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Modification of Plasma-sprayed TiO₂ Coatings Characteristics via Controlling the In-flight Temperature and Velocity of the Powder Particles

Jan Cizek, Ivo Dlouhy, Filip Siska, and Khiam Aik Khor

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The study presents a comprehensive research on the plasma spray fabrication of TiO₂ coatings with microstructural properties adjustable via controlling the respective in-flight properties of the feedstock particles. The in-flight properties can be, in return, governed by tuning the plasma system spray parameters. By determining and linking the two interrelationships, a connection between the important coating characteristics (composition, microstructure, surface and mechanical properties) to the plasma system settings was established. It was shown that by changing the values of six parameters representing the flexibility of the plasma system, the temperatures and velocities of the particles within the jet can be altered from 2125 to 2830 K and 137 to 201 m s⁻¹, respectively. The values of the in-flight temperature critically influenced the efficiency of the coating build-up (values ranging from 8 to 84 μm per 1 torch pass) and the content of anatase phase in the fabricated coatings (0-5.8%), while the in-flight velocity of the TiO₂ particles was found to be connected to the porosity of the coatings (ranging from 14.4 to 26.2%) and the adhesion strength at the coating-substrate interface (2.6 × difference).

Keywords in-flight properties, plasma spray, rutile, taguchi, titania, TiO₂

1. Introduction

Given the stringent requirements for their long-term functionality, reliability, and positive interference with the human tissues, the present-day hard tissue implants are often composite components fabricated from a number of various materials. Frequently, the latter condition is ensured by a deposition of bio-active layers onto the prostheses surfaces. Traditionally, calcium phosphates (CaP, e.g. HA, α-TCP) have been used for the task (Ref 1), owing to their good bio-active and osseo-inductive properties. However, the application of the CaP-based ceramics is generally associated with several negative factors stemming from their inherent inferior mechanical strength (Ref 2).

To resolve the difficulty, novel materials are being examined for the surface shielding and osseointegration

promotion of the implants. Titanium dioxide (TiO₂, “titania”) has exhibited enhanced biocompatible character at nano-metric feedstock scales (Ref 3-5) and has been proven to support osteoblast cells growth without negative effect on the respective cells viability (Ref 6-8). Further to that, the TiO₂ coatings generally exhibit superior hardness and adhesion bonding to the substrate as compared to their CaP counterparts.

The most versatile and widely employed technique for fabrication of the bio-material coatings on the implants is plasma spraying. In the process (Ref 9), the material feedstock is inserted into a jet of hot plasma generated by ionization and subsequent recombination of a mixture of gases. Within the jet, the particles are partially or fully molten and propelled toward pre-arranged substrates. Upon impact, the particles undergo a severe deformation (flattening, splashing, conforming to surface asperities) and solidify. The final coating consists of the mutually adherent solidified particles (“splats”) and other morphological attributes, such as internal porosity, inclusions and other impurities, and cracks. The respective quality of a coating (its morphological, physical, and chemical properties) is, apart from the feedstock materials, influenced by a number of diverse factors in the plasma spray deposition. One subset of the factors can be classified as the plasma spray system operational parameters.

The quality of the produced coatings directly influences the overall performance of the implant, and it is therefore imperative to control the process of its production. The aim of the paper was to evaluate the influence of six selected factors representing the plasma system settings on

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the final properties of the TiO₂ coatings with respect to the in-flight properties of the material during deposition. In the study, six coating sets were deposited under parameters leading to high/medium/low in-flight velocities and temperatures, and their respective properties were studied.

2. Experimental Setup

2.1 Powder Feedstock

A commercially available TiO₂ powder was used in the experiment (Amperit 782.1, HC Starck, Germany). To lessen the prospective variance of the in-flight properties of the individual particles within the plasma jet, the powder was sieved thoroughly. The efficacy of the sieving process was confirmed by a laser scattering measurement method (Fritsch Analysette NanoTec 22). The distribution range was measured as 32–45 μm fraction, with no $<3 \mu\text{m}$ dust detected in the powder. Despite its angular morphology (Fig. 1a and c), the powder exhibited good flowability.

The chemical composition analysis provided by the manufacturer (Table 1) was complemented by Rietveld XRD analysis (Ref 10) to ascertain the mutual ratio of the two most common TiO₂ polymorphs. It was found that the material consisted of a rutile phase with approximately 4.0% anatase content. In order to obtain the maximum content of the stable rutile phase (Ref 11), heat treatment of the powder feedstock was carried out (1270 K, 240 min) (Ref 12,13). A subsequent analysis confirmed the transformation of the tetragonal anatase phase into rutile with no orthorhombic brookite phase or other phases present (100% rutile).

As a consequence of the fused and crushed production route, the powders typically include small levels of internal porosity. This was confirmed by SEM observation of the powder cross section (Fig. 1b). Due to a shrinkage accompanying the anatase $\rightarrow$ rutile transformation (Ref 12), the performed heat treatment induced morphological changes in the material—the elevated temperature treatment of the feedstock contributed to a formation of additional internal porosity of the initially fused material (Fig. 1d). Due to the thresholding limits of the powder cross-section image analysis, helium pycnometry method was adopted to quantify the pores amount (13.6%).

2.2 In-flight Properties Measurement

The powder feedstock particles inserted into the jet are propelled and experience a rapid heat intake from the surrounding plasma. The two associated in-flight properties, i.e., the velocity of the particles and their respective surface temperature, govern the final characteristics of the fabricated coatings via controlling, e.g., the flattening and splashing behavior. In order to record the incidence, a fast-shutter CCD camera (Oseir, Ltd., Finland) equipped with laser stroboscope was positioned orthogonally to the axis of the plasma jet at the focus distance of 235 mm. The

somewhat longer distance ensured capturing the particles from the hot core as well as the colder jet periphery, thereby ensuring higher statistical reliability of the average values measurements.

A manual setting of the camera exposure values was used (40% aperture, 15 μs exposure time). Such setting yielded inferior number of captured particles as compared to automatic mode. However, the invariance of the background processing was ensured, further increasing the statistical reliability of the measured properties. To suppress the influences of fortuitous events, a long-term recording of 2 min per spray session was carried out, yielding at least 140 detected particles per measurement session.

2.3 Design of Experiment

For the in-flight measurements and coatings deposition, Praxair 4600 atmospheric plasma system equipped with SG100 (Praxair Surface Technologies, Inc., IN, USA) internal-feeding gun was used. Argon was used as the powder carrying gas, and a mixture of argon and helium was used as the arc forming gases. Six parameters were selected to represent the versatility of the system: (i) net power, flow of the (ii) main and (iii) auxiliary gases, (iv) powder feed rate, (v) flow of the carrier gas, and (vi) spray distance, i.e., the distance between the gun exit and the substrate. The six factors represent the most robust parameters influencing the properties of the generated jet and therefore the in-flight properties that the powder particles attain. Description of the individual factors could be found in the study (Ref 14). The powder feedrate parameter (amount of powder entering the jet per minute, provided in g cm^{-3} in the text) was quantified by an additional powder-collecting experiment at various powder feeder wheel revolutions (1–4 rpm).

Preliminary experiments on the stability of the used plasma system showed a high repeatability considering the characteristics of the generated plasma jet. The maximum variations of the particles in-flight properties were specified as 1% for temperature and 3% for velocity for multiple (5 $\times$) plasma jet ignitions under identical parameters levels.

The experimental layout for determination of the influence of the plasma system settings on the in-flight properties was then designed. In order to comprehend the potential factor interactions, the full-factorial design of experiment was supplemented by Taguchi design of experiment (Ref 15). Such statistical-based concept effectively combines the individual factor levels, resulting in a high efficiency of the experimental design while maintaining the primary information yield. By conducting the experimental work using this partial-factorial setup, the number of necessary measurements was substantially reduced (from $3^6 = 729$ to 18 for six three-level factors). Given the number of factors, their respective number of levels (three), involvement of the mutual bonds, and the reliability and repeatability of the results, the layout of a corresponding orthogonal array (L-18) could not be used in its standardized form for the experiments. Following

Fig. 1 Morphology and cross section of (a, b) original (c, d) heat treated TiO_2 powder

Table 1 Indicated chemical composition of TiO_2 powder

Compound	Mass fraction, %
TiO_2	Balance
Fe_2O_3	0.25
SiO_2	0.30

the procedure provided in Ref 15, a modification of the array along with re-assignment of the particular columns was carried out. The respective factors levels according to the adapted array are shown in Table 2. The measurements were carried out in random order to further increase the results reliability. The results obtained according to Taguchi design were then processed using ANOVA (analysis of variance) statistical procedure, and the detailed results of the analysis could be found in Ref 16.

2.4 Coatings Deposition

The aim of the presented study was to assess the variability in the properties of the final coatings with respect to the selected plasma system settings. Based on the results obtained according to Taguchi design, six combinations of the system settings leading to maximum/medium/minimum in-flight properties were selected for the subsequent coatings production. The six selected combinations are shown in Fig. 2 (denoted as A-F).

The coatings were deposited onto a commercially available high-quality Ti-6Al-4V alloy conforming to ASTM F136 Grade 5 standard (Ref 17). The substrates were electric wire-cut from a sheet into dimensions of $29.1 \times 24.1 \times 2.6 \text{ mm}^3$. Chemical degreasing of the surfaces was carried out, followed by a standardized grit-blasting procedure (640-840 μm SiC medium, 500 kPa pressure, 45°

blasting angle, 150 mm blasting distance) to maximize coating adhesion. The grit-blasting resulted in a surface roughness of $R_a = 5.1 \pm 0.3 \mu\text{m}$. The number of gun passes and the robot arm transverse speed were set as 10 and 100 mm s^{-1} , respectively, and the samples corresponding to the six individual sets were sprayed in batches to ensure uniformity of the results.

The adhesion strength of the deposited coatings was measured according to ASTM-C633 standard (Ref 18). The test specimens were Ti-6Al-4V cylindrical studs with a 25.4-mm diameter. The surface of the studs was, too, roughened by grit blasting prior to the deposition. Six series of samples were deposited under conditions A-F. Twelve specimens were fabricated per each set, all deposited en bloc to increase the results uniformity. Based on the observed coating build-up rates, the number of robot arm passes was modified for the individual sets so as to obtain coatings approximately 420 μm thick.

To provide a further insight into the mechanisms of the in-flight properties influence on the coatings characteristics, an additional experiment was carried out. The Ti-6Al-4V substrates were mirror-polished ($R_a = 0.47 \pm 0.007 \mu\text{m}$) using a standardized procedure. The SG100 gun was positioned in front of the substrates at defined spray distances, but no movement of the robot arm was executed. Instead, the substrates were shielded using a constructed shutter apparatus. After the initial stabilization of the plasma jet, the shutter was opened briefly. Using the procedure, it was possible to observe the flattening and splashing behavior of the individual impacting splats (Ref 19). The polished Ti-6Al-4V surface enabled easier splats observation, and, by eliminating the mechanical interlocking factor, the phenomenon was mainly driven by the particles in-flight properties. The dimensions of the samples were selected so as to comprise the entire cross

Table 2 Taguchi design of in-flight properties measurements

Run	Net power, kW	Main gas flow, l min ⁻¹	Auxiliary gas flow, l min ⁻¹	Feed rate, g min ⁻¹	Carrier gas flow, l min ⁻¹	Spray distance, mm	Measured in-flight	
							Temperature, K	Velocity, m s ⁻¹
1	7	20	10	11.7	3	75	2727	151
2	7	34	24	17.3	5	100	2277	141
3	7	48	38	22.9	7	125	2125	137
4	11	20	10	17.3	5	125	2600	146
5	11	34	24	22.9	7	75	2444	174
6	11	48	38	11.7	3	100	2388	196
7	15	20	24	22.9	3	100	2617	159
8	15	34	38	11.7	5	125	2449	193
9	15	48	10	17.3	7	75	2592	193
10	7	20	38	17.3	7	75	2267	134
11	7	34	10	22.9	3	100	2212	127
12	7	48	24	11.7	5	125	2373	176
13	11	20	24	11.7	7	125	2381	150
14	11	34	38	17.3	3	125	2830	201
15	11	48	10	22.9	5	75	2344	173
16	15	20	38	22.9	5	100	2593	176
17	15	34	10	11.7	7	100	2560	174
18	15	48	24	17.3	3	125	2362	194

Fig. 2 In-flight temperatures and velocities of TiO₂ particles and six combinations selected for coatings production (A-F, dark markers). The error bars represent standard deviations obtained during the in-flight measurements

section of the plasma jet at respective distances, allowing to study the differences between the splats deposited in the middle of the jet and within its colder peripheral areas. The plasma system settings used for the splats collection were identical to the six sets selected for the coatings productions as shown in Fig. 2.

2.5 Coatings Characterization

The morphology of the fabricated coatings was evaluated in SEM, using both top view of the coatings and their corresponding cross-sectional counterparts. In order to obtain information on the porosity of the coatings, three different methods were used: helium pycnometry and SEM image analysis were used for internal porosity evaluation, while mercury intrusion porosimetry provided information on the open porosity. The surface roughness

indicators of the coatings were measured according to ISO: 4287 standard (Ref 20) in two perpendicular directions to affect the potential effect of the spray direction.

To obtain information on the coating hardness and elastic modulus, five loading and unloading cycles (sample unloaded to 90% of the current load) were used for one indentation (MTS Nano Instruments, USA). Ten indentations per sample were carried out (Vickers indenter geometry, the maximum loading force 10 gf). Oliver-Pharr method (Ref 21) was used for determination of the respective elastic moduli.

The phase composition of the coatings was measured using X-ray diffractometry (Philips PW1710, The Netherlands), and the obtained spectra were assessed by Rietveld analysis (Ref 10) using TOPAS software (Bruker AXS Inc., USA). Merging two measured patterns prior to the analysis aided in removing casual errors in the detection (e.g., accidental noise delta-function peaks). The analysis allowed a quantitative determination of the coatings phase compositions and addressing the respective changes with respect to composition of the initial powder feedstock. The standardized patterns for the particular phases were collected from ICSD databases.

Polyamide-epoxy FM 1000 adhesive film was selected as a suitable agent (Cytec Engineered Materials, Inc., USA) for the subsequent adhesion testing of the prepared coatings. The tensile load was applied at a low constant rate of the cross-head (0.013 mm s⁻¹) under ambient conditions (24 °C, 80% humidity).

3. Results and Discussion

3.1 In-flight Properties

The measured velocities and surface temperatures of the TiO₂ particles during their short dwell times in the plasma jet are shown in Table 2 and Fig. 2, including the

respective standard deviations. The detailed analysis of influence of the respective plasma system settings on the in-flight properties was provided in the previous study (Ref 16). The measured temperatures of the TiO_2 particles varied between 2125 and 2830 K. The relatively big span of the range represents temperatures from close to the indicated melting point of the material (2143 K) (Ref 5) to well beyond the point. Further to that, the controlled variations in the plasma settings brought along a difference in the measured particle velocities from 137 to 201 m s^{-1} . Such difference corresponds to approximately $2.5 \times$ variation in the kinetic energy at the particle impact. Due to both phenomena, substantial differences in the fabricated coatings build-up processes (and therefore the respective final properties) were expected.

Based on the 18 combinations derived from Taguchi arrays setup, six samples were selected for subsequent coatings deposition and analyses. To facilitate transparent orientation in the six samples properties, a summarizing Table 3 is provided.

3.2 Coating Microstructure

Significant differences in the efficiency of the coatings build-up process under A-F conditions were observed: after 10 gun passes, the total thickness of the coatings varied from 82 to 841 μm (Table 3). Considering the corresponding in-flight properties, the thickness build-up appears to be strongly connected to the temperature (i.e., molten state) of the TiO_2 particles, while the effect of the velocity is not pronounced. In the case of the coating E, the lowest build-up rate could be caused by the coincidence of the relatively high velocity and low temperature, causing a frequent particle rebound.

The free surfaces of the A-F coatings are shown in Fig. 3. The top layers of the samples consist of fully- and semi-molten particles, and the corresponding average roughnesses are rather low for TiO_2 plasma deposition (Ref 22, Table 3). Surface cracking was observed for sample C (Fig. 3c). Rather than a consequence of its moderate in-flight properties, the cracks in the coating C could have originated as a consequence of internal stresses alleviation due to the increased coating thickness (841 μm). The topmost surfaces of coatings B,C exhibited superior splat spreading. This corresponds with the lowest values of surface roughness measured for the two coatings (Table 3). Contrary to this, the high in-flight velocity samples E, F exhibited high surface roughness where individual particles or splats were difficult to detect. Markedly, lower open porosity of the samples surfaces was recorded for samples B,C,F (Table 4), i.e., the samples with the highest in-flight temperatures. The reduction in the open porosity of the three combinations follows the observation of the spreading behavior of individual particles described in sect. 3.6. Closing of the open porosity channels on the sample surfaces was probably induced by the splashing nature of the impacting (semi)molten material.

The cross-section morphology of the coatings A-F is shown in Fig. 4. In general, the coatings exhibited moderate-sintered structure with partially visible individual splats

surrounded by small size pores. The amount of internal porosity in the coatings surpassed the internal porosity of the powder feedstock (13.62%) and was not interconnected to the thickness of the coatings. The highest internal porosity levels (Table 4) were observed in the relatively thin coatings A. The pores morphology in coatings A showed a transition between individual embedded pores and relatively long connected void chains spanning several splats. Further to that, the adherence to the substrate was apparently impaired as a clear gap along the entire interface was recorded. The observed features in coating A are probably a consequence of the low deposition in-flight properties, with the in-flight temperature nearing the melting point of TiO_2 . It could therefore be assumed that the observed porosity is a consequence of a statistically significant proportion of partially unmolten particles being deformed by low impact energies. A significant decrease in the porosity levels of the coatings was recorded for the coatings deposited under moderately higher in-flight velocities (C,D,E). Their structure exhibited superior level of fusing with the smallest average pore sizes (Table 4). Among these samples, the in-flight velocity had no measurable impact on the internal porosity content (Fig. 5), while the porosity values appeared to be driven by slight changes in the in-flight temperatures only. This observation is in direct contrast with the measured porosity of the coatings produced under high in-flight temperatures (samples B,F). For the two samples, there is a notable influence of the in-flight velocity of the particles, i.e., with overheating of the TiO_2 material over a certain range above the melting point, a different splat spreading (and, consequently, pores formation) mode is most likely triggered where a decline in the porosity may further be controlled via in-flight velocity.

The obtained information also leads to an assumption that two different temperature-dependent mechanisms are involved in the generation of pores: a reduced formation of the pores by increased temperature is counteracted by possible formation of different morphology voids and pores during the contraction of the material from elevated temperatures. This fact is supported by the observed differences in the morphology of the pores, which varied significantly between the (C,D,E; $T/T_m \sim 1.10$ -1.14) and (B,F; $T/T_m \sim 1.27$ -1.32) subsets, as shown in Fig. 4.

As observed from the surface view of the coatings, a presence of major cracks was detected in the cross sections of coatings C. Additionally, the cracking was also observed for sets B,F. The coatings B,C,F exhibited the highest in-flight temperatures during their respective deposition. Aside from the coatings superior thicknesses, the alleviation of the stresses via cracking in the samples might therefore be connected to the temperature at particle impact, most likely by influencing the magnitude of the secondary stresses (Ref 23).

3.3 Phase Composition

The collected XRD spectra of the plasma-sprayed TiO_2 coatings and that of the initial powder feedstock (100% rutile after the heat treatment) demonstrated minor differences. The main rutile peaks in the spectra were

Table 3 In-flight properties of the six selected combinations and respective coatings properties

Sample	Temperature, K	Velocity, m s ⁻¹	Coating thickness, μm	Surface roughness (R_a), μm	Hardness, GPa	Elastic modulus, GPa	Adhesion strength, MPa
A	2125	137	130	5.7	0.40	42	4.39
B	2727	151	768	4.8	0.23	37	4.23
C	2444	174	841	5.2	0.73	70	5.12
D	2381	150	517	5.3	0.58	32	6.17
E	2362	194	82	7.1	0.29	38	10.95
F	2830	201	750	5.7	0.16	35	7.58

Fig. 3 The structure of the produced TiO_2 coatings surfaces

preserved (Fig. 6). However, a presence of small doublet of peaks at 69.008° and 69.788° (previously not detected in the initial feedstock) indicated that a recrystallization of the rutile phase occurred during the deposition, with a preferred orientation of (011) and (002) crystallographic planes in all samples. Identical transformation was observed by Gouma and Mills (Ref 12) for TiO_2 heat

treated at temperatures exceeding 1270 K and in the rutile nanorods fabricated by Dong et al. (Ref 24).

Further to that, a presence of a peak at 25.281° pertaining to anatase phase was observed in all coatings, i.e., a small proportion of the rutile phase was converted into anatase during the spraying (Table 5). According to Pawlowski (Ref 25), such conversion is triggered at

temperatures below 2075 K, and its character depends on the respective cooling rate: rapid cooling rates associated with smaller particles results in the rutile $\rightarrow$ anatase conversion, as experimentally confirmed by Tomaszek et al. (Ref 26). Gaona and co-workers (Ref 27) observed a complementary effect: in the study, the original feedstock consisted mostly of anatase phase subsequently converted into rutile within HVOF deposition process. The content

Table 4 Measured porosity of the produced coatings

Sample	Internal porosity, %	Open porosity, %	Pore diameter, μm
A	26.2	14.0	3.53
B	24.2	7.0	3.69
C	16.9	6.1	2.32
D	15.7	12.1	3.02
E	14.4	11.2	2.94
F	20.8	7.0	2.48

of the retained anatase was linked to the in-flight properties, with higher particle temperatures corresponding to a higher residual anatase content.

In our study, the content of the anatase phase in the coatings followed the TiO_2 in-flight temperature, as shown in Fig. 7. The amount of detected brookite phase in the coatings was below significant threshold in all measured spectra. No Magnelli $\text{Ti}_x\text{O}_{2x-1}$ phases (Ref 22) were detected in the coatings, i.e., no reduction of the rutile phase observed, e.g., in Ref 25 occurred during the deposition process.

3.4 Elastic Moduli and Microhardness

It could be seen from Table 3 that the measured levels of the produced TiO_2 coatings hardness are lower than the values usually indicated for plasma-sprayed ceramic coatings. Despite the slightly lower hardness of the samples B,F (high in-flight temperature), the relative differ-

Fig. 4 The morphology of the produced TiO_2 coatings

Fig. 5 Internal porosity of coatings produced under different in-flight particle properties

Fig. 6 Measured XRD spectra of powder feedstock and produced coatings. Anatase phase peak at 25.281° is denoted by asterisk (*), all other peaks pertain to rutile phase

Table 5 Anatase content in the produced coatings

Sample	Phase content, %	
	Rutile	Anatase
Powder	100	0
A	97.6	2.4
B	94.2	5.8
C	96.4	3.6
D	97.8	2.2
E	97.8	2.2
F	94.8	5.2

ences between the investigated A-F coatings did not appear significantly dependent on the in-flight properties. The higher hardness of the moderate-properties coatings C,D could be connected to their respective inferior levels of porosity. However, the equally porous set E exhibited

Fig. 7 Anatase content in the coatings produced under different in-flight particle temperatures

low hardness, and the mutual connection to the porosity levels therefore needs to be further studied. The apparent relation of the coatings hardness to the in-flight properties observed in Ref 27 was not confirmed. The difference could probably be attributed to the slightly different character of the coatings produced by HVOF (Ref 27) and atmospheric plasma spraying.

The moduli of the fabricated coatings were expected to be significantly lower as compared to bulk TiO₂ (Ref 28). This was subsequently confirmed by the measurements. Also, the A-F coatings moduli exhibited up to 200% differences between the individual sets. However, no clear trend in connection to either in-flight properties of coatings morphology was discovered. As an origin of the moduli variation in-between the sets, another mechanism could probably be involved. As compared to the previous study on the biological HA coatings (Ref 14), the levels of hardness of TiO₂ coatings were comparable, while the elastic moduli of the titania materials were significantly higher.

3.5 Adhesion

The gaps observed at the interfaces in samples A,B were expected to deteriorate the adhesion strength of the coatings. Indeed, the low in-flight velocity samples (A,B) exhibited lower values of the adhesion strength than their high-velocity counterparts (E,F, Table 3). This is in accordance with the general concept of spreading behavior of the splats with various kinetic energies contained within the first deposited layer, i.e., at the prospective coating-substrate interface. During the testing, a number of samples from the sets C,F exhibited a premature decohesion failure. This fact could in fact be associated with the cracks observed in the respective sets microstructure, invalidating the prospective use of such coatings. In general, the adhesion strength of coatings may be adversely affected by the development of internal stresses at the interface. Considering the usual secondary stresses development with increasing coatings thickness, the adhesion strength of the relatively thick coatings B,C,F

Fig. 8 The spreading behavior of TiO_2 splats on polished Ti-6Al-4V substrates deposited under different in-flight properties

may have been influenced. However, the observed cracking of the coatings leading to alleviation of the stresses apparently resulted in suppressing its effect on adhesion and no direct interrelationship between the measured adhesion strength and the thickness of the coatings was determined (Table 3).

3.6 Single Splats

To assess the spreading behavior, in particular with reference to the in-flight properties, single splats were collected at conditions identical to A-F (Fig. 8). The TiO_2 splats collected under condition A exhibited minor splashing of the particles as compared to other combinations. This fact is possibly caused by the low in-flight temperature and velocity of the set and is further supported by observation of round splats collected from the periphery of the jet. In accordance to the coating top surface observations, the splats deposited under B,C conditions exhibited superior spreading with a notable disintegration of the particle cores. The network of tails present in the splats collected from a geometrical middle of the jet was missing for the splats collected from the jet peripheral areas. For the two conditions, no round splats were identified in the experiment. The D set splats from the middle of the jet had morphological features identical to set C splats (similar in-flight temperature and velocity). Unlike other sets, splats collected at the periphery of the jet under this condition exhibited a formation of tail rings around the splat centers (Fig. 8d). The formation of the rings could possibly be caused by a disconnection of the advancing semi-molten rim of the initially round splats. Splats

deposited under E,F conditions were morphologically analogous. They both retained the coherence of the particle cores with a significant amount of splashing at the splat periphery. As a consequence, a formation of relatively long tails was observed, possibly a consequence of the high velocity during the deposition. The spreading of the particles under conditions E,F is in accordance with the observed top coating morphology where no distinct splats could be observed. Given the results, it could be concluded that the factor governing the spreading behavior of the incoming particles is a concurrence of both the in-flight temperature and velocity with similar incidence intensity. The mutual incidence on the splashing behavior was observed for other materials as well (e.g., Al_2O_3 particles in Ref 29).

Dhiman et al. (Ref 30) suggested a dimensionless solidification parameter Θ defined as the ratio of solidified part to overall splat thickness during the solidification process. The parameter incorporates a number of factors; among others, the impact velocity of particles and thermal contact resistance between splats and surface are considered. Following the study, the TiO_2 coatings produced by plasma deposition could be classified into two groups with the in-flight velocity being the determinant factor:

1. low impact velocities ($\Theta \ll 1$); the splats will spread into a thin sheet and rupture internally, leading to extensive fragmentation. A small central splat surrounded by a ring of debris is produced; in our study, the samples A,B,C,D (i.e., velocity $< 174 \text{ m s}^{-1}$) exhibit this morphology
2. the rapid solidification obstructs the spreading liquid, and round splats with radial tails are created ($\Theta \sim 1$);

this was observed for the high in-flight velocity samples E,F

The TiO₂ splats exhibited a relatively high content of internal porosity. Further to that, it was observed that this porosity increases when a splat is deposited onto a previously deposited splat rather than the Ti-6Al-4V substrate itself: thermal conductivity of the underlying layer is therefore an important factor influencing the splats solidification behavior (Ref 30). Cracking of the deposited and solidified splats was observed; however, the cracks were not necessarily perpendicular to each other, as observed elsewhere (Ref 31). A qualitative image analysis observation indicated that the degree of splashing of individual particles is directly proportional to the diameter of the formed splats (as also observed e.g., in Ref 32 for Al₂O₃-13%TiO₂ 22-45 μm powders).

4. Conclusions

The relation of the in-flight properties of TiO₂ particles and the corresponding coatings characteristics was studied thoroughly in the paper. Combining the results of the temperature and velocity within the plasma jet with the respective coatings' cross section and top-layer analyses, surface roughness, porosity determination, XRD measurements, hardness and elastic moduli determination, adhesion strength testing, and single splats spreading observation, it can be concluded that

- adjusting the plasma system parameters could lead up to 33 and 47% differences in the in-flight temperature and velocity of the particles, respectively.
- the coating build-up (connected to the process deposition efficiency) of the plasma spray process is mainly driven by the in-flight temperature, linked to spray distance and net power factors.
- significant differences in the microstructure of the produced coatings are directly linked to the in-flight properties, with visible individual splats in the structures as a consequence of single droplets spreading character (controlled by the thermal conductivity of the underlying layers).
- the internal porosity of the samples is mainly connected to the in-flight temperature of the particles, with pore content ranging from 14.4 to 26.2% (of the six factors, the in-flight temperature is mainly driven by spray distance and net power factors). Decreased porosity content coatings can be prepared at moderately increased TiO₂ particles temperatures, while exceeding overheating of the material triggers a formation of additional porosity.
- the surface open porosity is connected to both in-flight temperature and velocity as a consequence of their mutual incidence on the splashing behavior of the incoming particles. Considering the difference to internal porosity of the coatings, the effect of the in-flight temperature is of temporary nature only and

is neglected inside the coatings by successive torch passes.

- cracking observed in the respective microstructures is connected to the in-flight temperature, with no correlation to the in-flight velocity, probably a consequence of secondary stresses alleviation.
- the plasma spray process resulted in a recrystallization of the initial rutile feedstock with a minor conversion to anatase phase only (<6%). The transformation extent is dependent on the in-flight temperature of the TiO₂ particles.
- no distinct dependence between the in-flight properties of the particles and the hardness of a elastic moduli of the fabricated coatings was observed. As such, the two properties might be controlled by other factors.
- the adhesion of the coatings is governed by the in-flight velocity of the particles forming the first deposited layers.

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