for a current of $I = 503 \, \text{A}$, an $\text{H}_2$ gas flow of $V = 6.2 \, \text{SLPM}$ and a stand-off distance of $s = 121 \, \text{mm}$. This set of parameters is close to specimen S10, which resulted in a resistivity of $\rho_{S10} = 0.390 \, \Omega \, \text{mm}$. This result is in the same order, which shows consistency with the model’s prediction.

![Figure 4](image.png)

Figure 4. Contour plot of the resistivity depending on the current and the gas flow $\text{H}_2$ with a constant stand-off distance of 120 mm.

The electrical resistivity of the $\text{TiO}_x/\text{Cr}_2\text{O}_3$ coatings, measured in this study, range from $\rho_{\text{min}} = 0.312 \, \Omega \, \text{mm}$ to $\rho_{\text{max}} = 1.592 \, \Omega \, \text{mm}$. The detected range is comparable to the minimal electrical resistivity of $\rho = 0.5 \, \Omega \, \text{mm}$ for TiO$_x$ coatings reported by Floristán et. al [5]. The reported minimum electrical resistivity for a plasma sprayed coating made of TiO$_x$ with a weight proportion of 20% Cr$_2$O$_3$ is $\rho = 2,000 \, \Omega \, \text{mm}$ [7], resulting in a difference of over three orders of magnitude. Within that study, however, the resistivity was measured through-thickness of the coating, while the herein presented resistivity was measured in-plane. This leads to the assumption that plasma sprayed TiO$_x$/Cr$_2$O$_3$ coatings exhibit anisotropic behaviour of the electrical resistivity, which may result from less splat boundaries in-plane than through-thickness. A similar anisotropy of about four orders of magnitude was found by Colmenares-Angulo et al. for plasma sprayed TiO$_2$ coatings [6]. They state that the difference results from differing stoichiometric distribution among splat regions.

The individual effects of each parameter are depicted in Figure 5. Furthermore, the correlation between the coatings’ resistivity and the net power of the plasma is added for comparison. An increase of the gas flow of $\text{H}_2$ leads to a decrease of the resistivity. This correlation is described by a decreased porosity and the reducing effect of $\text{H}_2$ on the particles, which results in a slightly increased oxygen deficiency in the suboxide phases. An increase of the current results in a decreased resistivity as well. This can be explained by the increase of available energy to accelerate the chemical reduction reaction. The overlapping effect shows in the graph of the net power, too. The stand-off distance, however, raises the electrical resistivity as it is increased. Mixing of the plasma jet with the surrounding atmosphere increases proportionally to the stand-off distance. The particles therefore experience a stronger oxidation
and less reduction with the H₂ within the plasma gas mixture. Additionally, the kinetic energy of the particles is less, which could result in a less dense coating, and thus raise its specific resistivity.

Figure 5. Prediction slice plots at the center point. The red line shows the linear correlation, while the band resembles the 95% confidence band of the resistivity for each individual parameter as well as the occurring net power of the plasma. The marks resemble the measured values. The remaining parameters were set to the values given in Table 2.

Within the variation of the stand-off distance the coating thickness of the TiOₓ/Cr₂O₃ coatings is negatively proportional as depicted on the left side of Figure 6. Hence, the deposition efficiency is decreasing with an increasing stand-off distance. The depicted scattering of the thickness results from additional influences on the deposition efficiency from the varied current and H₂ gas flow.

On the right side of Figure 6, the correlation between the electrical resistivity and the coating thickness of TiOₓ/Cr₂O₃ is shown. At coating thicknesses lower than 50 µm, an increased scattering of the resistivity is observed. This may result from a larger proportion of coating roughness to coating thickness. Large coating roughness in a thin coating may form narrow places, which in turn raise the electrical resistivity of the coating.
4. Conclusions
A regression model for the influence of the current, the H₂ proportion within the plasma gas mixture and the stand-off distance on the in-plane electrical resistivity of plasma sprayed TiOₓ/Cr₂O₃ coatings was successfully established. While all three factors are significant, the effect resulting from the stand-off distance is least significant. According to the established model, the minimal electrical resistivity of TiOₓ/Cr₂O₃ coatings is \( \rho_{\min} = 0.312 \ \Omega \text{mm} \). While the plasma spraying process alters the phase composition of the TiOₓ/Cr₂O₃ feedstock considerably, comparison with previous studies showed that the resulting phase composition within the TiOₓ/Cr₂O₃ coating is hardly affected.

Further investigations have to be conducted to verify the established regression model. Therefore, particle states as particle temperature and velocity within the plasma jet will be measured to associate these with the resulting microstructure and hence electrical resistivity of the coatings. The exact correlation between the phase compositions of TiOₓ/Cr₂O₃ feedstocks with the resulting phase composition of TiOₓ/Cr₂O₃ coatings must be examined in more detail. SEM and EDX analysis of the feedstocks as well as the coatings will yield significant insight. The clarification will help in understanding and controlling the possible tolerances for future application.

Acknowledgments
The presented investigations were carried out at RWTH Aachen University within the framework of the Collaborative Research Centre SFB1120-236616214 “Precision Melt Engineering” and funded by the Deutsche Forschungsgemeinschaft e.V. (DFG, German Research Foundation). The sponsorship and support are gratefully acknowledged.

References
[1] Bobzin K, Wietheger W, Knoch M A and Schacht A 2020 Heating behaviour of plasma sprayed TiOₓ/Cr₂O₃ coatings for injection moulding *Surface and Coatings Technology* 399 126199
[2] Scheitz S, Toma F-L, Berger L-M, Puschmann R, Sauchuck V and Kusnezoff M 2011 Thermally sprayed multilayer ceramic heating elements *Thermal Spray Bulletin* 11 88–92
[3] Hayfield P C S 1981 Electrode material, electrode and electrochemical cell *US4422917*
[4] Andersson S, Sundholm A and Magnéli A 1959 A Homologous Series of Mixed Titanium Chromium Oxides Tiₙ₋₂Cr₂O₂n-₁ Isomorphous with the Series TiₓO₂n-₁ and VₓO₂n-₁ *Acta Chemica Scandinavica* 13 989–97
[5] Floristán M, Fontarnau R, Killinger A and Gadow R 2010 Development of electrically conductive plasma sprayed coatings on glass ceramic substrates Surface and Coatings Technology 205 1021–8

[6] Colmenares-Angulo J R, Cannillo V, Lusvarghi L, Sola A and Sampath S 2009 Role of process type and process conditions on phase content and physical properties of thermal sprayed TiO$_2$ coatings J Mater Sci 44 2276–87

[7] Trache R, Berger L-M, Toma F-L, Saaro S, Lima R and Marple B 2011 Electrical Resistivity of Thermally Sprayed Cr$_2$O$_3$-TiO$_2$ Coatings Conference proceedings: Int. Thermal Spray Conf., 27.-29. Sept. 2011, Hamburg

[8] Montgomery D C 2013 Design and analysis of experiments (Hoboken NJ: John Wiley & Sons Inc)

[9] Bobzin K, Wietheger W, Heinemann H and Schacht A 2020 Supplementary data for: Parameter Study on the Electric Resistivity of Plasma Sprayed TiO$_2$/Cr$_2$O$_3$ Coatings http://hdl.handle.net/21.11102/32b4f333-d6df-45c9-a539-e90a1162fc13

[10] Somiya S, Hirano S and Kamiya S 1978 Phase Relations of the Cr$_2$O$_3$-TiO$_2$ System J. Solid State Chem. 25 273–84

[11] Liu Y and West A R 2013 Semiconductor-Insulator Transition in Undoped Rutile, TiO$_2$, Ceramics J. Am. Ceram. Soc. 96 218–22