Manufacturing of composite titanium-titanium nitride coatings by reactive very low pressure plasma spraying (R-VLPPS)

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Abstract. Very Low Pressure Plasma Spraying (VLPPS) is an emerging spray process nowadays intensively studied by many research centers in the World. To date, studies are mostly focused on the manufacturing of ceramic or metallic coatings. None refers to composite coatings manufacturing by reactive plasma spraying under very low pressure (i.e., ~150 Pa). This paper aims at presenting the carried-out developments and some results concerning the manufacturing of composite coatings by reactive spraying. Titanium was selected as metallic material in order to deposit titanium-nitride titanium coatings (Ti-TiN). Nitrogen was used as plasma gas and was injected along an Ar-H₂-N₂ plasma jet via a secondary injector in order to reach the nitrogen content on the substrate surface. Thus, different kind of reactive mechanisms were highlighted. Resulting coatings were characterized by Scanning Electron Microscopy (SEM) observations. Porous microstructures are clearly identified and the deposits exhibit condensed vapours and molten particles. Glow Discharge Optical Emission Spectroscopy (GDOES) analysis evidenced nitrogen inside the deposits and X-Ray Diffraction (XRD) analysis confirmed the formation of titanium nitride phases, such as TiN and Ti₂N, depending upon the location of the nitrogen injection. Microhardness values as high as 800 VHN were measured on manufactured samples (to be compared to 220 VHN for pure titanium VLPPS-manufactured coatings).

1. Introduction

Plasma spraying is an enabling technology aiming at manufacturing thick (i.e., from a few hundreds micrometers to a few millimeters) coatings onto components to provide them with unique functional properties, such as enhanced resistances to wear and corrosion, thermal insulation, etc. Plasma spraying consists in injecting a feedstock material made of micrometer-sized particles into a high-energy plasma flow (depending upon the plasma gas mixture and the power parameters, corresponding usually to a mass enthalpy of about 20 MJ.kg⁻¹, conventional value) exiting a torch at elevated velocities (in the order of 1000 m.s⁻¹ when considering an anode nozzle diameter of about 6 mm, a volume flow rate of plasma gas mixture of about 50 L.min⁻¹ and an electric power of about 50 kW). The feedstock particles are molten by heat transfers from the high-energy flow and simultaneously accelerated towards the surface to be covered (i.e., the substrate) where they form, after impact, spreading and rapid solidification (i.e., cooling rate of about 10⁵ to 10⁶ K.s⁻¹, characteristic value), individual flattened lamellae, the stacking of which forming a coating.

Plasma spraying exhibits multiple advantages, among which - the large variety of feedstock materials that can be sprayed (i.e., alloys, ceramics, polymers, composites), the large variety of substrate...
compositions (i.e., alloys, ceramics, polymers, composites), the formation of unique non-equilibrium structures thanks to the high solidification rate, the high feedstock throughput (i.e., from 3 to 10 kg.h\(^{-1}\), conventional values), the capability of manufacturing multi-layered or graded coatings by adjusting the feedstock composition, etc. Several drawbacks limit however its applicability. Among them, only materials exhibiting congruent melting behavior can be processed i.e. materials having a melting temperature distinct by at least 300 K of their vaporization temperature.

Reactive plasma spraying appears as a palliative solution to circumvent this drawback. It consists in inducing reactions in between a precursor and a reactive gas to form non-congruent melting materials. The very first attempts were made during the mid-80’s by shrouding a plasma flow expanding at atmospheric pressure and injecting reactive gases inside. In such a configuration, reactions occur in between molten particles and the reactive gaseous species (the mechanism depends upon the ratio of the kinematic viscosity of gas to that of liquid). This configuration was never fully satisfactory due to its main drawbacks: 1) the entrapment of air in the plasma flow, meanwhile the shroud at its periphery, due to the flow recirculation of the extremity of the shroud. Air entrapment leads to in-flight oxidation of particles; 2) the limited interaction time in between the molten particle and the reactive species (> 1ms); 3) the rather low efficiency of the reaction which takes place in between a liquid (the molten particle) and a gas (the reactive species); 4) the thermal losses due to the cooling of the shroud, etc.

Very-low pressure plasma spraying (VLPPS) is an emerging technology which aims at operating the plasma torch under an absolute pressure of about 100 Pa of a neutral atmosphere (i.e., Argon). This way, the plasma flow expands at the exit of the torch to form a jet of about 1 m long, characteristic value. This process is based on a different deposition mechanism, in regard to conventional plasma spraying, either at atmospheric pressure (for APS) or at low pressure (20000 Pa, characteristic value for VPS): the coating is manufactured, pass by pass, mostly by the condensation of vapors instead of the solidification of molten particles. Indeed, feedstock particles vaporization occurs in the plasma core, at the exit of the torch. The plasma jet carries then the vapors towards the substrate to cover where they condense to form the coating. Because of the Knudsen effect leading to the decrease in heat and momentum transfer between the plasma jet and particles, VLPPS requires to work with fine feedstock powder.

Reactive – very-low pressure plasma spraying (R-VLPPS) takes advantage of the long dwell-time of the vapors to induce their reaction with a gaseous precursor, injected in the plasma flow either as plasma forming gas and/or downstream the plasma flow to form, in situ, new species that condense onto the substrate.

This study aims at demonstrating the potential of this reactive process and considers, as demonstrative precursors, Titanium and Nitrogen, in view of forming Titanium nitrides, materials exhibiting a non-congruent melting behavior, and for this reason impossible to plasma spray in a conventional way.

2. Experimental details

Plasma atomized pure titanium powder provided by RAYMOR INDUSTRIES INC. (Boisbriand, QC, Canada), with a size distribution ranging from 5 µm (d\(_{10}\)) to 25 µm (d\(_{90}\)) and an average size diameter (d\(_{50}\)) of 13 µm, was used as starting feedstock material (see figure 1). Three different configurations were considered to inject the reactive species, Nitrogen, in the plasma flow. The first way considers Nitrogen as the primary plasma forming gas. The second way uses a ring-shaped injector (figure 2) located downstream, close to the substrate surface (i.e., 8 mm). The third way is a combination of the two first ones.
Copper plates of 70×30×2 mm³ were used as substrates. In order to improve the adhesion of the coatings, the substrates were degreased in ethanol vapors and grit-blasted (with α-Al2O3 grits of 250 µm, average dimension) prior spraying. They exhibited an average surface roughness of 12 µm and an average maximum peak-to-valley ratio of 126 µm. In order to evidence the different nitriding mechanisms, substrate temperature was considered as an operating parameter. A water-box was used to cool the substrates during spraying. The substrate temperature was monitored using type K thermocouples of 800 µm in diameter brazed at the front of the substrate to avoid through-thickness conductive losses and thermal resistances in between the samples and the sample-holder. Indeed, the rather long spray distance and the rarefied atmosphere do not damage the thermocouples during tests.

2.1. **VLPPS system and experimental conditions**

The experiments were carried out thank to a VLPPS device developed in the lab. This device is depicted in figure 3. It is made of an operating chamber of 12 m³. The pumping system allows varying the chamber pressure during operation from 150 Pa to 5 kPa. It is also equipped with a 53 kW F4-type plasma torch installed on a 6 axis robot. The effect of the nitrogen flow rate in the plasma jet, the location of nitrogen injection and the substrate temperature was evidenced via five sets of parameters, as detailed in Erreur ! Source du renvoi introuvable. while chamber pressure, spray distance and velocity were unchanged.
Table 1. Operating parameters

| Parameter                                           | F4  |
|-----------------------------------------------------|-----|
| Anode internal diameter at torch exit (mm)          | 6   |
| Chamber pressure (Pa)                               | 150 |
| Feedstock powder rate (g.min\(^{-1}\))              | 1.0 |
| Spray distance (mm)                                 | 900 |
| Spray velocity (mm.s\(^{-1}\))                      | 200 |

| Parameters                                         | Set 1 | Set 2 | Set 3 |
|----------------------------------------------------|-------|-------|-------|
| Arc current intensity (A)                           | 500   | 600   |       |
| Arc voltage (V)                                     | 85    | 90    |       |
| Ar plasma forming gas flow (L.min\(^{-1}\))        | 4     | 4     |       |
| \(\text{H}_2\) plasma forming gas flow (L.min\(^{-1}\)) | 3     | 3     |       |
| \(\text{N}_2\) plasma forming gas flow (L.min\(^{-1}\)) | 23    | 30    |       |
| Plasma mass enthalpy (MJ.kg\(^{-1}\))              | 30    | 38    |       |
| Nitrogen flow rate in ring-shaped injector (L.min\(^{-1}\)) | /     | /     | 5     |
| Substrate temperature (°C)                          | 150   | 800   | 800   |

2.2. Characterization of coating structural features and mechanical properties

Coating cross-sections and coating surface morphologies were observed using a JEOL JSM-5800LV scanning electron microscope (SEM) in back-scattered electron mode to point out the chemical contrast into the deposits. A LEITZ MINILOAD-2 Vickers tester was used to measure the microhardness of the coatings. A load of 25 g and a dwell-time of 30 s were selected. An X-ray diffractometer (XRD, D8 Advance, BRUCKER AXS, Germany) with a CoK\(\alpha\) anti-cathode (\(\lambda_{\text{Co}} = 0.179 \text{ nm}\)) was employed to determine the phase composition of the coatings (scanning step: 0.02°). Glow Discharge Optical Emission Spectroscopy (GDOES, GD-Profiler 2, HORIBAJOBIN-YVON) was used to quantify the chemical composition of Ti-TiN coatings. Nano indentation test (NHT) were implemented on Ti-TiN coatings to evaluate phase hardnes. The indenter type is Berkovich and the loading was linear. The contact load was fixed to 2.5 mN and the maximum depth to 125 nm. Results were obtained by the “Oliver and Pharr” method.
3. Results and discussion

3.1. Effect of Nitrogen content as plasma gas forming

SEM observations of Ti-TiN coating cross-sections manufactured using set 1 and set 2 are presented in figure 4. The average deposited thickness per pass was of 0.2 µm with set 1 and 0.15 µm with set 2. The coatings exhibit, from a general point of view, a structure composed of majority condensed Titanium vapors. Such a structure does not correspond in this case to the staking of lamellae resulting from the spreading and the solidification of molten impinging droplets as evidenced in figure 5 depicting the OES spectra and in figure 6 displaying a high resolution fractured cross-section of a typical coating manufactured with this process. The lamellar structure results from a chemical contrast, at this stage of the analysis very likely to areas enriched in nitrogen.

Coatings exhibit some voids. The coatings manufactured with set 2 seem to exhibit a lower total macroscopic void content compared to set 1. It is nevertheless impossible at this stage to be conclusive due to the smallest voids which are not detected due to the image resolution limit. The total void content of those coatings has been estimated to 5%, average value, by Ultra-Small Angle X-rays Scattering (USAXS) performed at the Advanced Photon Source (Argonne National Laboratory, Argonne, IL, USA).

Glow Discharge Optical Emission Spectroscopy (GDOES) analyses allow quantifying the average Nitrogen concentration through thickness in the coatings. In average, the atomic concentration increases from 9%at. to 18%at. for corresponding plasma mass enthalpy of \( h = 30 \text{ MJ.kg}^{-1} \) and \( h = 38 \text{ MJ.kg}^{-1} \) (figure 6). One can notice the presence of copper in the coating, corresponding to the diffusion from the substrate to the coating at elevated temperature (\( \geq 800 \text{ K} \)).

![Figure 4. SEM observations of Ti-TiN coatings elaborated by VLPPS.](image-url)
Figure 5. OES spectra on Ar-H$_2$N$_2$ plasma without and with titanium powder on 300-900 nm

Figure 6. Typical fractured view of a Ti coating manufactured by R-VLPPS.

Figure 7. GDOES quantitative analysis of titanium coatings manufactured with nitrogen as primary plasma forming gas, a) $\text{h} = 30 \text{ MJ.kg}^{-1}$ and b) $\text{h} = 38 \text{ MJ.kg}^{-1}$. 
3.2. Effect of Nitrogen content as primary plasma forming gas and Nitrogen injected through the ring-shaped injector

Figure 8 displays the typical structures of Titanium coatings manufactured with Nitrogen as primary plasma forming gas coupled with Nitrogen injected close to the substrate through the secondary ring injector. The comparison is done for parameters from set 2 and set 3. The coating architectures do not change significantly compared to the previous case: a lamellar structure is clearly identified again.

![Figure 8. SEM observations of Ti-TiN coating cross-sections elaborated by VLPPS.](image)

Figure 8. SEM observations of Ti-TiN coating cross-sections elaborated by VLPPS.

Figure 9 presents the average Nitrogen atomic concentration gradient through thickness. It is in the range of 25%. From this result, it has been proved the injector ring allows hence increasing the average concentration of nitrogen in the coatings, from 18%at to 25%at, respectively.

![Figure 9. GDOES quantitative analysis of titanium coatings manufactured with Nitrogen as primary plasma forming gas and Nitrogen injected close to the substrate through the ring-shaped injector.](image)

Figure 9. GDOES quantitative analysis of titanium coatings manufactured with Nitrogen as primary plasma forming gas and Nitrogen injected close to the substrate through the ring-shaped injector.

3.3. Comparison of coating structures and identification of mechanisms occurring during coating deposition

Nitrogen atomic concentration gradients through coating thickness clearly indicate the presence of Nitrogen in the coatings. Figure 10 displays the XRD patterns of those deposited materials. This characterization technique allows identifying phases, meaning how Nitrogen is bounded in the structure. The XRD patterns reveal the presence of Titanium nitrides exhibiting two main stoechiometric compositions: TiN, TiN$_{0.3}$ and Ti$_2$N. The Rietveld refining allows quantifying the respective phase amounts. However, this technique, applied to the presented patterns, appeared to be not conclusive, since
nitride amounts vary in very large ratio, depending upon the selected refining criteria. Other techniques, such as IR spectroscopy, should very likely permit to better quantify those amounts. Works are in progress.

In table 2 are given Ti-TiN coating Vickers hardness obtained from nano-indentation measurements which were performed on splats.

**Figure 10.** XRD pattern obtained on Ti coating and Ti-TiN coatings elaborated by VLPPS from set 1, 2 and 3

**Table 2.** NHT results obtained on Ti-TiN coatings elaborated from set 2 and set 3, for different locations on the coatings

| NHT location in the coating | Ar-H₂-N₂ (set 2) | Ar-H₂-N₂ with ring shaped injector (set 3) |
|-----------------------------|------------------|------------------------------------------|
| Splat – center              | (1209 ± 262) HV  | (1394 ± 300) HV                          |
| Splat – side                |                  | (1453 ± 286) HV                          |

The average Vickers hardness of Ti coatings elaborated by VLPPS is (220 ± 12) HVN. Compared to this value, the hardness of Ti-TiN coatings is higher, showing the strengthening of the coatings by titanium nitrides formation during spraying. However, the standard deviation on the average values is huge, around 300 HVN. This shows that Ti-TiN coatings are not homogeneous and nitriding mechanisms are not complete due to the partial powder particle vaporization.
Conclusion

Very low pressure plasma spraying was implemented to manufacture Ti-TiN composite coatings. In order to elaborate these deposits, two ways were studied. Firstly, nitrogen was used as plasma gas forming for two mass flow rates, leading to $\dot{h} = 30 \text{ MJ.kg}^{-1}$ and $38 \text{ MJ.kg}^{-1}$, respectively. In both cases, OES measurements show the titanium powder particles vaporization. However, in the case of the lower plasma mass enthalpy, coatings exhibit a lamellar microstructure and some spherical particles were observed, revealing the partial particle heat treatment. Nitrogen content of the coatings was evaluated by GDOES analysis. In relation with the increase of plasma enthalpy, the nitrogen atomic content is improved from 9%at. to 18%at. XRD pattern confirm the formation of titanium nitride during the spraying. Different stoechiometric compositions of titanium nitrides were determined such as TiN and TiN$_{0.3}$.

Secondly, nitrogen was injected as primary plasma gas and via a ring-shaped injector localized close the surface substrate in order to enrich the substrate surrounding with Nitrogen species. For this configuration, coating microstructures do not change significantly compared to the first ones. A condensed architecture can be identified. GDOES measurements have shown the atomic Nitrogen content into these coatings reaches 25%at. and XRD patterns reveal the formation of Ti$_2$N phase which can be explained by the nitriding mechanisms taking place on the substrate surface during the particle re-solidification. Compared to the average hardness titanium coating elaborated by VLPPS, (220 ± 12) HVN, composite Ti-TiN coatings present an improved average hardness, (1350 ± 283) HVN. The significant standard deviations express a partial nitriding of titanium powder particles during spraying. To promote once more the nitriding mechanisms, other ways can be considered as increase the nitrogen content in the spraying surrounding. But some experiments have demonstrated deposits elaborated with too high nitrogen content are weakened illustrated by a lot of cracks and delamination. Work is in progress to explore the nitriding efficiency by reducing the titanium thickness deposited per pass, possibly promoting the nitrogen diffusion into the coatings and titanium nitride formation.

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