Structural and mechanical characterization of titanium nitride layers obtained by plasma thermal spraying

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Keywords

Plasma thermal spraying, titanium nitride, microlayers, wear resistance, hardness

1. Introduction

The scientific, technological and industrial past decade has required the creation of new materials, in order to satisfy the various conditions of static and dynamic loading in corrosive environments at high temperatures.

Titanium nitride (TiN) is a ceramic material, which has a high wear resistance and mechanical strength, also a low friction coefficient at high temperatures [1]. Titanium nitride is used to perform the hard coatings on the cutting tools, and on the components in the petrochemical industry, frequently subjected to complex abrasive wear and corrosion [2].

Typically, this ceramic material is deposited on the metallic substrates by PVD and CVD methods, but these methods have a low efficiency owing to the low thickness of the microlayers, less than 10µm [3]. It was shown that the performance of titanium nitride microlayers depends on the thickness, so the thicker microlayers lead to a better wear and corrosion resistance. Titanium nitride is also, a biocompatible ceramic material, owing to their high mechanical characteristics, good wear and corrosion resistance, so it is used in medicine to cover the hip, the knee implants and the dental implants [4].

2. Titanium nitride formation by plasma thermal spraying process

Plasma thermal spraying of titanium powder in nitrogen atmosphere is a complex process which combines in the same time the both aspects: plasma thermal spraying of the titanium powders and chemical reactions, which occur during the spraying process.

In figure 1 is presented the schematic diagram of the thermal spraying system in nitrogen plasma jet.

Due to the high temperatures, the titanium powder particles melt into the plasma jet and they are guided by the nitrogen gas stream directly to the substrate. The particles reach the surface of the substrate in plastic and molten state, and adhere to the substrate by specific mechanisms. From the direct reaction between the molten titanium particles and the nitrogen, the titanium-based compounds (TiN_2, Ti_2N, TiO_2) appear, in various microscopic forms [5].

3. Experimental program

The experimental program aimed to obtain the deposited microlayers on titanium alloy substrates disks (Ti6Al4V), of 5 mm thickness, using the titanium powder particles, of less than 30 µm in size, by thermal spraying technique in nitrogen plasma at four spraying distances, d_p (140; 120; 100 and 80 mm).

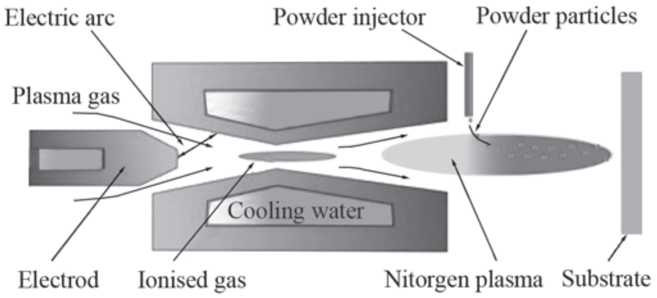

Figure 1. Schematic diagram of the thermal spraying system in nitrogen plasma jet [5].

The obtained coatings by plasma thermal spraying method were subjected to macro, and microscopic examinations, to thickness determination of the microlayers, and HV0.1 hardness and roughness measurements.

4. Experimental results

4.1 Macro-microscopic examination

The macroscopic examinations performed in accordance with EN 1321:2006 showed the microlayers aspect. In the figure 2, the deposited microlayers aspect is presented.

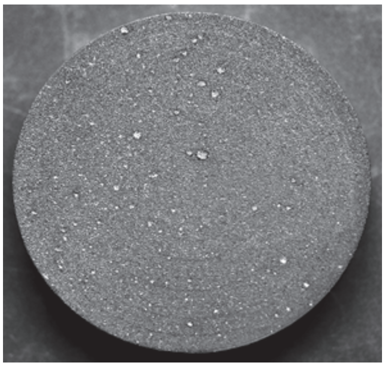

Figure 2. Macrostructure, Sample 1.

On the microlayers surfaces of the titanium nitride layers, the spherical particles of titanium nitride were been observed.

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These particles are resulted by rapid solidification of the molten titanium in nitrogen plasma jet.

4.2. Determination of the deposited microlayers thickness

The value of the microlayers thickness are presented in the Table 1.

Table 1. Values of microlayers thickness.

Sample	Microlayer thickness [µm]		
	Individual values	Mean value	Mean square deviation, σ^2
1	92, 89, 87, 91, 90, 92	90.8	5.3
2	105, 108, 112, 111, 114	110.0	6.6
3	127, 131, 132, 120, 131	128.2	10.4
4	140, 122, 154, 141, 130	137.4	12.6

The variation of maximum and minimum microlayers thickness of the analyzed variants is shown in Figure 3.

It must be mentioned that, the lowest values of the microlayers thickness (87-92 µm) was obtained at sample 1 at the biggest thermal spraying distance (140 µm). By decreasing the spraying distance, the values of the microlayers thickness are increased, reaching at sample 4 at values between 122 and 154 µm.

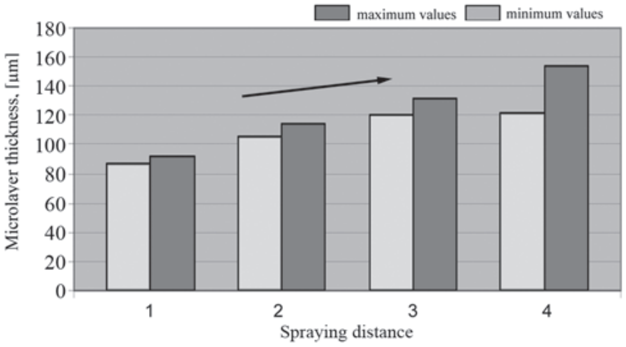

Figure 3. Microlayers thickness variation function of spraying distance.

4.3. Determination of the microlayers roughness

The determination of the surface roughness was made by evaluating the average roughness, Ra and the measurements results are presented in Table 2. The Figure 4 shows the values of average roughness, Ra function of the spraying distance.

Table 2. Values of average roughness, Ra.

Sample	Average roughness Ra [µm]		
	Individual values	Mean value	Mean square deviation, σ^2
1	5.58; 5.91; 5.35; 6.29; 5.45	5.7	0.43
2	5.29; 5.36; 5.42; 4.27; 5.27	5.1	0.38
3	3.90, 3.99, 3.13, 3.65, 3.42	3.6	0.27
4	2.38; 2.54; 2.68; 2.33; 2.63	2.5	0.18

By modifying the spraying distance, from 140 mm to 80 mm, it can be observed the tendency of decreasing the roughness average values, Ra from 5.7 µm, at sample 1 to 2.5 µm, at sample 4. This is possible, because at shorter distances, the particles of the sprayed material are molten in the flame, thus when are reaching the substrate being in molten state are splattered, resulting a lamellar structure. By increasing the spraying distance, the particles leaves the heated zone of the flame and will have a lower temperature, passing from molten to plastic state, so during the impact with the substrate their form will remain almost spherical, resulting an increased value of the roughness.

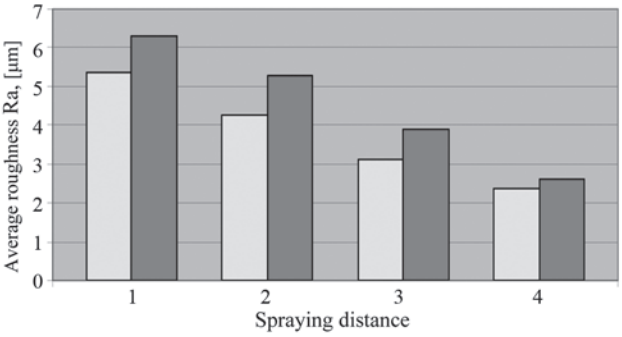

Figure 4. Microlayers roughness variation function of spraying distance.

4.4. Microscopic examinations

The structural characteristics (structure, phase constituents, etc.) of the deposited microlayers (DM) and the metallic substrate (MS) were evaluated by metallographic examination according to EN1321: 2006, as:

- the base metal (BM), titanium alloy Ti6Al4V has biphasic $\alpha + \beta$ structure, the β phase having predominantly a lamellar form in the base matrix (Figure 5).

Figure 5. Base metal microstructure, 100x.

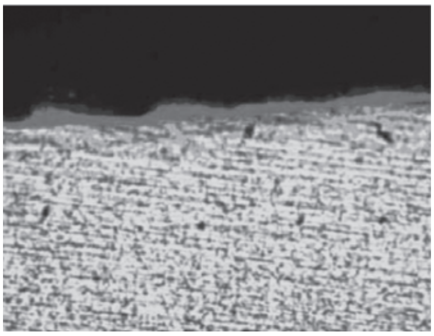

Figure 6. Interface microstructure microlayer-substrate, 100x.

- the deposited microlayers (DM) of the samples 1, 2, 3 and 4 have the structures composed of titanium nitride precipitation with spherical agglomerations, and the thickness of the microlayers is not uniform in the same variant (Figure 6).

It is observed a continuous adherence on the crossing zone of the microlayers to titanium alloy substrate. No cracks or microcracks were been observed in the examined zones.

4.5. Determination of the deposited microlayers hardness

The HV0.1 hardness test was made on the cross section of the deposited microlayers, at samples 1 ... 4. The measurements results are presented in Table 3.

In Figure 7, it is shown the variation of local hardening, on the examined zones of the deposited microlayers by plasma thermal spraying (samples 1 ... 4)

Table 3. Hardness values.

Examined zones	HV0,1 Hardness		
	Minimum value	Maximum value	Mean value
Sample 1, (140 mm)	658	750	704
Sample 2, (120 mm)	662	778	720
Sample 3, (100 mm)	673	808	740
Sample 4, (80 mm)	696	836	766
BM- Ti6Al4V	326	339	330
Titanium alloy Ti6Al4V according ASTM B 348	-	349	-

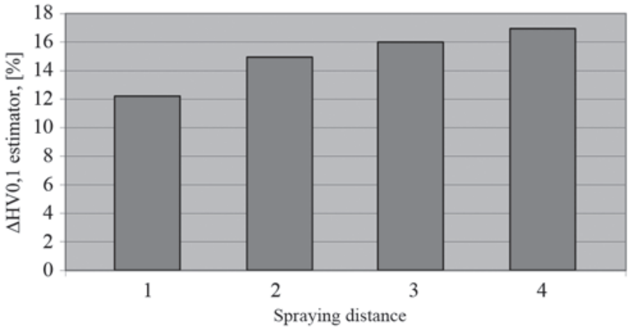

Figure 7. Variation of ΔHV0.1 function of spraying distance.

By increasing the thermal spraying distance (d_p), the layers hardness has the tendency to increase the local hardening estimator from 12.1 to 17.0%. In this case, it is not possible to appear the structural embrittlement phenomena due to the hard microstructures, which characterize the development of titanium nitride compound (TiN) as globular particles and as matrix in the basic structure.

5. Conclusions

5.1. The experimental program made in order to perform and to evaluate the quality of the titanium nitride microlayers obtained by plasma thermal spraying of titanium powder in nitrogen plasma jet had the aim to determine the chemical composition, the roughness, the specific microstructures and the hardness of these microlayers.

5.2. The titanium nitride microlayers deposited by plasma thermal spraying in nitrogen plasma jet of the titanium powder on titanium alloy substrate allowed the obtaining of new advanced materials having a high hardness between 658 and 836 HV0.1. No cracks were been observed on the microlayers surface or in the cross section of the joints.

5.3. The titanium nitride obtaining process by plasma thermal spraying in nitrogen plasma jet in the analyzed variants (1, 2, 3, and 4) can be achieved even in the industrial conditions, in order to cover the strong stressed components subjected to wear and corrosion. The deposited microlayers have the thicknesses between 100 and 137μm, and the surface roughness is less than 6.29 μm.

Acknowledgement

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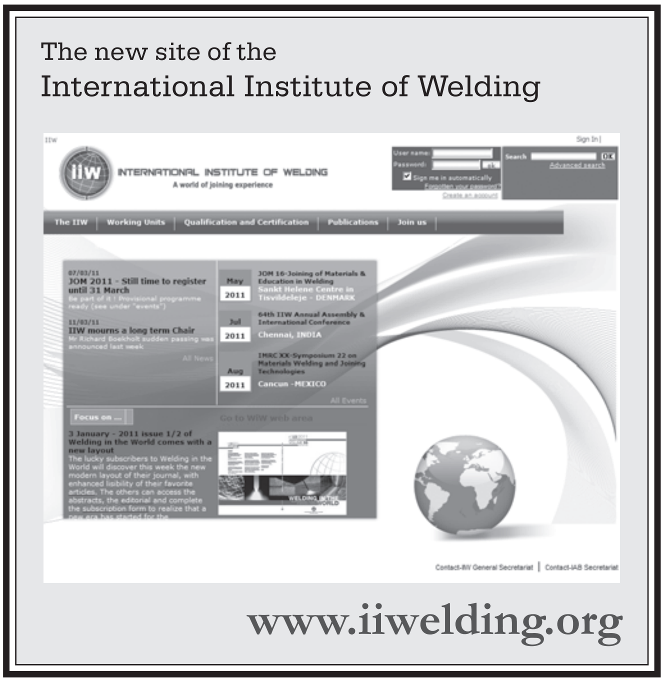

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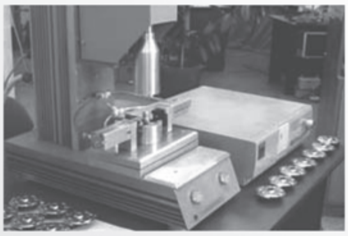
Ultrasonic Welding Laboratory

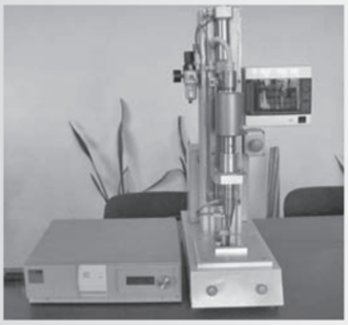
Research directions:

- Applied research for experimental development of new materials joining technologies for industrial applications
    - Ultrasonic welding of non-ferrous metallic materials: Cu, Al, CuZn37
    - Ultrasonic welding of thermoplastics materials: PC, ABS, PEHD
    - Ultrasonic welding of new materials, composites, with ”shape memory” and biocompatible: CuZnAl, NiTiCu, NiT6V
- Study of the interface phenomena, microstructure quality and metallurgical constituents in ultrasonic welding of metallic materials
- Conception, realisation and experiments of new ultrasonic joining equipments for plastics and metallic materials
- Conception and calibration of the mechanical resonator

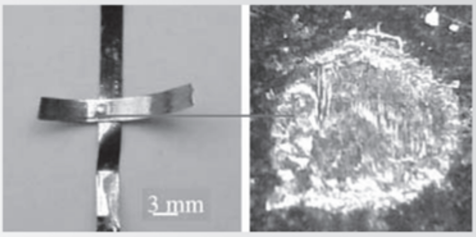


Equipments

- **Ultrasonic equipment for metallic material joining,** 3000 W / 20 kHz
- **Ultrasonic equipment for plastic material joining, 2500** W / 20 kHz
- **Equipment for liquid media activation in sonochemistry,** 2000 W / 20kHz
- **Hybrid welding equipment, resistance and with ultrasounds,** 3000W /20kHz 36kVA / 220V
- **Testing equipment (sonometer) for electro-ultraacoustical systems – resonant frequency and acoustical impedance,** 100 Hz- 99kHz
- **Testing equipment (sonometer) for electro-ultraacoustical systems in working - resonant frequency,** 100-99kHz
- **Software for ultrasonic calibration, KRELL ENGINNERING.** Design and configuration of ultra-acoustical devices:
    - piezoceramic converters for liquid reaction media;
    - sonotrodes for plastics and metallic materials welding.



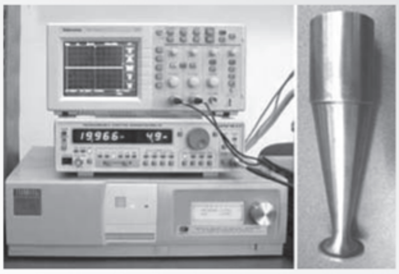
Application examples



Welding bands of NiTiCu +NiTiCu
(20μm +20μm)

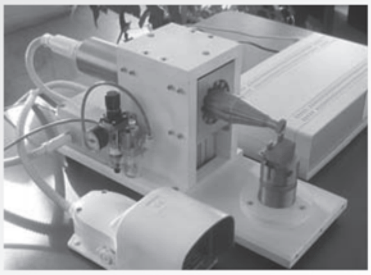
Ultrasounds welding, 4 rivet joints,
PC +6 % fiber in automotive micromotors

Copper pipe welds with ultrasouds
(0,8mm + 0.8mm)



Conception and calibration of
the mechanical resonator

Cavitational equipment,
500 W / 20 kHz



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- design and production of sonotrodes
- technical development for US welding applications
- training of personnel
- consulting

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