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Plasma-sprayed Ti-6Al-4V coatings in a reactive nitrogen atmosphere up to 250 kPa

V.GUIPONT, R.MOLINS, M.JEANDIN, Evry / F
G.BARBEZAT, Wholen, CH

Abstract

Two spherical Ti-6Al-4V (25-45 μm and 45-75 μm) powders, were sprayed in a CAPS system ("Controlled Atmosphere Plasma Spraying") operating in a coupled mode: High-Pressure Plasma Spraying (HPPS) and Reactive Plasma Spraying (RPS). Four different pressure settings up to 250 kPa with reactive nitrogen atmosphere were tested in order to assess the influence of chamber pressure and chamber atmosphere on the deposition of Ti-6Al-4V coatings. The microstructures and phase compositions of the plasma sprayed Ti-6Al-4V coatings were studied using standard X-ray diffraction (XRD) and electron probe microanalysis (EPMA) with help of electron microscopy techniques (SEM and TEM). These established the pressure-assisted nitriding of the Ti-6Al-4V in the CAPS chamber with fine and coarse TiN precipitates embedded in a α-Ti matrix. A High-Pressure coupled with RPS enhanced the nitriding of the Ti-6Al-4V powder with a content of nitrogen which was all the higher because particle size was low.

1 Introduction

“In-situ” chemical reactions between the melted material and its gaseous environment are generally inherent to the thermal spray process. If these chemical reactions are promoted and controlled, this characterizes the reactive plasma spraying (RPS) mode. This very powerful spraying technique allows to manufacture composite materials, intermetallic alloys and reinforced or toughened ceramics [1]. Already with conventional APS (atmospheric or air plasma spraying) mode, oxide compounds of metallic materials are synthetized and located at the lamella boundary. If low oxide contents are generally targeted, a rather high oxide content might be interesting to enhance tribological properties for example. Thus, the APS mode can be considered as the most common “reactive” plasma spraying mode to achieve multi-phased or composite oxidized coatings. In case of titanium coatings sprayed in the APS mode (with or without nitrogen in the plasma gas), titanium particles react to form an oxinitride of titanium and a solid solution of α-Ti that contains both nitrogen and oxygen [2].
More generally, RPS coatings can be achieved when bringing liquid, gaseous or solid precursors into contact with the sprayed material at a high temperature. To promote the chemical reaction, the reactants can be the dissociated species or elements that form or interact with the plasma itself or the gaseous species of the surrounding atmosphere of the process. Moreover, if the reactive atmosphere is in contact with the deposit that is held at a high temperature during spraying, further reactions can occur after impact and solidification of the droplet. “In-situ” synthetized carbides or nitrides are the two types of RPS coatings that are always studied and corresponds to these various RPS operating routes [3-7].In some works, pure titanium powder have been sprayed using RF plasma equipment with nitrogen content in the plasma gas [8]. In other works, titanium coatings containing titanium nitrides were synthetized in a surrounding nitrogen atmosphere. The latter mode is one of the most convenient potential industrial process for wear and corrosion-resistant coatings [9,10]. This mode could operate with a DC plasma gun operating with injected nitrogen reactive gas in a shrouding reactor [11] or with a controlled nitrogen atmosphere at different gas pressures in a chamber [12,13].
The aim of the present work was to achieve Ti-6Al-4V nitrided coatings using high-pressure plasma spraying (HPPS) coupled with reactive plasma spraying in a reactive nitrogen atmosphere, namely HPRPS (High Pressure Reactive Plasma Spraying). The influence of chamber pressure and the influence of chamber atmosphere with some experiments using air atmosphere were studied. In addition, two spherical Ti-6Al-4V (25-45 μm and 45-75 μm) powders were sprayed in order to assess the influence of particle size on the resulting nitriding process.The formation of nitrided compounds was studied using standard X-ray diffraction (XRD) and electron probe microanalysis (EPMA) with help of scanning and transmission electron microscopy techniques (SEM and TEM) in order to assess the pressure-assisted nitriding of the Ti-6Al-4V.

2 Materials and Processes

2.1 Powders

Two different spherical, pre-alloyed and low-oxygen content Ti-6Al-4V powders (PyroGenesis Inc., Canada) were used corresponding with two different particle size range: 25-45 μm and 45-75 μm. A SEM cross-section view of the powder (chemical etching with “Kroll” reagent) showed the martensitic structure of the Ti-6Al-4V alloy, **Fig.1**.

2.2 High-Pressure Reactive Plasma Spraying (HPRPS)

Plasma spraying experiments were carried out using a multi-process plasma equipment (CAPS, Sulzer-Metco, Switzerland) with a F4-MB plasma gun. The CAPS system has an 18 m^3 chamber, which could operate in a controlled atmosphere of air, argon or nitrogen from 2 kPa to 350 kPa. The plasma spraying

parameters are given in **Table 1**. The same Ar/He plasma mixture was used for all HPRPS pressure settings. Some experiments with air instead of nitrogen were performed and APS coating with Ar/H_2 plasma was sprayed as a reference. The addition of N_2 in the plasma was studied in the HPRPS mode. Further experiments with a shorter spraying distance (75 mm) were done at 250kPa with a nitrogen atmosphere.

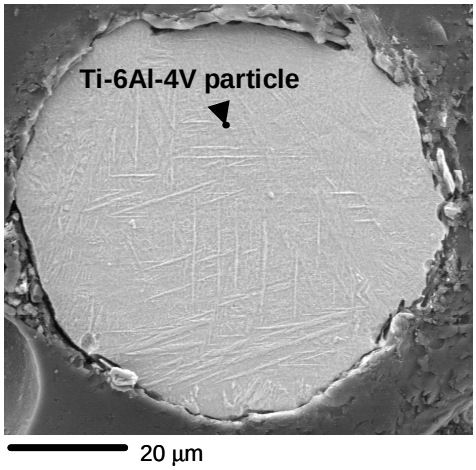


Fig. 1. Cross-section SEM image of a typical Ti-6Al-4V particle (45-75µm size range).

Table1. Plasma spray parameters

Reactive Plasma Spraying				
Atmosphere	Nitrogen			
Pressure (kPa)	100	150	200	250
Plasma (l/min)	Ar:50/He:30, I=700A Ar:50/He:30/N_2:2, I=650A			
Ti-6Al-4V	45-75 µm or 25-45 µm			
Distance	130 mm			
Cooling gas	argon			
Atmospheric Plasma Spraying				
Atmosphere	Air			
Pressure (kPa)	100		100	250
Plasma (l/min)	Ar:47/H_2:10 I=650A		Ar:50/He:30 I=700A	
Ti-6Al-4V	45-75 µm			
Distance	130 mm			
Cooling gas	air			

2.3 Sample analysis

As-sprayed samples were placed in a dry chamber under vacuum to prevent any further oxidation. Phase analysis were performed using XRD D-500 goniometer (Siemens, Germany) with Co Kα radiation (800W) on the surface of the as-sprayed coatings (irradiated area = 10 mm²). EPMA quantitative analyses of cross-sections (with fittings for the Ti and N elements) were carried out using a SX 50 microprobe (Cameca, France) in the WDS. Cross-section observations of as –sprayed or etched coatings ("Kroll" reagent) were performed using a DSM 982 Gemini SEM (Zeiss, Germany) with back-scattered electron (BSE) detector. Parallel foils of the coating were ion-thinned and analysed with a 300kV EM430-T TEM (FEI, the Netherlands) coupled with EDS analysis.

3 Results and discussion

3.1 HPRPS process in nitrogen atmosphere

In a previous work [14] using Ar/He in argon atmosphere up to 250 kPa, it was shown that the pressure concentrated the energy density within the HPPS plasma and improved the heat transfer between the plasma and the particle. When comparing an argon atmosphere with a nitrogen atmosphere, it was calculated that the temperature of the plasma decreased more quickly along the plasma axis in a nitrogen atmosphere [15]. Nevertheless, Ar/He plasma rather than Ar/H_2 plasma (used in the conventional APS mode) showed the advantage to operate up to 250 kPa without overheating and damaging of the plasma nozzle for a nearly similar plasma effective electric power, **Fig. 2**.

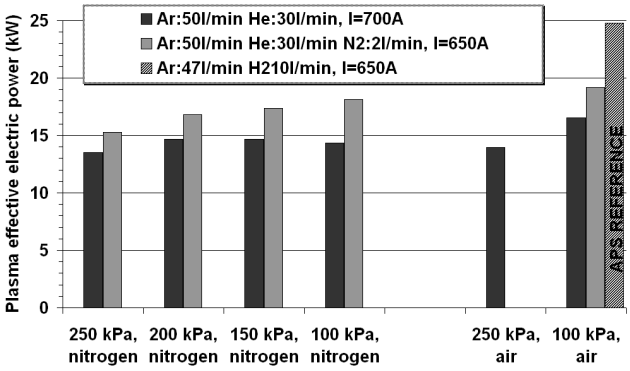


Fig. 2. Plasma effective electric power (F4-MB gun)

The same plasma gas mixtures were kept whatever the applied pressure. However, when adding a low content of N_2 gas, it was necessary to reduce the arc current down to 650A to avoid any damage to the nozzle due to the high enthalpy of N_2 plasma gas (nearly similar to that of H_2). For this ternary plasma gas mixture, a rather slight decreasing of the plasma effective electric power was obtained when pressure increased. Note that HPRPS selected conditions were all with a lower plasma power than that for APS. Nevertheless, this selected parameters with the cooling of the substrate allowed the explicit influence of surrounding reactive gas pressure to be assessed. This aspect was a key issue of this study.

3.2 Influence of atmosphere on plasma-sprayed Ti-6Al-4V

3.2.1 Typical phase composition

Typical XRD diagrams of as-sprayed Ti-6Al-4V coatings were selected to bring to the fore the titanium compounds (with help of the JCPDS cards) that could crystallize during the process, **Fig. 3**.

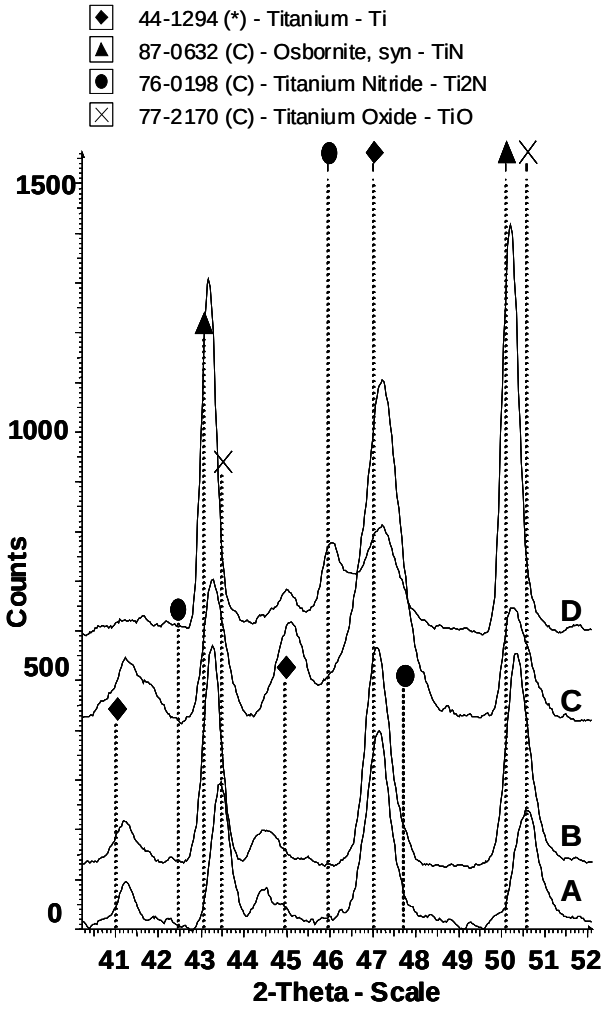


Fig. 3. XRD Diagrams: A: APS (100kPa, air atm., Ar/H_2 plasma), B: HPPS (250 kPa, air, Ar/He plasma), C: RPS (100 kPa, N_2 atm., Ar/He/N_2 plasma), D: HPRPS (250kPa, N_2 atm., Ar/He plasma)

If TiO and TiN peaks overlap, this could correspond to a titanium oxi-nitride phase. However, if Ti-6Al-4V coatings in air and nitrogen atmosphere are compared (A and D diagrams), a difference between these two compounds was clearly exhibited, i.e. TiO for APS and TiN for HPRPS. Spraying Ti-6Al-4V coatings in HPPS (Profile B) led to a titanium oxi-nitride. A high TiN content and a low α-Ti content were obtained in the HPRPS mode. In this case Ti_2N peak was also identified. These results are in agreement with those obtained for pure titanium [12]

3.2.2 Pressure-assisted nitriding of Ti-6Al-4V

On the basis of the value of the (200) peak area of the TiN phase (2θ=50.1°), a qualitative assessment of the nitriding level was obtained as a function of nitrogen pressure in the CAPS chamber, **Fig. 4**. This diagram featured the influence of the particle size and that of nitrogen in the plasma gas.

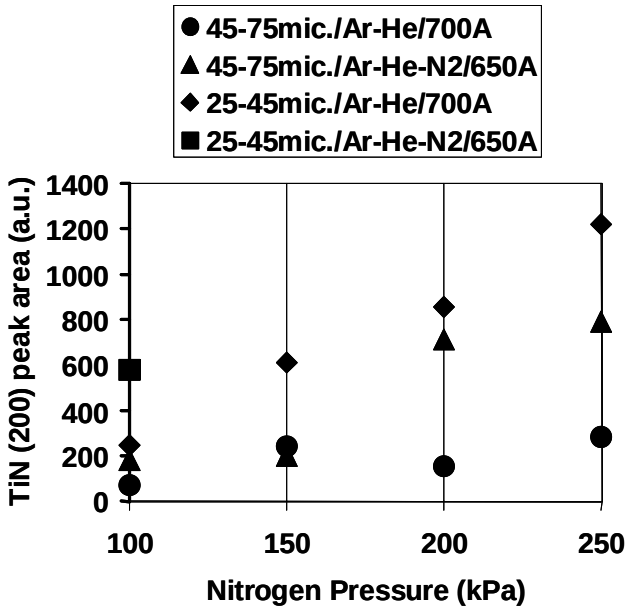


Fig.4. TiN (200) XRD peak area for different HPRPS conditions.

The higher content of TiN was qualitatively determined for the HPRPS Ti-6Al-4V coating using the smaller particle size. In this case, pressure effect can be said to be linear. This established clearly the gas pressure effect on the nitriding process in the HPRPS mode using nitrogen atmosphere. This effect was promoted by the use of a rather fine Ti-6Al-4V powder. Further nitriding could be obtained, provided that 25-45µm Ti-6Al-4V powder is sprayed in the HPRPS mode using an Ar/He/N_2 plasma. Unfortunately, only one result in the RPS mode (100 kPa, N_2 atm.) was available. Furthermore, pressure settings higher than 250 kPa could be interesting too. But, further investigation is needed to define suitable plasma parameters at 350 kPa for example.

3.3 Nitrided Ti-6Al-4V coating microstructure

3.3.1 Nitrogen distribution within coatings

Using EPMA of HPRPS cross-sections (200 kPa, Ar/He plasma, 25-45 µm specimen), the quantitative distribution of the main constitutive elements (Ti, Al, V, N, O) was measured along a direction perpendicular to the coating surface. Typical distribution of the nitrogen element within the lamellar HPRPS coatings could be obtained, **Fig. 5**.

The diagram could be divided in three different regions. These regions corresponded to three different lamellae. Two of these lamellae were rich in nitrogen as well shown in the diagram (from 0 to 10 µm and from 18 to 24 µm) by mean of the nitrogen weight percentage which was rather high and constant in the range of 11-15%. The third lamella (from 10 to 18 µm) was a low-nitrogen content lamella (0-3%) that could be considered as a Ti-6Al-4V lamella.

Note that the specimen was free of oxygen except the regions wherein pores were filled with mounting organic resin.

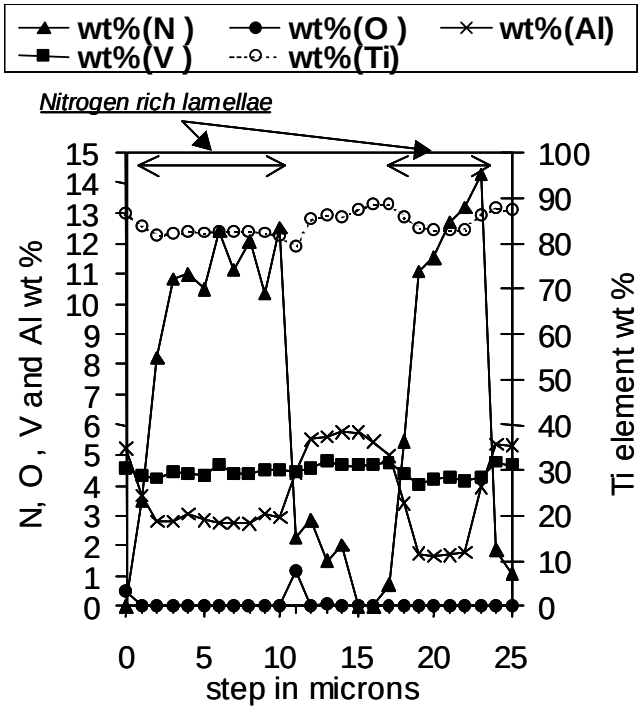


Fig.5. EPMA profiles on HPRPS specimen

This typical distribution of nitrogen within HPRPS coating showed that nitrogen was rather homogeneously distributed on a micrometric scale within a nitrided lamella. However, nitrided lamellae were randomly located near non- or poorly- nitrided lamellae. The resulting material can be considered as a Ti-6Al-4V based matrix composite with TiN-rich lamellar addition (the size of which is the size of a splat). Despite the pressure-assisted nitriding, this quantitative analysis showed that the nitriding process did not affect homogeneously all the sprayed particles. Further work is needed to better control the TiN distribution within the HPRPS coatings. Argon cooling should probably be no longer used to allow a better atmosphere homogenisation.

Furthermore, it was observed in nitrogen-rich regions that the weight percentages of all the Ti-6Al-4V constitutive elements decreased, with a steep gradient for Al, i.e. from 6% down to 2-3%. No particular Ti, Al or V increase in the rest of the coating that could rebalance this chemical removal was detected using EPMA. This fact exhibited one distinctive characteristic of Ti-6Al-4V reactive spraying compared to pure Ti. One may assume (but need confirmation) that intermediate Ti-Al-V compounds could form then be evaporated during the HPRPS process.

3.3.2 Coating microstructure

SEM views of etched cross-section were achieved for RPS and HPRPS coatings (25-45µm particle size) using Ar/He/N_2 or Ar/He plasma gas mixture respectively, **Fig. 6**. These coatings were selected according to the different TiN contents obtained by XRD qualitative (see section 3.2.2) and because of the very different coating features. Using nitrogen in the plasma gas in the RPS mode (100 kPa, N_2) resulted in a well-flattened and dense typical lamella structure, **Fig 6-a-1**. Nitrogen-rich regions were in dark grey while light grey regions corresponded to non-nitrided (or less-nitrided) lamellae using BSE SEM. Nitrided dark regions were homogeneously distributed and were for around 50% of the coating. Using a high and reactive pressure at 250 kPa (Ar/He plasma), large dark nitrided regions were observed, **Fig 6-b-1**. In this case, a coating morphology with round particles was observed. The high nitrogen content within HPRPS coatings showed that the particles were melted, nitrided and probably partially solidified before impinging. Nevertheless, the flattening ratio was sufficient to form a plasma-sprayed coating.

At higher magnification, very different nitrided microstructures were exhibited, **Figs. 6-a-2 and 6-b-2**. The well-flattened RPS lamellae were with a small-sized and homogeneous microstructure in the nitrided region. Some smooth and glassy regions were attributed to the Ti-6Al-4V material (not represented in the figure). This feature corresponded to an homogeneous removal of Ti alloy or N-rich Ti alloy. This was confirmed by TEM analysis, **Fig. 7–a**. Microcrystalline TiN particles were embedded and homogeneously distributed in a pure or N-rich α-Ti matrix. On the other hand, the highly nitrided agglomerated HPRPS particles exhibited an heterogeneous microstructure, as shown by selective chemical etching, **Fig 6-b-2**. Ti-N phases (TiN and/or Ti_2N phases) with a typical inner dendritic microstructure and some dense layer at the particle periphery were observed [16]. The Ti-N compound was actually a corrosion resistant phase and could not be etched by “Kroll” reagent. This revealed large areas with both fine and coarse Ti-N dendrites. TEM view of this coating allowed to observe the corresponding micro-scaled TiN particles and submicro-scaled TiN precipitates, **Fig. 7-b**. These microcrystalline TiN particles were surrounded by an α-Ti alloy. Fine TiN precipitates corresponded to a high solidification rate while coarser TiN particles were nitrided and partially solidified before impacted. As a confirmation of this, it was observed that the dense peripherical layer was identified as sequence of coarse TiN particles. TiN or Ti_2N could not be easily detected using SEM of etched coatings and Ti_2N was not yet detected by TEM.

Decreasing the spraying distance to 75 mm led to HPRPS coatings with a well-flattened lamella structure and with a TiN content similar to that of the RPS coating sprayed at 100kPa using Ar/He/N_2 plasma. This means that the nitriding process occurred mainly during the particle flight and could easily form high-nitrided titanium compounds in the pressure–assisted process. Further investigation is needed to determine a spraying distance suitable for building-up well-flattened coatings with the highest content of nitrided titanium compounds.

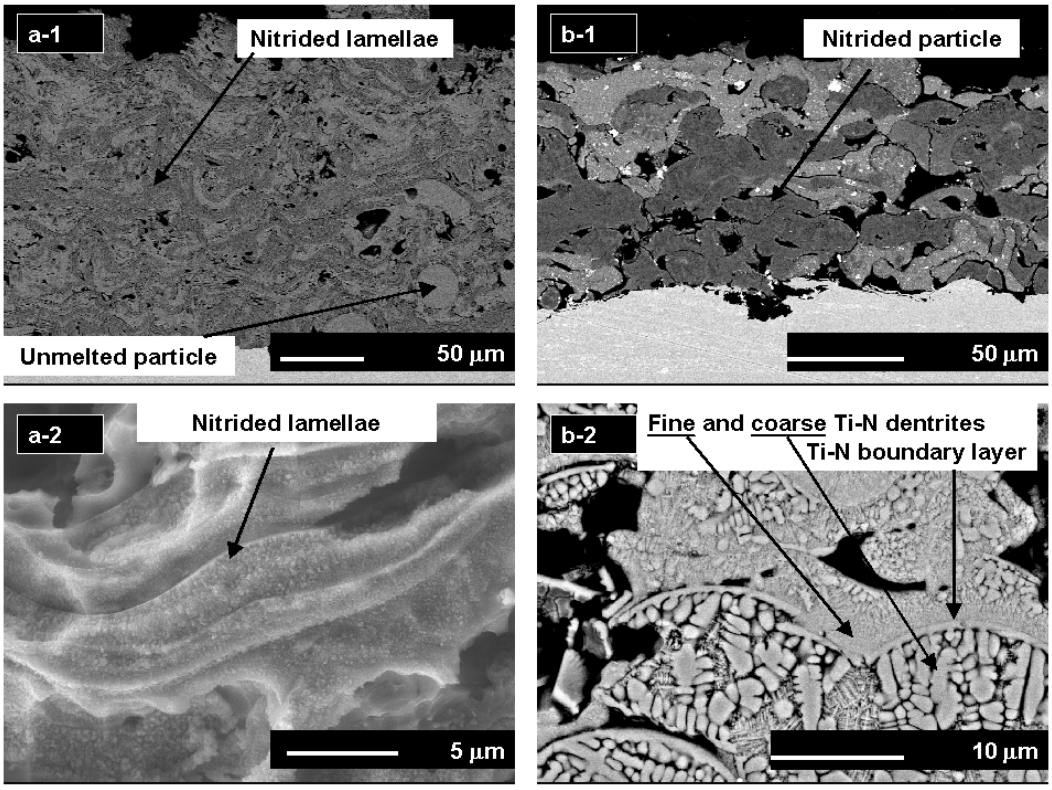


Fig.6. SEM views, a: RPS (100 kPa, N2 atm., Ar/He/N_2 plasma), b: HPRPS (250kPa, N2 atm., Ar/He plasma)

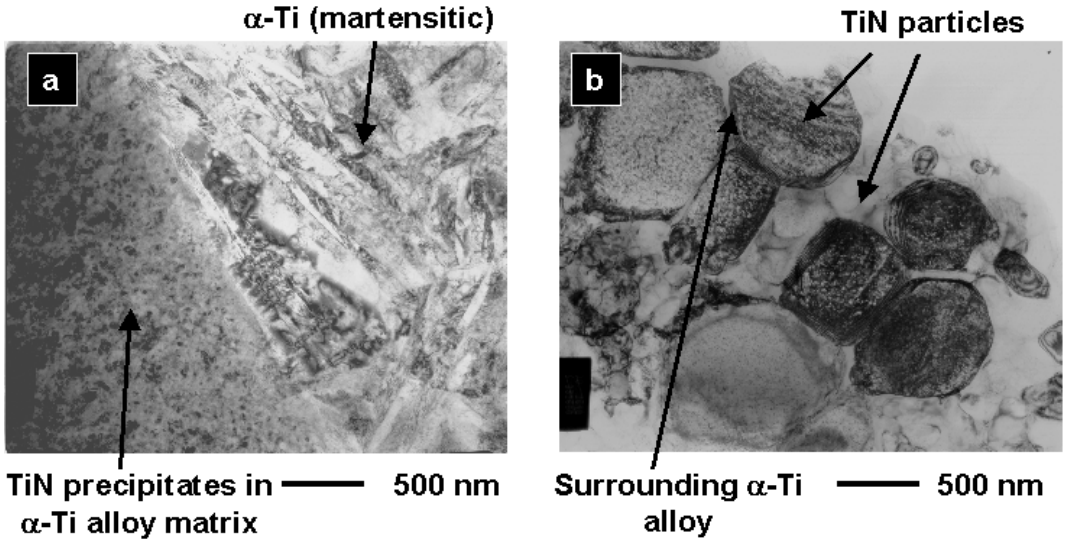


Fig.7. TEM views, a: RPS (100 kPa, N_2 atm., Ar/He/N_2 plasma), b: HPRPS (250kPa, N_2 atm., Ar/He plasma)

4 Conclusions

Pressure-assisted nitriding of plasma-sprayed Ti-6Al-4V was obtained using CAPS up to 250kPa. Pressure effect is a key parameter to carry out highly-nitrided Ti-based coatings because the nitrogen reacts mainly during the particle flight to form TiN or Ti_2N. With an increased pressure, it was possible to form nitrided lamellae within the coating even with a short spraying distance. The use of nitrogen in the plasma gas was not necessary to obtain a high nitrogen content. Using a rather low enthalpy Ar-He plasma gas mixture coupled with a high-pressure of nitrogen in the chamber, HPRPS Ti-6Al-4V coatings at 250 kPa with small particle size powder exhibited the highest TiN content with some Ti_2N phase. Pressure improved the heat transfer between the plasma and the particles and allowed the use of a low enthalpy plasma to melt the particles. In these conditions, the “in-situ” nitriding process was so efficient that a typical dendritic growth of fine and coarse TiN particulates was observed within sprayed lamella as confirmed by TEM. A lower nitrogen content within HPRPS or RPS Ti-6Al-4V coatings led to a lower TiN content without typical TiN dendrites but with very fine microcrystallized TiN and/or N-rich titanium solid solution and residual Ti-

6Al-4V martensitic phase. A promising application could be the tailoring of Ti-6Al-4V-based matrix composites with TiN-rich lamellae containing titanium hard phases of different micro-scaled sizes that could improve wear properties. Work is in progress to characterize the TiN hard phase within HPRPS coatings using nano-indentation coupled with atomic force microscopy.
Some significant removal of Ti-Al-V was detected in the N-rich lamellae of Ti-6Al-4V using EPMA and TEM analyses. Further work is needed to explain this particular phenomenon and to discuss the role of Al and V on the nitriding process. The particle size is another key parameter to manufacture nitrided Ti-based coatings. If fragmentation into fine particles occurred during the spraying process, it led to fine TiN round particulates. The direct use of ultra-fine or nanoscaled Ti based powder could be very interesting, especially in case of co-spraying for the achievement of nitrides reinforced composite coatings for example.

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