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Bruno Courant, Jean-Jacques Hantzpergue, Stéphane Benayoun. Surface treatment of titanium by laser irradiation to improve resistance to dry-sliding friction. *Wear*, 1999, 236 (1-2), pp.39-46. 10.1016/S0043-1648(99)00254-9 . hal-04117737

**HAL Id: hal-04117737**

**<https://hal.science/hal-04117737v1>**

Submitted on 9 Nov 2023

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# Surface treatment of titanium by laser irradiation to improve resistance to dry-sliding friction

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This experimental study was performed with intent to improve the surface properties of titanium and to minimize the friction on ceramic. Its main object was to strengthen the resistance against wear resulting from dry-sliding contact. Titanium-covered or not, graphite powder was irradiated and superficially melted by means of a pulsed Nd–YAG laser beam. Different irradiations were carried out, changing the distance between irradiated surface and laser beam focal plane. The variations in the dry-sliding friction coefficient were recorded using a pin-on-disc tribometer. An optimum irradiation of graphite-covered titanium generated hard granular titanium carbide and lubricating graphite inclusions which drastically reduced dry friction and wear of the Laser-Melted Zone. In this way, a self-lubricating composite coating has been successfully synthesized on titanium from the laser melting process.

*Keywords:* Antiwear treatment; Dry-sliding friction; Laser melting; Self-lubricating coating; Titanium

## 1. Introduction

Titanium and its alloys are materials used in aeronautics or astronautics because of their light density and toughness comparable to the best steels. However, their behaviour during dry friction with sliding or rolling contact is rarely satisfactory.

Surface melting by laser irradiation with material adding is the process that allows the most possibilities among the surface treatments which are able to improve the tribological behaviour of metallic materials. The addition elements are varied, e.g., other metal [1], nitrogen [2], bore [3] or carbon [4]. Acting on the irradiation parameters, it is possible to range strongly the concentration of addition element in the transformed zone (Laser-Melted Zone) and also its thickness from about 10  $\mu\text{m}$  up to some millimeters. The power laser beam allows to irradiate and to modify locally the surface of the parts, like other energy beams. Moreover, its use is easier because the surface does not need to be in vacuum during irradiation, contrary to the use of ion or electron beams.

Great progress has been recently noticed concerning the synthesis of coatings reinforced by particles of ceramic such as titanium carbide (TiC) [5], and the development of low friction and antiwear coatings [6], with a view to improve the resistance of the coated materials to dry friction.

A previous study [7] concerned the formation of surface alloys made of titanium  $\alpha\text{-Ti}$  and carbide,  $\text{TiC}_{1-x}$ . The pulsed laser irradiation of titanium surfaces covered with a graphite powder deposit 20  $\mu\text{m}$  thick allowed the Vickers microhardness in the Laser-Melted Zone to be multiplied by four.

Graphite as a solid lubricant has been well-known for a long time [8]. The mechanisms of friction and wear [9] are clarified for this self-lubricating solid, and also its lubrication mechanism [10]. Such a material can be mixed with sintered metals to achieve self-lubricating characteristics [11].

The purpose of this study is to improve the surface properties of titanium and to minimize especially the friction on ceramic and the wear by dry-sliding contact. Irradiation of titanium by pulsed Nd–YAG laser beam with deposition of graphite powder gives two possibilities. The first one squares with the surface melting which induces partial carbidation and hardening of the metal, as

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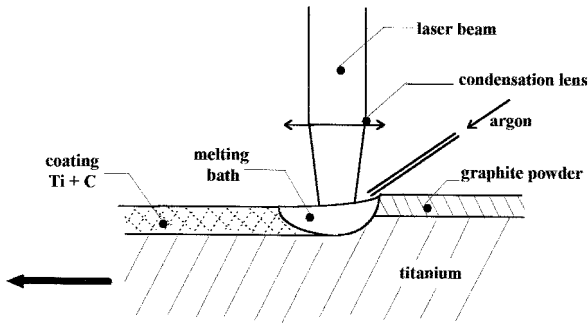


Fig. 1. Formation of coatings made of titanium and carbon by laser irradiation of titanium covered with graphite powder.

the result of the formation of surface alloy. The second one squares with the incorporation of a strong graphite amount under inclusion state which induces the surface synthesis of a real self-lubricating composite material.

## 2. Experiments

The surface of titanium was irradiated by means of a Nd-YAG laser beam which was pulsed by relaxed mode. Wavelength of laser radiation was  $1.064 \mu\text{m}$ , whereas maximum transmitted power was 300 W. The samples were square ( $20 \times 20 \text{ mm}^2$ ) titanium foils 3.2 mm thick, with grade of 99.67%. Each titanium sample was polished before irradiation in order to exhibit always the same surface state. Addition material was graphite powder of micrometric grain size (1 to 2  $\mu\text{m}$ ). This powder was mixed with water and ethanol to obtain regular deposit on titanium surface. The graphite deposit was then dried in hot air. Thickness of graphite deposit ranged always between 18 and 22  $\mu\text{m}$ . This one was deduced from the weighings before and after graphite deposition, knowing the area of deposit and the specific mass of graphite.

Table 1

Operative parameters of pulsed irradiation

The values have been selected from numerous experiments achieved during a preliminary study [12].

$E$ (J)	$\tau$ (ms)	$f$ ( $\text{s}^{-1}$ )	$V$ ( $\text{mm s}^{-1}$ )	$\Delta Y$ ( $\mu\text{m}$ )
$5.0 \pm 0.3$	$12.0 \pm 0.1$	$25.0 \pm 0.1$	7.34	500

Table 2

Distances between focal plane and irradiated sample surface corresponding to the different irradiation conditions

Irradiation condition	Distance of focal plane (mm)
1	-0.3
2	4.7
3	7.7
4	9.7
5	14.7

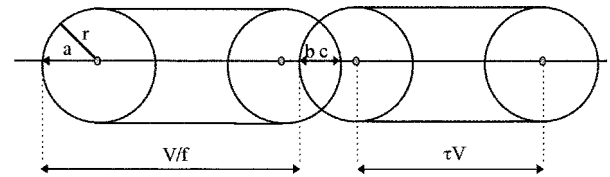


Fig. 2. Schemas of the area irradiated during one pulse and the superposition of two areas successively irradiated.

The titanium samples, with or without graphite deposit, were mounted on an  $X$ - $Y$  numerically driven table and then were irradiated by scanning of the pulsed laser beam. Their surface therefore melted with or without carbidation of titanium. The titanium surfaces without graphite deposit were blackened in smoke to induce a strong absorption of the laser radiation as for titanium covered with graphite. An argon flow ( $10 \text{ dm}^3 \text{ min}^{-1}$ ) prevented the oxidation of titanium and graphite during their irradiation (Fig. 1). The first micrometer depth of the samples was then analysed with the electron microprobe by energy dispersion spectrometry (EDS). Under these circumstances, the surface oxygen content always was below the detection threshold, i.e., below the atom percentage by about 3% [12].

The testing of the dry-sliding friction was performed with a pin-on-disc tribometer. The plane titanium sample was mounted on the rotary holder after irradiation and rubbed on a spherical ceramic pin (6 mm diameter ruby ball) with the load force,  $L$ . The friction force,  $F$ , was measured by an inductive sensor which recorded the strain of the pin holder arm. The friction coefficient,  $F/L$ , was recorded vs. the rotation number under the conditions of dry-sliding in moist air at  $25^\circ\text{C}$  with relative moisture content of about 60%. The parameters for these friction tests were chosen as follows:

- load force,  $L$  (5 N);
- friction track radius (4 mm); and
- rotation speed ( $120 \text{ turns min}^{-1}$ ).

The relief induced on titanium sample by laser melting prevented the use of a profilometer to measure the wear of the disc after pin-on-disc tests. Titanium sample and ruby

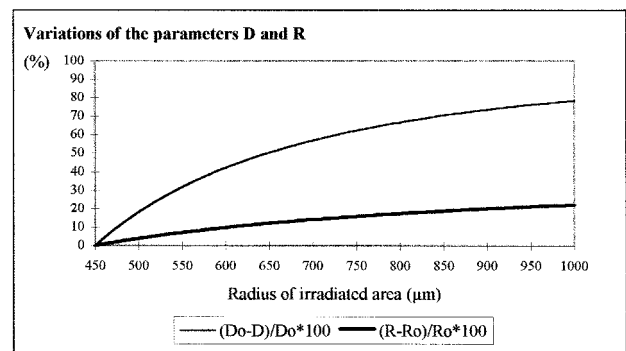


Fig. 3. Relative variations of the pertinent parameters  $D$  and  $R$  vs. radius,  $r$ , of area irradiated during one pulse.

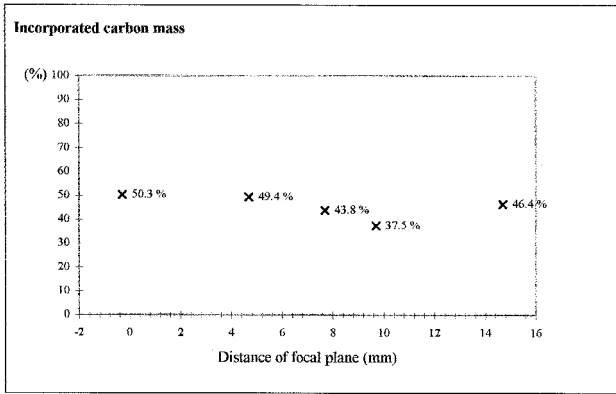


Fig. 4. Mass percentage of incorporated carbon vs. distance between focal plane and irradiated sample surface. This percentage is related to the irradiated carbon mass.

ball were therefore weighed before and after friction test to deduce the mass loss resulting from wear.

### 3. Irradiation conditions

The irradiation conditions were dependent on the operative parameters below:

- pulse energy,  $E$ ;
- pulse duration,  $\tau$ ;
- frequency of pulse generating,  $f$ ;
- scanning speed along the axis  $X$  of the laser beam,  $V$ ;
- and
- translation along the axis  $Y$  between two scanings of the beam,  $\Delta Y$ .

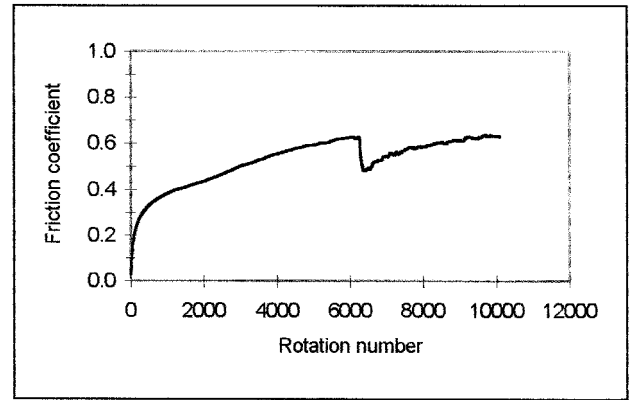


Fig. 6. Evolution of the friction coefficient of the titanium sample blackened in smoke and then irradiated under condition (5).

The same values of operative parameters were used for all the irradiations (Table 1). Only distance between focal plane and sample surface was modified (Table 2). This distance was deduced from the distance between sample surface and condensation lens of the beam, knowing the focal length, i.e., 62.4 mm. So, only the radius of the laser beam in the interaction plane,  $r$ , was modified for the different irradiations. Two pertinent parameters directly regulated the heat transfer induced in the metal volume from the irradiation and therefore regulated the thickness of the resulting Melted Zone [13]. This concerned the surface density of energy deposited by each pulse,  $D$ , and the superposition ratio of two areas successively irradiated,  $R$ . These two parameters are dependent on the four operative parameters  $E$ ,  $\tau$ ,  $f$  and  $V$ , and also on the radius of

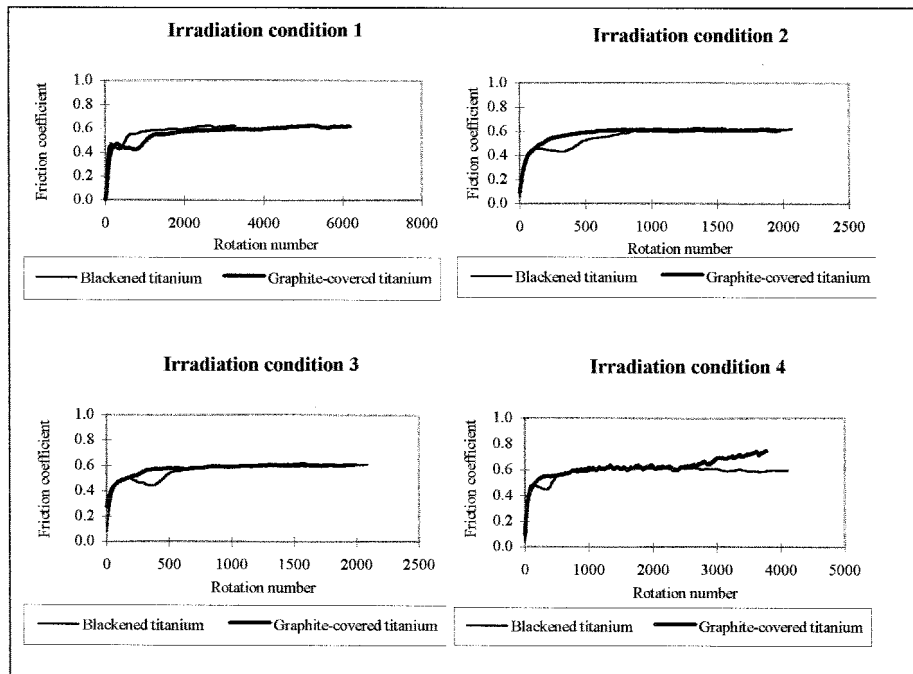


Fig. 5. Evolutions of the friction coefficient, after irradiation under conditions (1) to (4), of titanium samples either blackened in smoke, or covered with graphite powder layer 20  $\mu\text{m}$  thick.

area irradiated during each pulse,  $r$ . According to Fig. 2, the parameters  $D$  and  $R$  are defined by expressions (1) and (2) below:

$$D = \frac{E}{2\tau Vr + \pi r^2}, \quad (1)$$

$$R = \frac{\overline{bc}}{\overline{ac}} = \frac{2r + \left(\tau - \frac{1}{f}\right)V}{2r + \tau V}. \quad (2)$$

A preliminary study [13] showed from weighings that the percentage of carbon incorporated into titanium by metal surface melting was strongly dependent on the superposition ratio,  $R$ . For different irradiation conditions with the ratio  $R = 0.9$ , the incorporated mass percentage ranged from 53.3% to 72.5%. With the ratio  $R = 0.5$ , this one ranged only from 17.1% to 36.9%. A strong superposi-

tion ratio reduces the losses of graphite powder by ejecta and therefore increases the proportion of carbon incorporated into titanium.

As shown in Fig. 3, the radius growth of the area irradiated during one pulse produces a decrease of energy density,  $D$ , very superior to the increase of superposition ratio,  $R$ . Area irradiated during one pulse is greater if distance between sample surface and focal plane of beam is longer. The small increase of superposition ratio,  $R$ , has little influence on the quantity of incorporated carbon. In compensation, the strong decrease of energy density,  $D$ , reduces strongly the thickness of the Laser-Melted Zone which is more enriched with carbon. It is therefore possible to obtain a Laser-Melted Zone made of metallic titanium ( $\alpha$ -Ti) and titanium carbide ( $\text{TiC}_{1-x}$ ) which encloses numerous graphite inclusions. These inclusions resulted from the graphite quantity which have not been dissolved

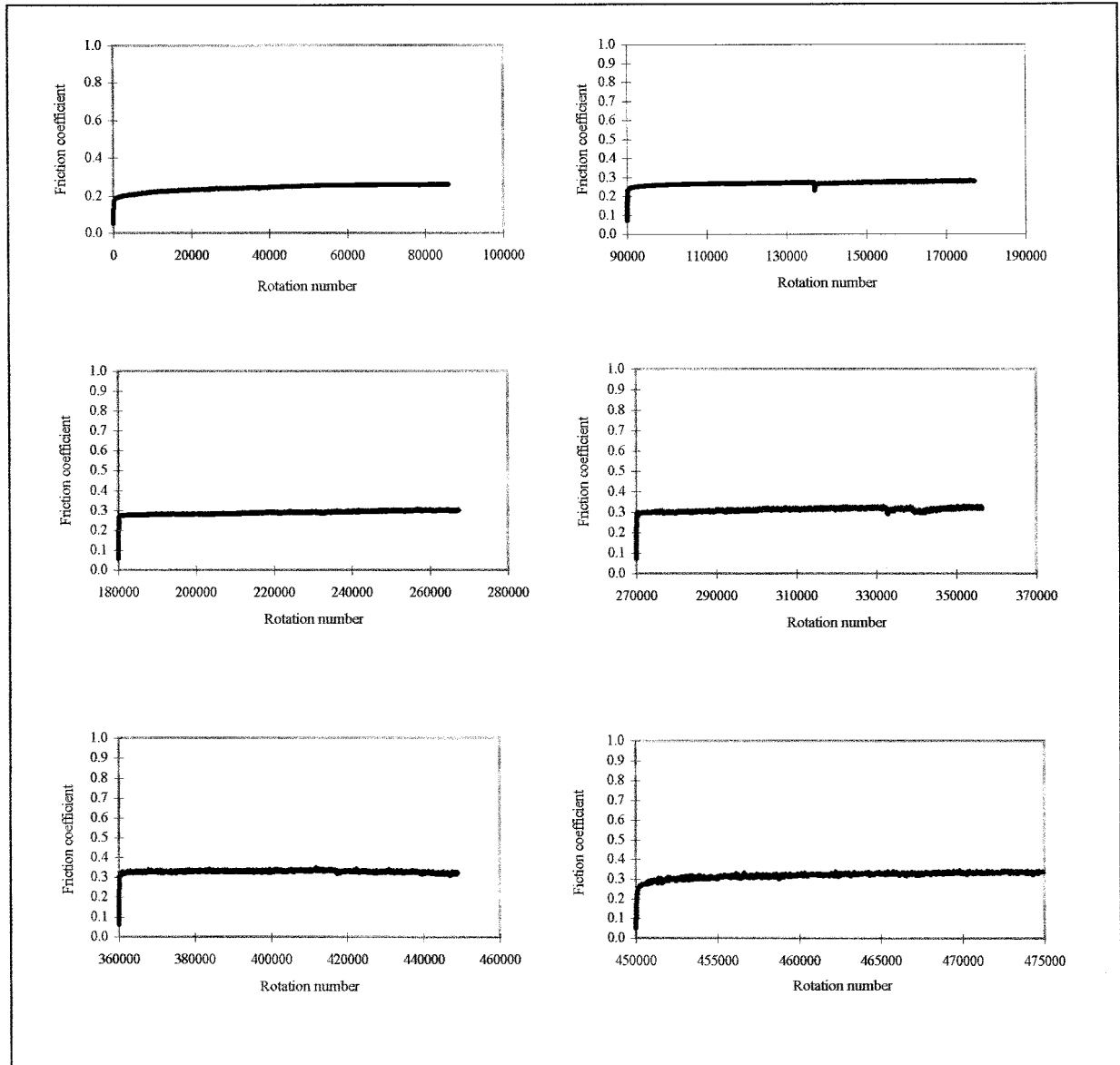


Fig. 7. Evolution of the friction coefficient of the titanium sample covered with graphite powder layer 20  $\mu\text{m}$  thick and then irradiated under condition (5).

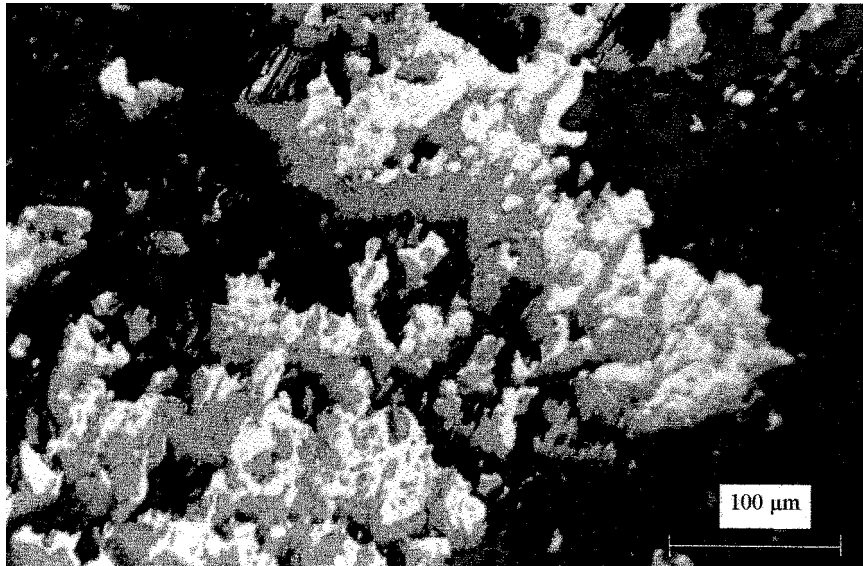


Fig. 8. Feature of the friction track after 475 000 rotations on titanium; the Laser-Melted Zone is rich in graphite inclusions.

in the melting bath. This presence of graphite in the Laser-Melted Zone allows us to expect an improved tribological behaviour.

#### 4. Results and discussion

A titanium foil covered with graphite deposit 20  $\mu\text{m}$  thick and a titanium foil blackened in smoke were irradiated for each distance given in Table 2. The objective was to appraise the actual influence of carbon incorporated into titanium of the Laser-Melted Zone.

The mass percentage of incorporated carbon is plotted vs. the distance between focal plane and irradiated surface (Fig. 4). This percentage is weakly dependent on this

distance. On the other hand, the energy density,  $D$ , is a decreasing function of this same distance. Therefore, the more the focal plane is distant, the more the Laser-Melted Zone is thin and the more the global concentration of carbon incorporated to titanium is increased.

The variations in friction coefficients are compared between titanium samples with or without pre-deposit of graphite (Fig. 5) which were irradiated in conditions (1) to (4) (Table 2). No improvement of tribological behaviour of titanium sliding on ceramic (ruby) was noticed after these irradiations which induced melting of the metal surface.

Friction tests by sliding on non-modified titanium surface have been discussed in a preliminary study [14]. Three successive transitional periods of friction and wear were recorded before a virtually steady state was reached.

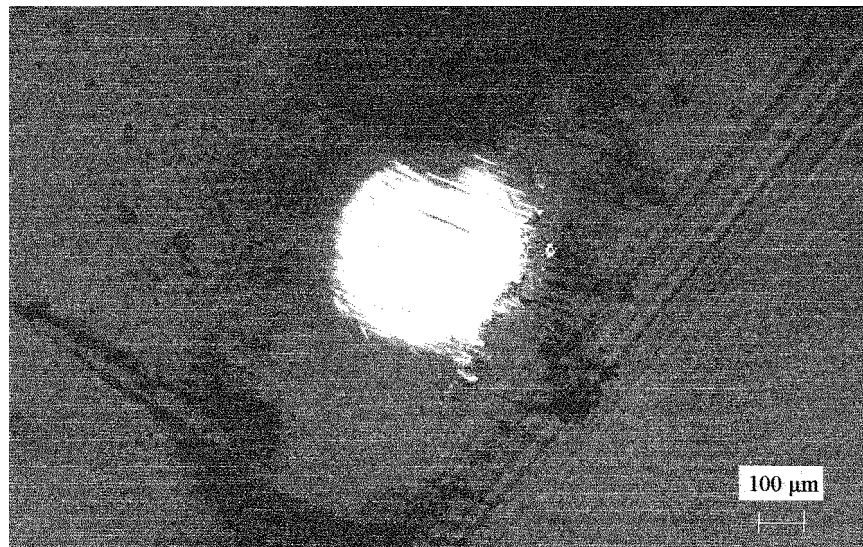


Fig. 9. Feature of the ruby ball after friction on titanium surface rich in graphite inclusions during 475 000 rotations. The feeding suggests a weak titanium transfer on ceramic (ruby) by adhesion.

- The first was characterized by a fast increase of friction coefficient and corresponded to the accommodation of the sliding contact between both bodies, with titanium adhesion on the ruby ball and formation of a transfer layer. Titanium first suffered from adhesive wear.

- The second period began after stripping and fragmentation of the transfer layer to give fine titanium flakes as third body. Accumulation of these particles on friction track and morphology of these particles induced a weak decrease of friction. The adhesive wear was softened during this period.

- The third friction period was characterized by a strong increase of friction whereas formation of scratches on the track disclosed that titanium was subject to abrasive wear. The grinding of the third body gave finer particles which became oxidized, hard and abrasive.

- The abrasive wear was continuing and the coefficient of friction between titanium and ceramic stabilized about 0.6 during the fourth and last period.

Surface melting of titanium covered with graphite deposit induces partial carbidation of the metal. The particles

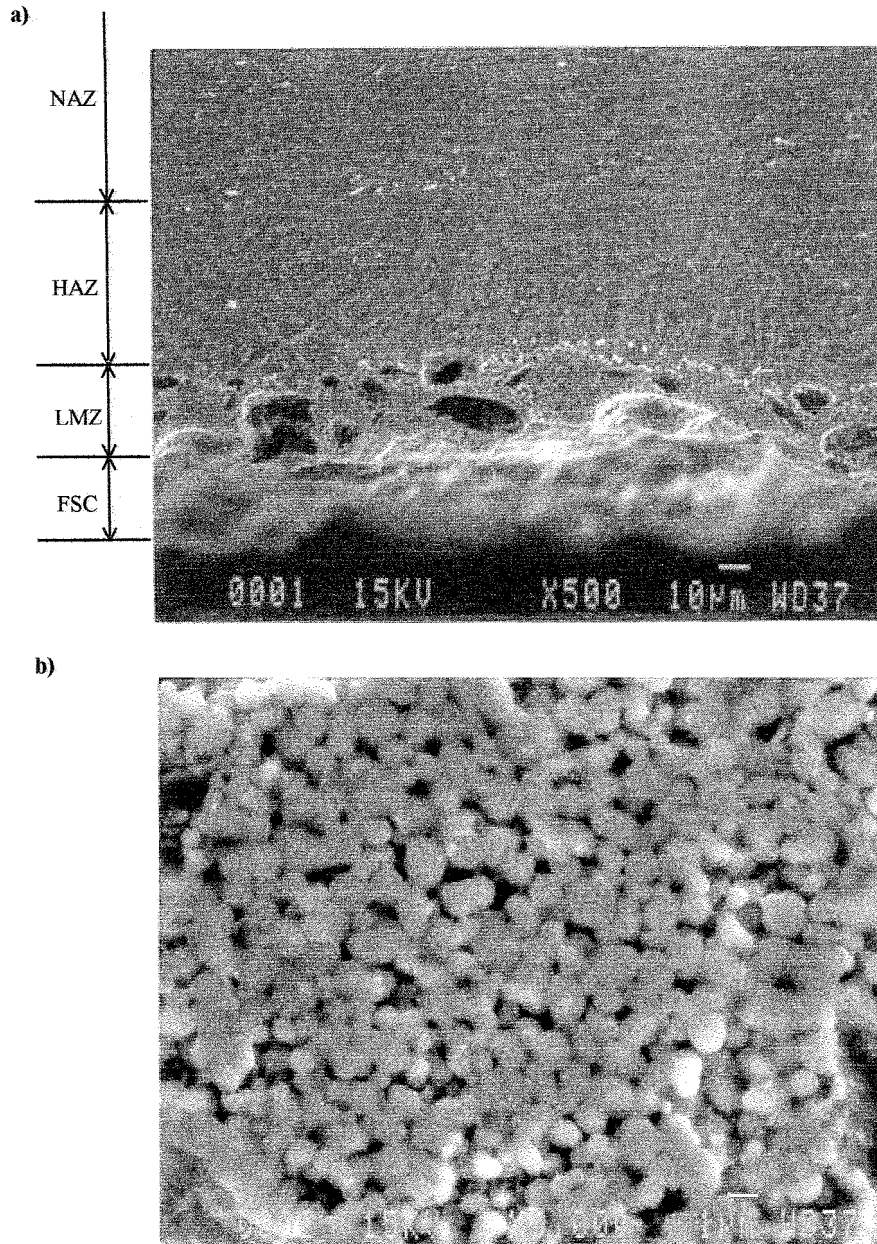


Fig. 10. Scanning electron microscopy micrographies of the cross-section of the titanium sample covered with graphite powder and irradiated in condition (5). (a) NAZ = Non-Affected Zone of titanium with equiaxis microstructure; HAZ = Heat-Affected Zone of titanium ( $\sim 50 \mu\text{m}$  thick) with acicular microstructure; LMZ = Laser-Melted Zone ( $\sim 20 \mu\text{m}$  thick) as composite coating made of  $\alpha\text{-Ti}$ ,  $TiC_{1-x}$  and C (graphite); FSC = free surface of coating: (1)  $\alpha\text{-Ti} \rightarrow$  hexagonal metallic titanium as matrix; (2)  $TiC_{1-x} \rightarrow$  granular titanium carbide (grain size  $\sim 1 \mu\text{m}$ ); (3) C  $\rightarrow$  carbon under the state of graphite inclusions of size  $2\text{--}20 \mu\text{m}$ . (b) Local view of the Laser-Melted Zone (LMZ) showing the granular structure of the phase  $TiC_{1-x}$  (grain size  $0.5\text{--}1.5 \mu\text{m}$ ).

of the synthesized hard phase  $\text{TiC}_{1-x}$  are abrasive. The titanium transfer layer on ruby ball is subject to abrasive wear and this wear process prevents fragmentation of the layer with titanium flake formation. Weak decrease of friction coefficient is therefore prevented, except for the irradiation condition (1) where abrasive phase  $\text{TiC}_{1-x}$  is in the minority compared with ductile phase of metallic titanium.

A different behaviour is recorded for titanium irradiated under condition (5). The friction coefficient slowly increases during 6000 rotations up to a value about 0.6 (Fig. 6). Wear of friction track and third body then become suddenly visible whereas friction coefficient decreases up to about 0.5 because of the formation of third body. The friction coefficient then slowly reaches its previous value of 0.6. The same periods of friction and wear follow one another as for irradiation conditions (1) to (4), but they are much longer. A thinner titanium layer is melted with condition (5) because the laser beam is very defocused on sample surface. Titanium is blackened in smoke before irradiation only to allow stronger absorption of the laser radiation. In this case, the weak amount of deposited amorphous carbon is less diluted in titanium of Laser-Melted Zone than under conditions (1) to (4). The presence of this carbon probably reduces titanium transfer on ceramic during the first period and therefore slows down friction increase.

The strength of sliding friction on ceramic is minimized and resistance to wear of titanium is strongly improved (Fig. 7) after treatment by deposition of graphite layer 20  $\mu\text{m}$  thick and then irradiation under condition (5). Friction coefficient does not exceed 0.35 after 475000 rotations, whereas no mass loss of the titanium sample and the ruby ball is recorded. Friction track is shallow and lack of scratches suggests the lack of abrasive wear (Fig. 8). Third body as a very fine grey powder is generated in infinitesimal amount. Adhesion of titanium on ceramic takes place because a fading of contact surface on ruby ball is apparent (Fig. 9). The very thin Laser-Melted Zone about 20  $\mu\text{m}$  thick on this titanium sample contains titanium carbide,  $\text{TiC}_{1-x}$ , but also numerous big inclusions of graphite (Fig. 10). This graphite acts as solid lubricant during sliding. Hard phase  $\text{TiC}_{1-x}$  and graphite reduce much the titanium transfer by adhesion on the ceramic and therefore, slow down much the wear of the metal.

## 5. Conclusion

It is possible to modify superposition ratio,  $R$ , of the pulses and also energy density,  $D$ , deposited on irradiated surface by each pulse, by changing distance between graphite-covered titanium surface and focal plane of the pulsed laser beam. Energy density strongly acts on total concentration of incorporated carbon in Laser-Melted Zone.

Tribological behaviour of titanium is slightly modified if this surface zone is only made of a cermet resulting from the mixture of titanium carbide as hard phase with metallic titanium as ductile phase. But this behaviour is much improved if the Laser-Melted Zone is more enriched with carbon, owing to optimisation of the irradiation conditions. Such a surface zone is also made of a third phase in the form of numerous graphite inclusions acting as solid lubricant. Dry-sliding friction between ceramic and titanium treated in this manner is minimized whereas adhesive wear of the metal is reduced much, and its abrasive wear is prevented, by the self-lubricating composite coating synthesized from the laser melting process.

## Acknowledgements

The authors are grateful to Dr. L. Fouilland-Paillé (ENSAM, Châlons-en Champagne, France) and Dr. S. Ettaqi (ENSAM, Meknès, Maroc) for their helpful discussions. They also wish to thank Dr. A. Perronet (LAMM, Saint-Nazaire, France) for her contribution to Fig. 10.

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