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Tribological performance of \( \alpha \)-Fe(Cr)-Fe\(_2\)B-FeB and \( \alpha \)-Fe(Cr)-h-BN coatings obtained by laser melting

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\( \alpha \)-Fe(Cr)-h-BN and \( \alpha \)-Fe(Cr)-Fe\(_2\)B-FeB coatings on X30Cr13 stainless steel are synthesized by laser melting with incorporation of hexagonal boron nitride, or by alloying of boron. The additive powders are deposited on steel before pulsed irradiation by Nd-YAG laser beam. The solidification structures of the obtained coatings are investigated by optical microscopy and X-ray diffraction. The mechanical properties are investigated by nanoindentation and the tribological behaviour is characterized on pin-on-disc tribometer, under dry-sliding conditions with different loads and a temperature range 25–500 °C. h-BN-\( \alpha \)-Fe(Cr) and Fe\(_2\)B-\( \alpha \)-Fe(Cr) coatings have average hardnesses 10.0 and 14.5 GPa, respectively, while hardness of untreated stainless steel is 4.2 GPa. In comparison with this untreated steel, the sliding contact on ceramic (ruby) of such coating shows a lower coefficient friction and a definitively better wear resistance.

Keywords: Composite and boride coatings; Laser melting; Nanoindentation; Wear resistance; Energy dissipation; Temperature effects

1. Introduction

The stainless steels are largely used in applications where a good corrosion resistance is necessary. However, their properties, such as the hardness and the wear and friction behaviour are not always satisfactory. The surface treatment with a power laser is an attractive method, compared to the other processes like the electroplating [1], the ionic implantation [2] and the physical or chemical deposition from a vapour phase (PVD and CVD) [3,4].

Irradiation by high energy density beam produced from a power laser is convenient to locally modify and treat metal surfaces by melting with incorporation of foreign element or other material. Indeed, such a process contributes to reinforce the adhesive or abrasive wear resistance of treated metal, in consequence of the formation of a multiphase alloy made of the ductile metal phase and one or several hard phases, such as carbides, nitrides or borides [5,6,7]. Recent articles showed that it is possible to use this process in order to improve the resistance to corrosion [8] or oxidation [9] of metallic materials. In the present study, this process is used to increase the wear resistance of a treated X30Cr13 stainless steel. We do not search to underline the relationship between the tribological behaviour and the laser processing parameters or the solidification rate. We used a power laser, which is pulsed and so, four operative parameters are required and must be optimized in order to increase the wear resistance and minimize the friction. The surface of the moving sample is submitted to a multi-pulse irradiation. Being confronted with transient phenomena in the temperature evolution, it is difficult to relate the four laser processing parameters and the interaction time, compared with the case of a continuous irradiation.

In this work, we studied the tribological properties induced by surface alloying from the melting by irradiation with a pulsed Nd-YAG laser beam on a X30Cr13 stainless steel. The chemical composition of steel surface is first modified by the fusion, either with addition of boron, or with incorporation of hexagonal boron nitride (h-BN). Boron is a non-metal element, which forms very hard covalent compounds, such
as iron borides (hardness: 12–16 GPa) by combination with metals. Whereas hexagonal boron nitride is a ceramic having a lamellar structure [10] and a low friction coefficient [11], comparable to graphite. After each treatment of laser irradiation, the structural state of the melting zone as a coating is characterized by metallographic analysis and X-ray diffraction, whereas its elementary composition of the melted zone is checked by X-ray microanalysis. The principal mechanical characteristics for such a coating, elasticity modulus and hardness, are deduced from nanindentation tests. Moreover, the tribological behaviour during dry-sliding is tested in order to find the optimal laser treatment to obtain coatings exhibiting the best resistance to wear, characterized by a reduced friction coefficient and a minimum wear rate.

2. Experimental procedure

2.1. Materials and specimen preparation

The X30Cr13 stainless steel used as a substrate is in the ferrito-martensitic state. Its chemical composition is given in Table 1. The steel substrates are discs with a diameter 25 mm and thickness 5 mm.

Before the laser treatment, the steel substrates are polished to paper 1000 and cleaned in ethanol with ultrason in order to exhibit always the identical and uniform surface state. Then, they are covered with a pulverulent layer (micrometric granulometry), either of boron, or hexagonal boron nitride (h-BN). These powdery materials are first mixed with ethanol and colloidion to obtain regular predeposits on stainless steel surface. The boron or h-BN predeposit is dried in hot air. Thickness of predeposit is deduced from the weighing before and after deposition, knowing the area of deposit and specific mass of powder. It always ranged between 18 and 20 µm.

2.2. Laser irradiation processing

Laser surface alloying is carried out using a 300 W Nd-YAG laser beam (λ = 1.06 µm) with a spot of diameter 1.26 mm. The samples are mounted on a numerically driven X–Y table and then irradiated on a 16 mm x 16 mm area (Fig. 1). A dry argon flow at 12 l min⁻¹ is used as a gas shield to prevent surface oxidation during irradiation.

The operative parameters of laser irradiation are:
- pulse energy, E;
- pulse duration, τ;
- frequency of pulse generating, F;
- scanning speed, V, for the laser beam along the X axis;
- translation, ΔY, fixed at 0.50 mm along the Y axis, between two scanning of the laser beam;
- scanning speed, V_Y, fixed at 70 mm s⁻¹ for the laser beam along the Y axis.

The four pertinent parameters [12,13] of the laser irradiation are dependent on the operative parameters E, τ, F, V and also on the beam radius, r. They are defined by the following expressions:
- energy surface density,
  \[ D = \frac{E}{S_1} \]  
- pulse power,
  \[ P = \frac{E}{\tau} \]  
- temporal emission rate,
  \[ B = \frac{\tau F}{r} \]  
- superposition rate between two zones successively irradiated (Fig. 2),
  \[ R = \frac{\Delta Y}{\Delta V} = \frac{2r + (\tau - 1/F)V}{2r + \tau V} \]

The value of this last parameter is fixed at R = 0.95 [12,13]. In Eq (1), S_1 represents the irradiated area during the impulsation. Supposing that the beam form is perfectly circular of radius, r, this surface is defined by the following expression:

\[ S_1 = \pi r^2 \]
Table 2: Operative and pertinent parameters of laser irradiation

| Sample | Operative parameters | Pertinent parameters |
|--------|---------------------|---------------------|
|        | $E$ (J) | $\tau$ (s) | $F$ (Hz) | $V$ ($10^{-3}$ m s$^{-1}$) | $R$ | $R$ | $D$ ($10^{-3}$ J m$^{-1}$) | $P$ (W) |
| B      | 3.7     | 0.010   | 40.0   | 3.8    | 0.95   | 0.40   | 1.78    | 300 |
| BN     | 4.3     | 0.012   | 40.0   | 3.8    | 0.94   | 0.48   | 2.07    | 292 |

The operative and pertinent irradiation parameters used to carry out the laser surface alloying are given in Table 2.

2.5. Microstructural characterization

After irradiation treatment, the samples are cross-cut transversely to the passes of laser beam, included in resin and polished up to a $1/262$ m diamond finish. They undergo then a chemical etching in aqueous solution of hydrofluoric and nitric acid. The microstructures resulting from solidification are observed by optical microscopy and the phases formed in the melting zone are identified by means of a Bruker D5005 X-ray diffractometer. The used radiation source is the specturm line $K$ of copper with graphite filter. On the other hand, the distribution in coating depth of the added elements (boron and nitrogen) is determined by X-ray microanalysis using an electron microprobe and a wavelength dispersion spectrometer (WDS).

2.4. Mechanical characterizations

2.4.1. Nanoindentation

This nanoindentation technique with the capacity of controlling the loadings as small as about 10 micro-Newton ($\mu$N) is used to measure mechanical properties of the melting zones or coatings on metallographic cross-section. Hardness, $H$, and modulus of elasticity, $E$, can be deduced from the load–displacement curves ($P$–$h$) using the following formulas [14]:

$$H = \frac{P_{\text{max}}}{A}$$

(6)

$$E_i = \frac{\sqrt{\pi/2} \cdot S}{\sqrt{A}}$$

(7)

$$\frac{1}{E_r} = \left(1 - \nu^2\right) + \left(1 - \nu_i^2\right)$$

(8)

where $P$ is the indentation load and $P_{\text{max}}$ is the peak indentation load, $h$ is the displacement of the indenter, $A$ is the projected contact area, $S$ is the contact stiffness, $\nu$ is the Poisson’s ratio of the work-material, and $E_r$ is the reduced modulus of elasticity integrating the effect of elastic deformation from the indenter. $E_i$ and $\nu_i$ are respectively, the modulus of elasticity and Poisson’s ratio of indenter.

In this study, the continuous stiffness measurement (CSM) method is used to measure the contact stiffness, $S$. This technique and the analysis procedure are detailed in Refs. [15,16]. The nanoindentation experiments are carried out on a MTS nanoindenter NanoXP$^\text{TM}$ with a Berkovich diamond indenter (Fig. 3). The instrument is calibrated by using a standard fused silica sample prior to measuring the mechanical properties of the modified metal. The drift rate is preset to $0.05$ mm/s before the beginning of each indentation test. All the load–displacement curves used to determine hardness and modulus of elasticity are corrected considering the thermal drift. The displacement control is used in the nanoindentation experiment and the load is dependent on the indenter penetration depth. A X–Y table with a calibrated distance from the indenter to an optical microscope is used for accurate positioning of the indents. A step of 20 $\mu$m between indentation points is preset to minimize the interaction between plastic zones induced by the adjacent indentations while maintaining a sufficient number of indentation points (>10).

2.4.2. Friction and wear tests

Unidirectional sliding friction and wear tests with a pin-on-disc configuration (CSEM Tribometer) are performed on the coatings, using a ruby ($\text{Al}_2\text{O}_3$) ball with a diameter of 6 mm as pin (Fig. 4). After irradiation treatment the obtained coating is first grinded in order to eliminate the relief generated by surface melting. Then its surface is polished with a $1 \mu$m grade diamond paste up to reach the roughness of $R_a = 0.30 \mu$m. All the friction and wear tests are first carried out under dry-sliding conditions at room temperature and different normal loads. Supplementary measurements are made in argon environment at different temperatures and under a normal load of 2 N. The Hertzian stress of 500–1200 MPa correspond to the normal loads ranging between 1 and 10 N (Table 3). The operative parameters controlled during the rubbing tests are given in Table 4. For comparison, similar tribological tests of friction and wear are performed on uncoated X30Cr13 stainless steel.
Fig. 4. Schema of the pin-on-disc tribometer.

Table 3
Hertzian stress (MPa) of BN and B samples submitted to different loads

| Load force (N) | BN sample | B sample |
|---------------|-----------|----------|
| 1             | 782       | 796      |
| 2             | 985       | 1003     |
| 5             | 1337      | 1361     |
| 10            | 1685      | 1715     |

During the tests the friction coefficient was recorded versus sliding distance and after the tests the profiles of wear tracks are recorded with a Dektat 3ST surface profilometer for the evaluation of the wear resistance. The friction coefficient, $\mu$, is averaged over a sliding distance $d = 3.014$ m and the volume wear rate, $K$ ($m^3 N^{-1} m^{-1}$), is calculated following the Archard’s equation [17]:

$$K = \frac{V}{FNd}$$  \hspace{1cm} (9)

where $V$ is the worn volume, $F$ the normal load and $d$ the total sliding distance. The wear of the materials in sliding contact is considered as resulting from energy dissipation due to the friction between the contacting bodies.

3. Results and discussion

3.1. Composition and microstructure

Metallographic analysis of the stainless steel after surface melting with boron addition or h-BN incorporation revealed three distinct regions: laser melting zone (LMZ), heat affected zone (HAZ) and non-affected zone (NAZ) that corresponds to the steel matrix. Coatings of 300–400 $\mu$m thick are easily obtained by laser melting.

In the borided coating (sample B), the solidification begins at the interface between LMZ and HAZ. A plane front growth is observed at the bottom of LMZ (Fig. 5). The plane solid-

Table 4
Operative parameters for the tribological tests

| Load force | Friction track radius | Sliding speed | Total turn number | Test temperature |
|------------|-----------------------|---------------|------------------|-----------------|
| 1, 2, 5 and 10N | 6 mm                   | 50 mm/s $^{-1}$ | 80,000 turns     | 25, 300 and 500 $^\circ$C |

Fig. 5. Optical micrographs of the sample B.
Fig. 6. Optical micrographs of the sample BN.

Solidification front starts from the HAZ–LMZ interface and then becomes unstable. Subsequently, a fine structure is solidified. This microstructure reveals numerous and fine cellular dendrites. These crystal growth phenomena are governed by the temperature gradient, $G$, and the solidification rate, $V_s$. The ratio $G/V_s$ controls the morphology whereas the product $GV_s$ determines the size characteristics of the microstructure [18]. Fig. 5 shows that randomly oriented dendrites occurred. This is explained by the great superposition rate ($R = 0.95$). Its action perturbs the liquid flows and also the temperature fields. The strong turbulences generated in melting bath hinder a regular dendritic growth. In the coating with incorporated h-BN (sample BN), a relatively homogeneous microstructure is observed (Fig. 6).

The typical X-ray diffraction patterns of the Fe(Cr) untreated steel (X30Cr13 substrate) and the coatings of iron borides-Fe(Cr) alloy (sample B) and h-BN-Fe(Cr) composite (sample BN) are shown in Fig. 7. The solid solutions $\alpha$-Fe(Cr) and $\gamma$-Fe(Cr) as residual austenite are detected, and also the phase h-BN (hexagonal boron nitride) and the iron borides FeB, Fe$_2$B and Fe$_3$B$_6$ as metastable phase. This is attributed to the non-equilibrium solidification condition resulting from a high cooling rate [19,20]. The results concerning the melting zones as composite coating (sample BN) and borided coating (sample B) are summarized in Table 5. It also indicates the volume ratios of the phases h-BN and Fe$_2$B calculated from the masses of h-BN or boron incorporated in LMZ and deduced from weighing, considering a uniform distribution of these phases [21]. The boron concentration in LMZ for two types of treatment, measured by WDS, corresponds to the stoechiometric formulas BN or B. In the laser treatment with boron addition, the boron concentration in LMZ was estimated at 35 at.%, whereas in the treatment with h-BN addition, the boron concentration reached the value of 7.5 at.%. For the two treatments, the boron distribution in LMZ was always uniform.

3.2. Hardness and modulus of elasticity

Nanohardness and Young modulus of the h-BN-Fe(Cr) composite and iron borides-Fe(Cr) alloy as coatings samples BN and B, and the untreated steel as substrate (X30Cr13) are evaluated by nanoindentation. Results are shown in Table 4.
Table 5

Effective thickness of melted zone, constituent phases, volume ratio of h-BN with the assumption that Fe2B is the one and only boride phase and mean hardness of the untreated steel and the laser melted zones

| Sample           | Thickness of melted zone (μm) | Volume ratio (%) of h-BN or Fe2B | Constituent phases observed by XDR | Mean hardness (GPa) | Young modulus (GPa) |
|------------------|-------------------------------|----------------------------------|-----------------------------------|--------------------|--------------------|
| X30Cr13 substrate-Fe(Cr) | -                             | -                                | α-Fe(Cr)                          | 4.2 ± 0.1          | 235 ± 6            |
| BN               | 293 ± 94                      | 1.0 ± 0.6                        | h-BN + α-Fe(Cr) + γ-Fe(Cr)        | 10.0 ± 0.2         | 232 ± 4            |
| B                | 317 ± 55                      | 20.1 ± 0.1                       | α-Fe(Cr) + Fe2B + a few FeB and Fe23B | 14.2 ± 0.1         | 240 ± 6            |

Their evolutions versus depth are graphically represented in Fig. 8.

Depending on the samples, the hardness can increase up to 350 or 275%, in LMZ, for the samples treated with incorporation of boron or h-BN, respectively. For these samples, three fields are distinguished on the nanohardness profiles (Fig. 8). LMZ is characterized by the stronger nanohardness and able to reach to up to 16 GPa (sample B). The nanohardness decreases abruptly up to 200–250 μm in the depth and then it decreases gradually through the HAZ up to 300–500 μm where the characteristic value of the untreated stainless steel (4 GPa) is reached. For LMZ of sample B the strong nanohardness is attributed to the presence of the hard phases Fe2B and FeB [22–24]. On the other hand, the sample BN has the strongest nanohardness (11 GPa), which is recorded in LMZ prior to decrease slowly in depth. This nanohardness value of h-BN-Fe(Cr) composite coating is comparable with the value obtained by Dekempeneer et al. [25]. For the two types of coatings the hardness remains constant in depth, in accord with the boron content, which is also constant in depth.

The Young’s modulus in borided coating (sample B) is increased between 270 and 300 GPa whereas it is not increased for the sample BN treated with incorporation of h-BN (240 GPa). Bindal and coworkers [26–28] worked out a boride thin film by thermochemical diffusion on low carbon steels. They determined by microindentation Young’s moduli of 284 and 343 GPa for the phases FeB and Fe2B, respectively. Whereas a hexagonal boron nitride thin film has a 180 GPa Young’s modulus for a 14 GPa hardness [29,30].

3.3. Tribological behaviour at room temperature

3.3.1. Wear at different loads

The laser melting zones (LMZ) as h-BN-Fe(Cr) composite (sample BN) or borided alloy (sample B) coatings exhibited better tribological behaviours than the untreated steel (X30Cr13 substrate). The variations in wear rate are plotted as a function of normal load in Fig. 9.

The wear rate of untreated steel increases almost linearly with the load, reaching a value \( \sim 277 \times 10^{-15} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1} \), whereas the treated samples, BN and B, show a low wear rate \( K = 11 \times 10^{-15} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1} \) until a load of 5 N. At 10 N, their wear rates are strongly increased \( K = 95-113 \times 10^{-15} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1} \). The characteristic plateau, corresponding to the weak wear rates for the samples B and BN is often related to the formation of surface films. A similar behaviour exists for the wear rates of aluminum based particle-reinforced composites [31–33].
Microscopic observations reveal that the morphology of worn surface after rubbing varies with the applied load, because of the formation of the third body between first bodies. It can play a major role for improving the wear resistance. When the load is below 5 N, the particles of third body adhered to the worn surface. Beyond 5 N, the amount of particles on this surface decreases and at 10 N the third body has disappeared whereas the worn surface is rough (Figs. 10 and 11). The results of microscopic observations corresponding to the plateau in the wear rate curves and the rough worn track suggest that different wear mechanisms appeared on α-Fe(Cr), α-Fe(Cr)-Fe₂B-FeB and α-Fe(Cr)-h-BN coatings (samples BN and B) at different loads.

The presence of hexagonal boron nitride within the metal matrix, α-Fe(Cr), and the third body layer ensure the wear rate lowering at the loads ranging between 1 and 5 N. This is attributed to the lamellar structure of h-BN that makes it easy to deform so that the stress concentration imposed by the wear counterpart is dissipated and severe wear of metal matrix is avoided [34]. Concerning the borided alloy coating, their strong wear resistance is attributed to the hard iron boride phases. The wear rate of the borided sample B is very low compared with the rates for the untreated steel (X30Cr13 substrate). For the two types of coatings on X30Cr13 stainless steel (samples B and BN), the microstructure is very modified. It has become fine-grained and contributes to increases the hardness and to may reduce the wear in the contact with the ruby ball.

Beyond 5 N, the wear in the α-Fe(Cr)-Fe₂B-FeB and α-Fe(Cr)-h-BN coatings is strongly abrasive, i.e. the wear particles are abrasive and they scratch directly the worn surface of rubbing track.

The cross profiles of wear tracks are shown in Fig. 12. A sharp decrease of the depth and width of wear track is noticed for the steel surfaces modified by laser melting with boron addition (sample B) or h-BN incorporation (sample BN).

3.3.2. Energy dissipation in friction

In Fig. 13, the evolution of friction coefficient as a function of applied load is shown.

The average friction coefficient of the treated samples is always inferior to that of the untreated steel (X30Cr13 substrate) at different loads.
Wear processes in sliding contacts are considered as resulting from energy dissipation due to the friction between the contacting bodies. Up to now, Huq et al. [35] proposed a procedure to correlate the volumetric wear loss of one first body with the dissipated energy for pin-on-disc tests. The calculation of the dissipated energy in different tribological contacts is reviewed [36–38].

Mohrbacher et al. [39] introduced the concept of cumulative dissipated energy, \( E_d \), for bi-directional sliding contact conditions:

\[
E_d = \sum F_t d
\]

with \( F_t \) the tangential force and \( d \) the linear displacement for one cycle.

Huq and Celis [38] used this model to express the wear rate as a worn volume per unit of friction energy in pin-on-disc unidirectional sliding tests. The cumulative dissipated friction energy, \( E_d \), is calculated in such sliding test conditions from the following expression:

\[
E_d = \mu F_N V_g t
\]

with \( t \) the duration of the sliding test, \( V_g \) the sliding velocity, \( \mu \) the variable friction coefficient and \( F_N \) the applied normal load. Here, the test conditions are always \( V_g = 0.05 \text{ m/s} \) and \( t = 6000 \text{ s} \).

The obtained results are given in Table 6. A non-linear increase in wear rate of the treated samples, BN and B, with the increase of cumulated friction energy, as with the increase of applied load, is observed. In return, the wear rate increases almost linearly versus this energy in the case of untreated stainless steel.

### 3.4. Tribological behaviour at high temperatures

After the friction and wear tests at the standard temperature (25 °C) and under various loads, the tribological behaviour at higher temperatures is investigated. The applied
temperatures are 25, 300 and 500 °C at a normal load of 2 N and the other parameters are identical to those indicated in Table 3.

The variations in friction coefficient and wear rate with the temperature are shown in Table 7 and Fig. 14. The average friction coefficients of the three samples decrease until 0.60 at the highest temperature (500 °C). However, the wear rate of untreated steel decreases strongly with the temperature increase whereas that of the two types of coatings increases considerably. At highest temperature, the average friction coefficients of the three specimens are reduced probably because their plasticity is increased.

On untreated steel, the rubbing tracks at the highest temperatures exhibit a positive relief (Figs. 15 and 16). The third body remained on the friction track therefore is adherent, compact and consolidated because an expansion of the matter volume is recorded. Notwithstanding, the Fe(Cr)-Fe2B-FeB and Fe(Cr)-h-BN coatings have their wear rate considerably increased with the temperature. In this last case, the third body can be abrasive particles of oxidized metal that cause an important removal of coating.

In literature, metal oxides are known to soften in high temperature. During friction process, softening oxide scale is easily removed from the track. It is accompanied by wear rate increase and friction coefficient decrease.

### 4. Conclusions

Chemical and structural modifications of the X30Cr13 stainless steel surface are possible using the laser irradiation in order to melt the metal surface covered with powdery hexagonal boron nitride (h-BN) or powdery boron.

On the one hand, ceramic–metal composite coatings are obtained, with h-BN as ceramic and the solid solution, Fe(Cr), as metal matrix. In the other hand, boron–chromium–iron alloy coatings are synthesized. Their constituent phases are Fe(Cr) and iron borides, Fe2B, FeB and Fe23B6.

The two kinds of synthesized coatings are harder than untreated stainless steel (4.2 GPa). Moreover, the average nanohardness of the Fe2B-Fe(Cr) alloy coatings (14.5 GPa) is stronger than the one of the h-BN-Fe(Cr) composite coatings (10.0 GPa). At the ambient temperature (25 °C) and under loads ranging between 1 and 10 N, the wear resistance of the coated X30Cr13 stainless steel is improved in the two cases. In the better circumstances, the wear rate is decreased up to 96% in comparison with the one of untreated steel.

### Table 7

| Temperature (°C) | X30Cr13 Substrate | BN Sample | B Sample |
|-----------------|-------------------|-----------|----------|
| 25              | 0.85 ± 0.05       | 0.77 ± 0.05 | 0.83 ± 0.05 |
| 300             | 0.70 ± 0.05       | 0.84 ± 0.05 | 0.81 ± 0.05 |
| 500             | 0.60 ± 0.05       | 0.56 ± 0.05 | 0.59 ± 0.05 |
The improved tribological behaviour resulting from the second treatment (boron addition) is principally attributed to the crystallization of hard iron borides. For the first treatment (h-BN incorporation) the improvement is attributed to the hardening resulting from the grain size reduction induced by fast solidification of the α-Fe(Cr) phase and also to the lubricating part sustained by the hexagonal phase of boron nitride.

The concept of wear rate in terms of energy dissipation is a useful tool to gain information about the potential changes in wear damage of the materials. The tribological behaviour as a function of the dissipated energy was analyzed. The wear rate of the coated stainless steel does not vary linearly, contrary to the untreated steel. There is effectively a critical load beyond which the growth of wear rate becomes important for the coatings synthesized by laser melting.

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