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Study of the laser remelting of a cold sprayed titanium layer.

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Abstract

Cold Gas Dynamic Spray is an emerging coating technology based on the use of a supersonic gas jet to accelerate (up to 1000 m/s) and to impact a powder, with size ranging from 1 to 50 µm in diameter, on a substrate. Due to the high speed, during the impact, the powder undergoes a severe plastic deformation such that it adheres on the substrate. Thanks to this method, it is possible to produce up to fully dense metallic coatings on substrates of different materials. With this technology, different kinds of powder (metals, polymers, ceramics, composite materials and nanocrystalline powders) or their mixing can be deposited. Among the various possible powders that can be deposited by cold spray, titanium is one of the most attractive materials thanks to its potential applications. A titanium layer produced onto a softer materials (i.e. aluminium alloys) could improve both the corrosion resistance and the wear properties of the components. However, the coating made with this technique could be affected by several problems, such as porosity, high roughness and low mechanical properties. A possible solution for this issues is the use of laser remelting post-deposition treatment. The present investigation deals with the application of a continuous wave diode laser in order to change the coating properties and metallographic structure. With this aim, laser remelting of a titanium cold sprayed layer were carried out on samples of grade 2 titanium alloy, 5 mm thick, obtained by cold spray technique, by using a 220 W diode laser at different scan speed. In order to avoid the influence of the particular substrate, the laser remelting process was carried after the detachment of the coating from the substrate. After laser treatments, light and SEM microscopy were carried out to analyze the geometry of remelted zone and the evolution of its microstructure morphology. Moreover, micro-hardness measurements were made to evaluate the mechanical properties. Three different metallurgical structures corresponding to the remelted zone, the heat affected zone and base material were observed. The remelted zone showed an elliptical shape, with a depth up to 0.7 mm and a martensitic microstructure. Furthermore, in this zone, hardness higher than the base material (more than threefold) was found. In conclusion, it is possible to affirm that the laser remelting is a promising technique to improve the superficial properties of titanium cold sprayed layers.

Keywords: : Cold Spray, Titanium, Laser Remelting, Diode Laser, Microstructure.

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1. Introduction

Cold gas dynamic spray technique (CGDS) is an additive technology [1] that makes use of a converging/diverging nozzle (known as De Laval nozzle) and a high pressure, heated gas source (usually nitrogen) to create a supersonic gas flow. Metallic particles, usually in the size range of 10–100 µm, are injected into this gas flow and propelled to supersonic velocities. Typical particle velocities range from 500 to 1000 m/s and a high kinetic energy causes the impingement of the particles onto the substrate [2]. Depending on the material and particle speed, the particles will either rebound from the substrate (with or without erosion) or bond with the substrate [3]. The speed at which bonding is achieved, is referred to as critical velocity and depends on the particle sizes, particles distribution and the substrate material. Macroscopic plastic deformation resulting from the high impact velocity is generally believed to be the main bonding mechanism for metallic coatings deposited on metallic substrates [4–5]. The high impact momentum of the particles causes mechanical interlocking varying, depending on the application conditions and the metals employed. In this process, coating deposition occurs at relatively low temperatures compared to other spray technologies. Moreover, during the process the sprayed particles remain in the solid state. The coatings produced through this technology, exhibit remarkably high densities

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and conductivities, good corrosion resistance and a high hardness due to their cold worked microstructure [6]. The process provides a solution for applications where conventional metal spraying processes, such as flame, arc, plasma and HVOF spraying are inappropriate, in which problems such as coating porosity, oxidation and low adhesion may occur [7-8]. Furthermore, this process could be the only chance to produce coatings of harder materials on heat treatable aluminium alloys, due to the presence of an aging temperature that is easily reached during the thermal spray processes. Titanium is one of the most attractive metal for cold spray, thanks the potential multiple applications. Bulk titanium is finding increasing application in many industrial field, due to its corrosion resistance, as well as the biomedical industry where it is utilized in implants, because of its biocompatibility [9]. Furthermore titanium and its alloys are finding an increasing widespread use in the aeronautic field, due to their compatibility with CFRP. On the other hand, the use of titanium alloys is limited by the high costs, the difficulty of machining and the complexity of manufacturing. The application of Ti cold spray on other bulk metals is a potentially viable method for such applications. Cold spray has the potential to be an effective and economical way of converting manufactured Ti powders directly to finished products and advanced surfaces. Despite these premises the cold sprayed coatings have a number of drawbacks: porosity, superficial roughness and so on; these drawbacks could be overcome through post spraying superficial treatments, such as laser remelting [10]. Moreover, the increasingly greater and more demand imposed on materials, makes more difficult or even impossible to combine the different properties required in one single material; this results into the needing to develop new methodologies to improve the superficial properties of metallic materials. For this purpose, post-treatment by laser has been developed [11]. Laser surface melting is a promising process to improve the performance of sprayed coatings [12–13]. Although laser surface remelting has been actively investigated and applied to improve wear and corrosion properties for various metals [12, 14-15], although in literature laser remelting of titanium alloys is present, there is no investigation reported on cold spray deposition treatments.

The present investigation deals with laser remelting of a grade 2 titanium layer obtained by cold spray technique. Remelting tests were performed using a 220 W diode laser at different scan speed. After laser treatments, optical and SEM microscopy were carried out to analyze the geometry of remelted zone and the evolution of its microstructure morphology. Moreover, micro-hardness tests were performed to evaluate its mechanical properties.

Three different metallurgical structure corresponding to the remelted zone, the heat affected zone and base material were observed. The remelted zone showed an elliptical shape, with a depth up to 0.7 mm and a martensitic microstructure. Furthermore, in this zone, a hardness higher than the base material (more than threefold) was found.

In conclusion, it is possible to affirm that the laser remelting is a promising technique to improve the superficial properties of titanium cold sprayed layers.

2. Material, equipment and experimental procedures

2.1. Coating production

Commercially pure (grade 2) titanium particles with a mean granulometry of 40 μm were deposited onto an AA 2024-T3 plates 2 mm thick. The chemical composition and the main properties of grade 2 titanium are summarized in Table 1. In Fig. 1 it is reported a SEM micrograph of the powders. It is possible to observe that the powders have an irregular shape and moreover some conglomerates having bigger dimension are visible. Commercial cold spray facility DYMET403J (Obninsk-Center for Powder Spraying) was used for spraying. In order to avoid titanium particles oxidation during the spraying process, the deposition was carried out adopting Helium as carrier gas [16-17]. A round-shaped exit nozzle, 4.8 mm in final diameter, was adopted. In Fig. 2, a sketch of low pressure gas dynamic spray process is reported.

The parameters for the spaying process were chosen taking into account the previous literature [18]. In particular the particles were sprayed at a velocity of 680 m/s with Helium gas at 600 °C while the chamber pressure was about 15 bars. Under these conditions, a superficial layer of cold sprayed titanium powder, 5 mm thick, was obtained on the substrate of aluminium plates. After the deposition the titanium layer was detached from the substrate by means of a precision micro cutting machine with automatic feed, Presi-Mecatome T201.

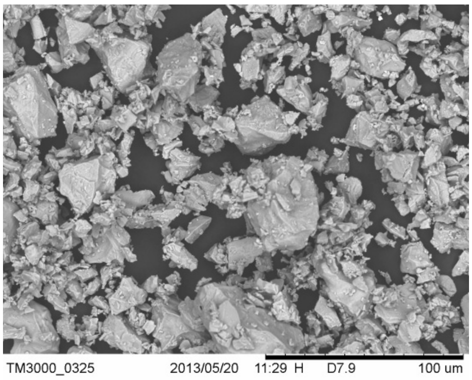


Fig. 1: SEM micrograph of the titanium powders before the spraying process.

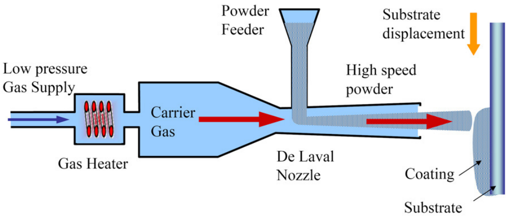


Fig. 2. Low pressure gas dynamic spray process schematization.

2.2. Laser equipment

The laser treatments were carried out by using a 220 W diode laser (IPG DLR-200-AC). The laser source is transferred via an optical fibre, 5 m in length, to a laser head and focused by a lens with a focusing length of 60 mm on the plate surface, that corresponds to a beam diameter, at the focusing point, of about 2 mm. The head was mounted on a 3+1 axis CNC system (Rofin finecut Y 340M). The laser system was computer controlled; this allows the generation of the geometric patterns and the set up of the laser power (P), the scan speed (Ss) and the modulation regime. Table 2 shows the detailed characteristics of the laser source. This kind of laser is usually adopted for surface treatments like as: cladding, heat treating, paint stripping, but it is also usable for brazing, soldering and plastic welding operations [19]. In the present work, it was adopted because of the good absorption from metals, at the diode wavelength and for the high efficiency and lower power consumption, compared to the traditional Nd:YAG or CO_2 laser source. The last characteristic is very important when environmental as well as process sustainability are considered.

2.3. Experimental procedures

Experimental tests were carried out at the maximum power (220W), changing scan speed in a wide range (200-1000 mm/min) in order to study the process itself. For each process condition, a single remelted track was carried out. During the tests, Argon was used as shielding gas [20]. The process conditions are summarized in Table 3.

From each remelted track, three sections were analyzed. Optical microscopy (Zeiss Stemi 2000 CS) and Scanning Electron Microscopy (Hitachi TM 3000) microscopy were performed, in order to record the macroscopic geometry of the remelted zone and the microstructure. Vickers micro-hardness measurements were performed, using a load of 1 N and spacing indentations of 0.2 mm, to evaluate the mechanical properties. Kroll’s reagent (2 ml HF, 6 ml HNO_3 and H_2O up to 100 ml) was adopted to point out the metallurgical microstructures, in particular grain boundaries and phase distribution.

Tab. 1: Chemical composition and main properties of grade 2 titanium alloy.

Element	**Ti**	**C**	**Fe**	**H**	**N**	**O**
Weight [%]	99.2	0.1	0.3	0.015	0.03	0.2

Physical and mechanical properties	**Value**	**Units**
Density	4.51	[g/cm^3]
Melting temperature (max)	1665	[°C]
Specific Heat	0.523	[J/kg,°C]
Thermal Conductivity	16.4	[W/m°C]
Tensile Strength	344	[MPa]
Yeld Strenght (at 0.2%)	275	[MPa]
Hardness	145	[HV]
Elongation at break	20	[%]
Young’s modulus	105	[GPa]

Tab. 2: Laser source characteristics (IPG-DRL-200-AC).

Characteristics	**Symbol**	**Value**	**Unit**
Emission centroid wavelength*	λc	975±5	[nm]
Emission Linewidth	Δλ	6	[nm]
Nominal power (min)	P	200	[W]
Modulation rate		50	[kHz]
Output fiber core diameter		200	[µm]
Collimated output beam diameter		5	[mm]
Beam parameter product	BPP	22	[mm*mrad]
Focus length of focusing lent		60	[mm]
Focused spot diameter	Ds	≈ 2	[mm]
Cooling system		air	--
Power consumption		600	[W]

Table 3 – Experimental parameters adopted in the remelting process.

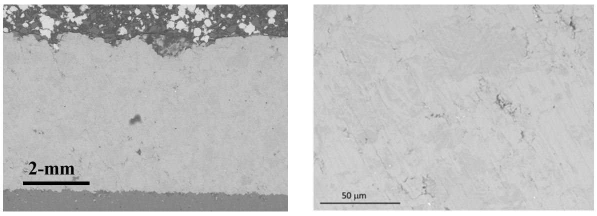
Experimental No.	**Ss [mm/min]**	**Fluence* [J/mm^2]**	**Irradiance** [W/mm^2]**
1	200	42	70
2	400	21	70
3	600	14	70
4	800	11	70
5	1000	8	70

* calculated as P/Ds*Ss;
** calculated as P/irradiated area.

Some macrographs were carried out on the surface of the sheets, in order to appreciate the surface appearance of the remelted tracks. For the remelted zone geometrical evaluations, the maximum width and the maximum depth of the tracks, were used as a response index.

3. Experimental results and discussion

In Fig. 3, a cross section of the cold sprayed layer, at different magnification, is reported. Looking at Fig. 3a, it is possible to see the thickness of the cold sprayed layer, approximately thicker than 5 mm. Such a result, allows to assess that this technique is able to produce thick titanium coatings on metallic substrate. Fig. 3b shows the good internal cohesion and the absence of macroporosity or other defects. Moreover, a good compaction rate is appreciable, i.e. the single splats are not visible and the coating has a good metallurgical continuity.



a) b)

Fig. 3: Macrograph of the cross section of the cold sprayed layer at different magnification.

In Fig. 4 a macrograph made on the top surface of the titanium plate after remelting is reported. In the picture the remelting tracks, carried out at different scan speed (increasing from left to right up to 1000 mm/min), are clearly visible. From Fig. 4, it is possible to appreciate an evident instability phenomenon in correspondence of both the run-in and the run-out, due to the boundary conditions, different than those obtained in the central zone. In fact, due to the lack of material on the specimen edges, the heat transfer changes, resulting in higher temperatures. On the other hand, when the process reaches the steady state conditions, a quite regular track, with no evident surface defects appears. Furthermore, in the firsts two tracks on the left of Fig. 4, it is possible to observe porosity presence. This is a clear symptom of overheating phenomena with consequent formation of the gaseous phase, able to eject part of the liquid far from the track. This indicates the use of too low scan speed (200 mm/min).

Referring to the experimental numbers stated in Table 3, it is possible to affirm that, after this first observation of the track surfaces, the conditions 1 (200 mm/min) and 2 (400 mm/min) produce an heat input too high, resulting in vaporization phenomenon, conversely the track 3 (600 mm/min) appears well defined, moreover, also the colour is as expected, i.e. silver. In Fig. 5 a macrograph carried out in the cross section of a track is reported; it is possible to observe the elliptical shape and how the remelted pool geometry was measured.

In Fig. 6 the maximum width and the maximum depth of the remelted pool were reported as a function of the laser fluence. From the figure, as expected, both width and depth increase as the laser fluence increases, up to a critical value. After that, the curves tend to an asymptote because of the overheating phenomena previously described. It is also interesting to observe that through the laser processing it is possible to remelt, up to 0.7 mm in depth, that is a value compatible with a coating.

During the remelting, the region involved in the process undergoes a great thermal gradient from the remelted pool to the base material; these spatial and temporal distributions of temperature produce a non-uniform microstructure, similar to what happens in laser beam welding. Consequently, three different zones are visible in the sections of the remelted track: base material (BM), heat affected zone (HAZ) and, of course, remelted zone (RZ).

The final microstructure of each zone depends on both the maximum temperature achieved and the cooling rate. Fig. 7 shows a micrograph of the base material made in the powder inner part. From the figure, a fully lamellar microstructure, with very thin lamellae, is observable. In Fig. 8, a micrograph of the HAZ is reported. In the figure, a microstructure similar to the one observed in the base material (Fig. 7), characterised by lamellae of coarser dimensions, is visible. This structure is the typical structure due to a certain heat input during the remelting process, that results in a growth of the grain dimensions; this is in agreement with the literature [21] and the physical phenomenon occurring during the process.

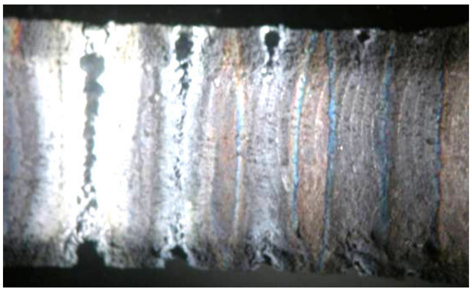


Fig. 4: Macrograph of the top surface of the titanium plate after the remelting process (the run-in is on the bottom).

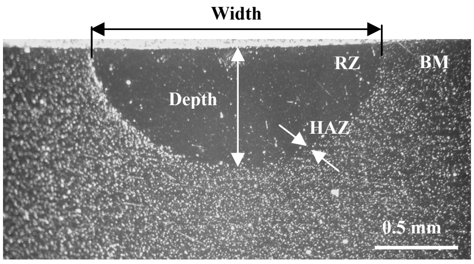


Fig. 5: Macrograph of the cross section of a single track, with indicated the measured geometry and the different metallurgical zones: Remelted Zone (RZ), Heat Affected Zone (HAZ) and Base Material (BM).

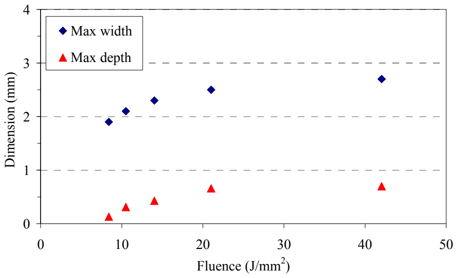


Fig. 6: Experimental measurements of the remelted pools dimensions as a function of laser fluence.

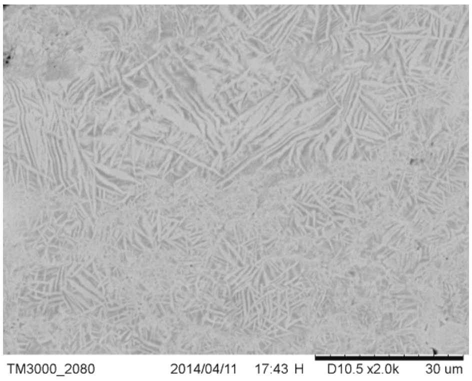


Fig. 7: SEM micrograph of the Base Material (BM).

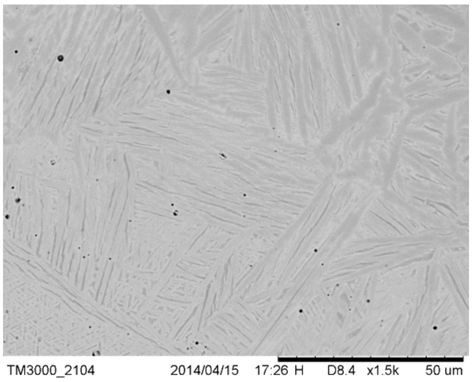


Fig. 8: SEM Micrograph of the Heat Affected Zone (HAZ).

In Fig. 9 the transition zone, between the base material and the above described HAZ, is shown. Looking at this image, it is clearly evident that the lamellae in the HAZ are bigger then the ones in the base material. In Fig. 10 the microstructure observed in the remelted zone (RZ) is reported. The microstructure evolution of the RZ during cooling is the following: during the solidification phase, bcc beta dendritic grain growth in the direction of the heat flow; when the temperature reaches the beta transus (i.e. 913°C), diffusionless transformation from beta to alpha martensitic structure occurs, when the cooling rate is high enough. The final microstructure is bimodal with equiaxial alpha grains and martensitic acicular alpha grains. The microstructure evolution observed is a straightforward result of the thin thickness of the sheet, that causes a rapid cooling rate even for the lower specific heat input condition. In Fig. 11 the transition zone between the remelted zone and the heat affected zone is showed. Some acicular martensitic alpha grains are also visible in the HAZ due to the high cooling rate experienced by this zone during the process.

In Table 4 the results of the Vickers micro hardness measurements in the different zones (BM, HAZ and RZ) are reported. It is important to point out that the grade 2 titanium in form of rolled sheet have a hardness of about 145 HV. The hardness of the base material is higher than the one typical of the Ti grade 2 in form of rolled sheet. This is usual for the cold spraying process since the sprayed particles undergo a plastic deformation, that results in a cold hardening. After all, it is possible to affirm that the whole cold spray process is a kind of cold working for the particles, resulting in a work hardening. As expected, the hardness in the HAZ is lower than the one measured in the base material. This result is in agreement with the microstructure observed in this zone (lamellae of coarser dimension) and its thermal history.

Table 4 – Results of the Vickers micro hardness measurements.

Laser fluence [J/mm^2]	**Hardness [HV]**		
	RZ	**HAZ**	**BM**
8	473	135	160
11	468	125	
14	485	128	
21	475	134	
42	480	130	

Conversely, the remelted zone (RZ) shows an high hardness, noticeably higher than the one measured in the base material. Such a result is due to the presence of acicular martensitic alpha grain within the remelted zone, due to the high cooling rate that occurs in this zone.

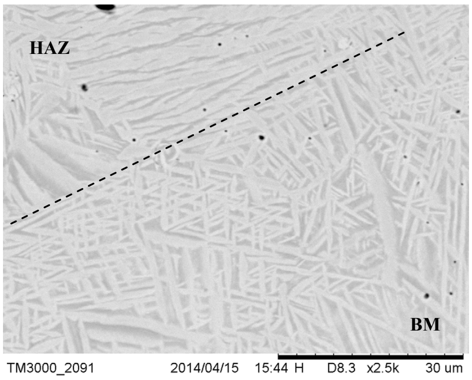


Fig. 9: SEM micrograph of the transition zone between the Base Material (BM) and the HAZ (on the top in the picture).

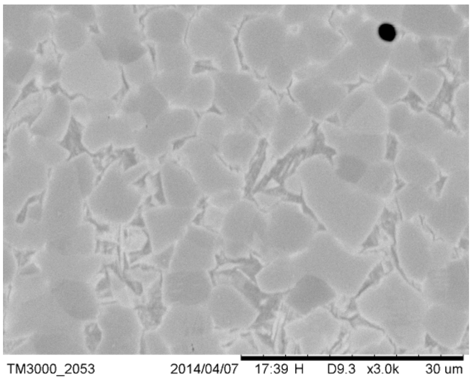


Fig. 10: SEM micrograph of the remelted zone (RZ).

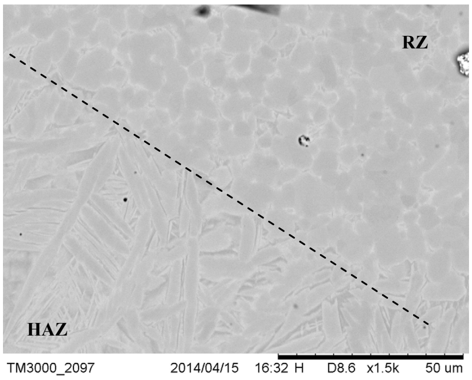


Fig. 11: SEM micrograph of the transition zone between the remelted zone (RZ) and the HAZ.

Conclusions

In this work, a diode laser was successfully used for the remelting of a titanium coating obtained by cold spray techniques. On the basis of the experimental results, the following main conclusions can be drawn:

- It has been confirmed that the cold spray deposition process is a technique that allows to produce dense and thick titanium coatings without macro-porosity and with a good internal cohesion.
- The laser equipment and the experimental conditions adopted allowed to achieve a remelting zone with a thickness up to 0.7 mm.
- The surface remelting was obtained for all the investigated combinations of the process parameters.
- The cross section of the remelted track showed the same elliptical shape for all the combinations of the process parameters, according to the thermal field induced by the laser beam.
- As expected, the dimensions of the melted pool increase as the laser fluence increases, up to a critical value.
- Fluences higher than 20 J/mm^2 result in material vaporization. Under these conditions, several cracks and porosities were produced on the remelted layer.
- After the remelting process, three different metallurgical zones can be observed: a remelted zone (RZ), a heat affected zone (HAZ) and the base material (BM).
- The final microstructure seems to be not dependent on the process parameters. The remelted zone showed a bimodal microstructures with the presence of both equiaxial alpha grains in the BM and HAZ zones, while an acicular martensitic alpha grains in RZ zone was observed.
- In the remelted zone a hardness higher than the ones measured in the base material was observed. This microstructure was produced by the fast cooling experienced by the material.

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References

[1] Irissou E., Legoux J. G., Ryabinin A. N., Jodoin B., and Moreau C., Review on Cold Spray Process and Technology: Part I-Intellectual Property, J.of Thermal Spray Technology, 2008; 17/4: 495-516.

[2] Schmidt T., Gaertner F., Kreye H., New Developments in Cold Spray Based on Higher Gas and Particle Temperatures, J. of Thermal Spray Technology, 2006; 15/ 4: 488-494.

[3] Astarita A., Durante M., Langella A., Montuori M., Squillace A. , Mechanical characterization of low pressure cold-sprayed metal coatings on aluminium, Surface and Interface Analysis, 2013; 45/10: 1530-1535.

[4] Morgan R., Fox P., Pattison J., Sutcliffe C., O'Neill W., Analysis of cold gas dynamically sprayed aluminium deposits, Materials Letters; 2004; 58/7-8: 1317-1320.

[5] Marrocco T., McCartney D., Shipway P., Sturgeon A., Production of titanium deposits by cold-gas dynamic spray: Numerical modeling and experimental characterization, J. of Thermal Spray Technology, 2006; 15/2: 263-272.

[6] Irissou E., Legoux J. G., Arsenault B., Moreau C., Investigation of Al-Al_2O_3 Cold Spray Coating Formation and Properties, J. of Thermal Spray Technology, 2007; 16/5-6: 661-668.

[7] Astarita A., Durante M., Langella A., Squillace A., Elevation of tribological properties of alloy Ti - 6% Al - 4%V upon formation of a rutile layer on the surface, Metal Science and Heat Treatment; 2013: 54/11: 662-666.

[8] Astarita A., Durante M., Langella A., Squillace A., Improving of steel superficial properties through thermal sprayed coatings, Int. J. Surface Science and Engineering, 2013; 7/4: 366-381.

[9] Boyer R., Collings E.W., Welsch G., Materials Properties Handbook: Titanium Alloys, ASM International, 1994, ISBN: 9780871704818.

[10] Bell T., Dong H., Tribological enhancement of titanium alloys. In: State Key Laboratory of Tribology-Tsinghua University, editors, Proceedings of the First Asian International Conference on Tribology, Tsinghua University Press, Beijing China, Tsinghua University Press, 1998, p. 421-427.

[11] Wang Y., Li C., Guo L., Tian W., Laser remelting of plasma sprayed nanostructured Al_2O_3-TiO_2 coatings at different laser power, Surface & Coatings Technology, 2010; 204: 3559-3566.

[12] Daurelio G., Minutolo F.M.C., Curcio F., Caiazzo F., Cinquepalmi M., High speed joining of polymeric plastics using different laser sources (CO_2, Nd-YAG and H.P.D.L.), Proceedings of SPIE, 2005; 5777/II: 903-906, art. no. 174.

[13] Singh B. Sidhu, Laser surface remelting to improve the erosion–corrosion resistance of nickel-chromium-aluminium-yttrium (NiCrAlY) plasma spray coatings, In: Kwok C.T, editors. Laser surface modifications of alloys for corrosion and erosion resistance, Cambridge UK, Woodhead Publishing Limited. 2012, p. 355-366.

[14] Yao Y., Li X., Wang Y.Y., Zhao W., G. Li, Liu R.P., Microstructural evolution and mechanical properties of Ti-Zr beta titanium alloy after laser surface remelting, J. of Alloys and Compounds, 2014; 583: 43-47.

[15] Ge Y., Wang W., Wang X., Cui Z., Xu B., Study on laser surface remelting of plasma-sprayed Al-Si/1 wt% nano-Si_3N_4 coating on AZ31B magnesium alloy, Applied Surface Science, 2013, 273: 122-127.

[16] Astarita A., Genna S., Leone C., Memola Capece Minutolo F., Paradiso V., Squillace A., Ti-6Al-4V Cutting by 100W fibre laser in both CW and modulated regime, Key Engineering Materials, 2013; 554-557: 1835-1844.

[17] Astarita A., Genna S., Leone C., Memola Capece Minutolo F., Paradiso V., Squillace A., Laser Cutting of Aluminum Sheets with a Superficial Cold Spray Titanium Coating, Key Engineering Materials, 2014; 611-612: 794-803.

[18] Moy C.K.S., Cairney J., Ranzi G., Jahedi M., Ringer S.P., Investigating the microstructure and composition of cold gas-dynamic spray (CGDS) Ti powder deposited on Al 6063 substrate, Surface & Coatings Technology, 2010; 204: 3739–3749.

[19] Gisario A., Barletta M., Veniali F., Document Surface reconstruction of porous substrates in sintered bronze by cw-high power diode laser, Optics and Lasers in Engineering, 2012; 50/9: 1306-1315.

[20] Sun Z., Annergren I., Pan D., Mai T.A., Effect of laser surface remelting on the corrosion behavior of commercially pure titanium sheet, Materials Science and Engineering A, 2003, 345/1-2: 293-300.

[21] Astarita A., Curioni M., Squillace A., Zhou X., Bellucci F., Thompson G.E. Beamish K. A., Corrosion behaviour of stainless steel-titanium alloy linear friction welded joints: Galvanic coupling; Materials and Corrosion, first published online: 6 FEB 2014, DOI:10.1002/maco.201307476.