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# Tribological study of diamond coatings on titanium alloys

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## Abstract

This paper presents the tribological characteristics of PACVD diamond coatings on titanium alloys. The coating morphology and quality have been investigated by SEM and Raman spectroscopy, and the surface roughness has been determined by AFM measurements. Friction and wear characteristics have been studied with a pin-on-disk tribometer as a function of the applied load, the sliding speed and the counterface material. For diamond-on-diamond contact, the dynamic friction coefficient stabilizes at a value of 0.05–0.08 after the surface polishing of diamond crystal tips. For non-diamond coated pins, a surface running in time at low sliding speed is necessary to avoid a coating spalling on the disk. After this step, the sliding speed can be increased to 1 m s<sup>-1</sup> with a friction coefficient equal to or lower than 0.1. The wear of the diamond-coated disk generally cannot be measured.

*Keywords:* Diamond coatings; Titanium alloys; Friction coefficient; Wear rate

## 1. Introduction

Because of its high hardness and chemical inertia, associated with both low friction and wear, the tribological performances of diamond are exceptional [1]. The friction characteristics of bulk diamond-on-diamond are known. In air, the friction coefficient is generally low, in the range 0.05–0.1, but it is higher in vacuum [1]. This difference occurs because the chemisorbed hydrogen and oxygen are removed from the surface, and a strong bonding occurs between the sliders [2]. Studies had first been carried out on single-crystals diamond. However, the tribological characteristics of CVD coatings are different to single-crystal diamond ones (which depend on the crystallographic orientations and the relative sliding direction [1]) because of their polycrystalline nature and the existence of non-diamond carbon at grain boundaries. Furthermore, the diamond coatings surface exhibits an important roughness which depends on both pretreatments of the substrate surface and deposition conditions [3,4]. These factors have obviously an important effect on the tribological properties of the coatings. For example, Hayward [5] has shown that the smooth-

est diamond coatings give the lowest friction coefficient, whatever the diamond quality. Friction and wear studies of diamond coatings were first carried out on coated silicon [6–9] or silicon carbide [10,11]. While these materials are ideal substrates for fundamental studies [12,13], they are not suitable for usual mechanical applications unlike titanium alloys or steels. The wear resistance of titanium alloys is generally improved by different processes including thermochemical pretreatments, physical (PVD) and chemical vapor deposition (CVD) [14]. However, the long exposure duration at high temperature required in most CVD or thermochemical techniques results in annealing of the substrates that affects the mechanical properties of the base material. Furthermore, the thermal expansion mismatch between diamond and titanium creates high residual stresses. Recently, diamond deposition was obtained at a moderate temperature ( $\leq 600^\circ\text{C}$ ), which allows to maintain the intrinsic properties of titanium alloys and to minimize the thermal stresses [15]. However, mechanical characterization is still necessary to test the adhesion of these coatings.

In this study we have investigated the diamond-on-diamond friction and wear properties of diamond-coated titanium alloy by using a pin-on-disk tribometer in ambient air. The friction coefficient and the wear rate were determined as a function of the sliding speed and the applied load. Other studies were performed with uncoated titanium alloy sliding

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against as-grown diamond coatings. These tribological results are linked with the coating morphology.

## 2. Experimental procedure

The disks, 16 or 34 mm in diameter and 5 mm thickness, were machined from commercial Ti-6Al-4V alloy. They were mechanically polished with different diamond pastes and then cleaned by acetone and ethanol.

Diamond deposition was carried out in a tubular reactor (60 mm in diameter) that crossed a wave-guide connected to a 6 kW microwave generator (2.45 GHz). The disks of 34 mm were placed on a rotating substrate-holder (10 rpm), that permits to enhance the coating homogeneity. Two types of coating were studied. The growth of type A coatings was carried out with a 1% CH<sub>4</sub>/H<sub>2</sub> mixture at 700°C while a 8% CO/H<sub>2</sub> mixture was employed with a substrate temperature of 600°C for coatings of type B. The total gas flow rate and the total pressure were fixed at 400 sccm and 1.33 kPa (10 Torr) respectively.

The surface morphology, faceted or not, and the average apparent grain size, *GZ*, were investigated by optical microscopy and scanning electron microscopy (SEM) together with the coating thickness on cross-sections. The coating quality, or diamond purity in percent with respect to non-diamond carbon, and the residual stresses were deduced from micro-Raman spectra. The purity of the coatings was evaluated from the integrated intensities of the diamond and non-diamond carbon peaks, taking into account a 75 factor for the ratio between graphite and diamond Raman scattering cross-sections [16]. These measurements were performed with a Dilor XY spectrometer, in back-scattering configuration, using a 514.5 nm Ar incident laser beam, with a 100 mW power and a spot size of 1 μm [15]. Atomic force microscopy (AFM) was employed to evaluate both the average surface roughness, *R<sub>a</sub>*, and the peak-to-valley height, *PV*, from several image analyses of 10 × 10 μm<sup>2</sup> surfaces. The variation on the whole surface was about ±10%.

The friction and wear tests were conducted by using a rotating pin-on-disk tribometer with a fixed pin. The radius of curvature of the hemispherical pin was 10 mm. The sliding speed was in the range 0.01–1 m s<sup>-1</sup> and the normal applied loads, *L*, were 1, 3 and 13 N. The tangential force was measured using a strain gauge located in a plane par-

allel to the friction one, through vertical leaf springs. The total wear rate, including both decrease of the pin height and depth of wear track on the disk, was measured during the test by a capacitive sensor of displacement. All sensor signals were recorded on a computer. The tests were performed in ambient air at relative humidity RH = 40–60%, during 1 to 50 h.

Diamond-coated Ti-6Al-4V samples were used as the disk. The pins were made from commercial Ti-6Al-4V. Tribological tests were carried out with uncoated and diamond-coated Ti-6Al-4V pins. In this latter case, the deposition conditions were identical for both counterfaces. The theoretical starting Hertzian contact pressure calculated on the basis of ideal sphere-on-plane geometry between two diamond-coated surfaces was 2.02 GPa when the normal load was 13 N, a Poisson's coefficient *ν* of 0.07 and a Young's modulus *E* of 1143 GPa being used in the calculation for polycrystalline diamond [17]. However, initial high actual micro-Hertzian stresses between the contacting asperity tips are obvious for such polycrystalline deposits. For uncoated titanium-alloy pin (*ν* = 0.3 and *E* = 110 GPa), the theoretical starting Hertzian contact pressure value was 0.67 GPa at 13 N.

After the friction and wear experiments, the worn surfaces were examined by SEM, AFM and studied by Raman spectroscopy. The final worn volumes of the disk and the pin were evaluated respectively from cross-sectional profiles of the wear track, and from the radius of the wear scar. The final wear rate (*W<sub>s</sub>*) was determined according to *W<sub>s</sub>* = *V*/*DL*, where *V* is the worn volume in m<sup>3</sup>, and *D* the sliding distance in m.

## 3. Results

### 3.1. Coating morphology and quality

The diamond growth conditions are given in Table 1 together with the average apparent grain size, the purity and the roughness values of diamond coatings of type A and B. The average surface roughness, which was calculated from a total of five or more measurements, increases as the grain size increases. The peak-to-valley value appears rather high, in the range 0.5–0.6 μm. However, before diamond deposition, the substrate surface displayed a scratched morphology resulting from an imperfect polishing (which

Table 1  
Diamond growth conditions and coatings characteristics

Coating type	Deposition temperature (°C)	Gas mixtures	<i>GZ</i> (μm)	Purity (%)	<i>R<sub>a</sub></i> (μm)	<i>PV</i> (μm)
A	700	1%CH <sub>4</sub> /H <sub>2</sub>	1.2 ± 0.1	92.1	0.080 ± 0.007	0.60 ± 0.05
B	600	8%CO/H <sub>2</sub>	0.8 ± 0.1	93.8	0.070 ± 0.006	0.50 ± 0.04

Average grain size (*GZ*) and diamond purity calculated from Raman analysis; average roughness (*R<sub>a</sub>*) and peak-to-valley height (*PV*) from AFM measurements.

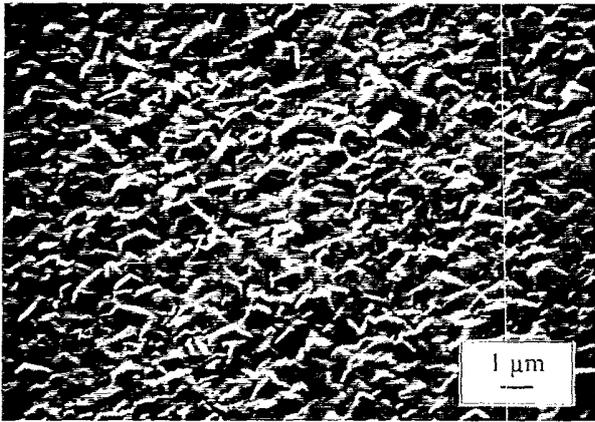


Fig. 1. SEM image of a diamond coating of type B deposited from 8% CO/H<sub>2</sub>, at 600°C, during 16 h, on a titanium-alloy disk.

can promote the adhesion of diamond coating by a mechanical effect). AFM analysis showed that the average roughness and the peak-to-valley height of initial substrates were respectively about 0.04 and 0.4 μm prior to coating. The final roughness which depends partly on this initial surface morphology is also influenced by the asperities due to the polycrystalline nature of the diamond coatings, as shown in Fig. 1 for type B. The deposit thicknesses were in the range 1.5–4 μm.

The two diamond coating types display typical Raman spectra (Fig. 2). Both spectra exhibit broad bands at 1140, 1350, 1450 and 1580 cm<sup>-1</sup>, which indicate an incorporation of amorphous and graphitic carbon [18–20]. The diamond purity is the lowest for coating A (Table 1). As it contains less apparent grain boundaries (*GZ* is greater for this film in Table 1), more amorphous or graphitic carbon would be incorporated between or inside subgrains than in coating of type B. The double peak, observed at 1335.1 and 1348.1 cm<sup>-1</sup> after decomposition of the experimental spectrum for coating A, and at 1334.1 and 1345.5 cm<sup>-1</sup> for coating B (Fig. 2) is assigned to polycrystalline diamond. The large shift and the partial splitting of this peak, when compared to 1332 cm<sup>-1</sup> for natural diamond, are attributed to the compressive residual stresses, which are thus in biaxial state [21–23]. The residual stresses are –6.2 GPa for coating A and –5.2 GPa for coating B as evaluated from Raman analysis [15]. The diamond grain quality, deduced from the width at half-maximum of the diamond peak, appears poorer for coatings A than for B. The broadening of the asymmetric peak diamond feature can be attributed to several phenomena such as the presence of more defective diamond, the higher dispersion of the crystallite orientation, and highly heterogeneous strain field occurring over micron dimension [24].

### 3.2. Diamond versus diamond-coated titanium-alloy friction tests

The friction coefficient versus the sliding distance of dia-

mond-coated pin and disk couple are shown in Fig. 3, for a 0.02 m s<sup>-1</sup> sliding speed and a load of 1, 3 and 13 N. The noisy fluctuations of the friction coefficient observed at 1 N are due to the surface roughness. After a longer test carried out in these conditions, the diamond coating on the disk is found to be intact as shown by SEM and indicated by the surface roughness values which remain constant.

At higher loads, the friction coefficient measured in the same track stabilizes at a value of about 0.08 for the coating of type A and 0.06 for the coating of type B (Fig. 3). The lower roughness of coating B [5] or its better diamond quality could explain this small difference. At each change of the applied load, we can observe a sharp peak which corresponds to the adaptation of the contact of both counterfaces. At the end of the test carried out at 13 N on the coating of type B, a wear track of 200 μm in width was formed on the diamond-coated disk. The high magnification image of this area shows that the worn surface is significantly polished (Fig. 4). In addition, AFM measurements within and just outside the wear track reveal a significant decrease of the surface roughness: the value of *R<sub>a</sub>* is divided by a factor 3, to reach 25 nm, and PV is equal to 0.32 μm (see Table 1 for comparison). These analyses confirm that only the tips of diamond grains have been polished, no spalling occurred and no grains have been pulled out during wear. The same observations have been made for coating of type A. The friction coefficient decreases also with the distance and the load, from 0.11 to 0.08 (Fig. 3a), and therefore with the surface roughness.

When increasing the sliding distance, at a sliding speed of 0.02 m s<sup>-1</sup> and a load of 13 N, the friction coefficient gradually increases after a distance of 250 m to reach 0.16 at 700 m. The worn surface of the pin shows an area where the titanium-alloy substrate is apparent. It presents a diamond/Ti-6Al-4V composite surface [15]. It is obvious that the Ti-6Al-4V contribution to the contact area has increased with the sliding distance. No variation of the total volume

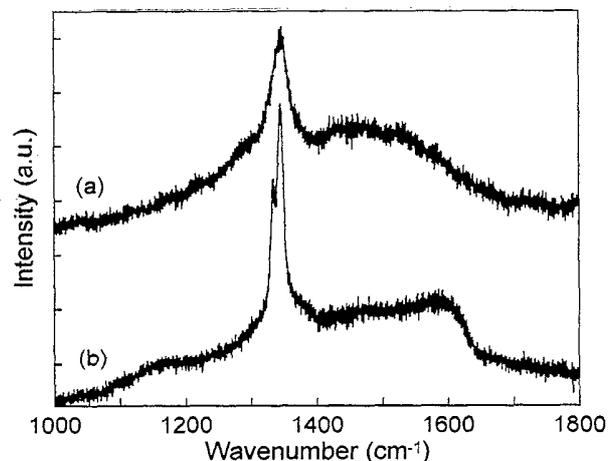


Fig. 2. Raman spectra of two diamond coatings deposited on titanium-alloy disks from: (a) 1% CH<sub>4</sub>/H<sub>2</sub> at 700°C (type A); (b) 8% CO/H<sub>2</sub> at 600°C (type B).

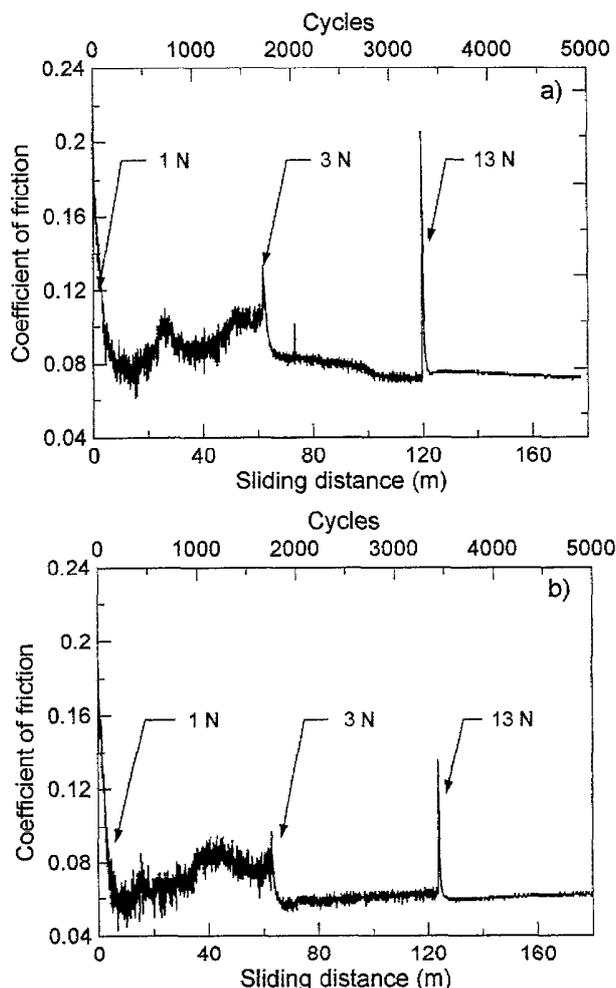


Fig. 3. Friction coefficient as a function of the sliding distance for several applied loads (1, 3, 13 N) at  $0.02 \text{ m s}^{-1}$ ; diamond-coated titanium-alloy pins sliding against diamond-coated titanium disks both deposited from: (a) 1%  $\text{CH}_4/\text{H}_2$  at  $700^\circ\text{C}$  (type A); (b) 8%  $\text{CO}/\text{H}_2$  at  $600^\circ\text{C}$  (type B).

wear rate as a function of the sliding distance was evidenced during the test because the vertical displacement was weak, a few micrometers at the end of the test. At this point, the final wear rate of the pin is indeed about  $6 \times 10^{-17} \text{ m}^3 (\text{N m})^{-1}$ . The wear of the diamond-coated disk is too low to be measurable and the wear track is just polished, as observed by SEM and confirmed by the AFM measurements. This lack of coating wear of the disk results from the short test duration due to the pin wearing more quickly. A longer test was carried out with a thicker diamond coating, about  $10 \mu\text{m}$  thick. After 3000 m, wear of the diamond-coated disk was still hardly measurable but the wear track was more polished as shown by AFM measurements. A wear measurement of the diamond-coated substrate would require a very thick diamond coating on a pin. However, it would be difficult to assess a general true wear behavior of the diamond-coated substrate because of the variation of contact pressure during the friction test, and because of the influence of initial surface roughness.

Optical microscopy and SEM observations of the wear surface do not reveal any coating failure or crack of the diamond coating of the disk. Furthermore, the residual stress values are similar before and after the friction tests. It can be concluded that no stress relaxation occurred in the coating. All these results confirm the high adhesion of the diamond coatings on titanium-based substrates [15, 25].

### 3.3. Diamond versus uncoated titanium-alloy friction test

Friction and wear tests were also carried out with uncoated titanium-alloy pins on titanium-alloy disks coated with a diamond film of type B. The friction coefficient was measured as a function of the sliding distance, for an applied load of 13 N. The sliding speed was fixed first at  $0.1 \text{ m s}^{-1}$  as shown in Fig. 5. At the beginning of the test, the fluctuations of the dynamic friction coefficient are very large and the mean value is high, in the 0.2–0.4 range. Then it decreases and after a sliding distance of about 2000 m, the friction coefficient reaches 0.1 and remains constant, except at about 4000 m where the test was interrupted. Farther than about 7000 m, the sliding speed is increased by steps in the range  $0.1\text{--}1 \text{ m s}^{-1}$ . The friction coefficient always reaches about 0.1 and remains constant, whatever the sliding speed. Other friction tests had been also performed previously in constant conditions, i.e. a load of 13 N and a sliding speed of  $0.1 \text{ m s}^{-1}$ , up to a distance of  $2 \times 10^4 \text{ m}$ . They are not reported here because similar results are obtained. A constant friction coefficient, in the 0.08–0.1 range, is reached after a running in period corresponding to a sliding distance ranging between 2000 and 3000 m.

The SEM observations of the wear tracks always show that the height of the diamond crystals asperities have decreased. Some wear debris, identified as titanium alloy by EDAX and therefore transferred from the pin, are also accumulated inside the diamond surface irregularities (Fig. 6). The average roughness and the peak-to-valley height are



Fig. 4. SEM image of the wear track formed on the diamond coating of Fig. 1 after a tribological test performed at several applied loads (1, 3, 13 N) and  $0.02 \text{ m s}^{-1}$ .

reduced by a factor 2.5, as measured by AFM. Except in one case where several scratches with a width of several micrometers are observed, at the end of a sliding test that does not present a noticeable difference in friction behavior, the wear of diamond coatings is negligible. During the running in time of the friction test corresponding to Fig. 5, the wear rate of the titanium-alloy pin is about  $6 \times 10^{-15} \text{ m}^3 (\text{N m})^{-1}$ . After this period, the wear is always very low, leading to a final wear rate of about  $6 \times 10^{-16} \text{ m}^3 (\text{N m})^{-1}$ . The examination of the titanium-alloy pin shows that its surface is scratched by the diamond asperities, leading to a large decrease of the contact pressure. Electron-probe microanalysis (EPMA) reveals the presence of titanium and oxygen on the worn surface of the pin that might be attributed to the formation of a native titanium oxide layer when bare titanium reacts with ambient air [15].

When some diamond coating scratching occurred, carbon is observed on the corresponding pin surface that may be due to the transfer of particles from the diamond coating. SEM images show that these particles have been embedded in the titanium alloy. The biggest particles are identified by Raman spectroscopy as diamond crystals with some graphitic impurities which might arise directly from the disk coating. A graphitization process due to a tribologically induced phase transformation would require a sufficiently high contact temperature that might not be reached here.

Other friction tests were carried out directly at a sliding speed equal to or greater than  $0.2 \text{ m s}^{-1}$  with a 13 N load. For example, after about 20 m at  $0.55 \text{ m s}^{-1}$ , the friction coefficient which is about 0.3 rises to an average value of 0.5. Large fluctuations of the friction coefficient are observed in accordance to the formation of a large and deep wear track as a result of diamond coating pull-out. These results confirm that a prolonged stage at a lower sliding speed ( $<0.2 \text{ m s}^{-1}$ ) is necessary to avoid an early coating failure. This coating detachment of high-stressed films is due to a strong

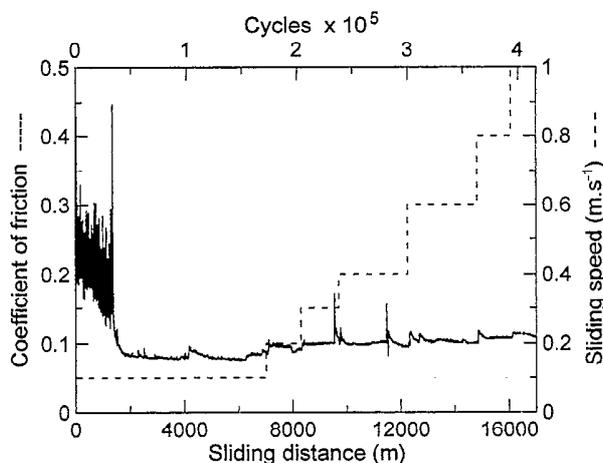


Fig. 5. Friction coefficient as a function of the sliding distance for an uncoated titanium alloy pin sliding against a diamond coating of type B, at 13 N and various sliding speeds in the range  $0.1\text{--}1 \text{ m s}^{-1}$ .

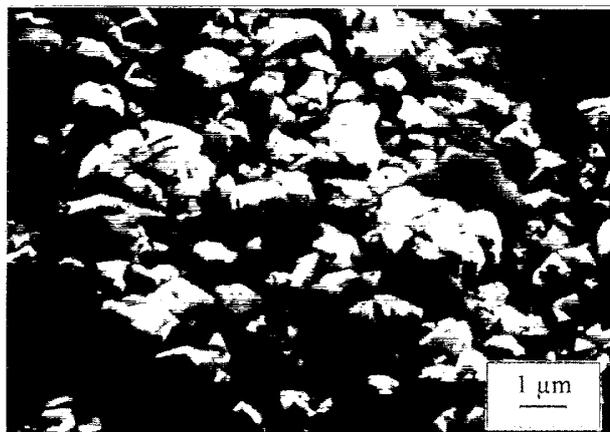


Fig. 6. SEM image of the wear track formed on the diamond-coated disk (type B) after a sliding test against a Ti-6Al-4V pin (applied load 13 N, various sliding speeds in the range  $0.1\text{--}1 \text{ m s}^{-1}$ , duration time 48 h).

friction and therefore high shear stress, the maximum of which is moreover located closer to the substrate surface according to Hamilton and Goodman [26], therefore closer to the interface.

#### 4. Conclusion

The diamond-on-diamond friction tests, carried out on coated titanium alloys, confirm the results obtained with other substrate types. After a short running in time, the friction coefficient is in the range  $0.05\text{--}0.08$  as previously reported by several authors for diamond-on-diamond, and the wear rate of the disk is very low. The surface roughness appears as the most important parameter. The influence of the coating quality seems weak but it should be more thoroughly examined for smooth coatings. The friction coefficient obviously changes when the diamond coating only remains on the edge of the pin, but the wear rate does not change drastically. No coating failure or crack, and no stress relaxation are observed on the disk track after the friction tests, even at high load. All these results confirm the good adhesion and the good diamond quality of the coatings, especially those deposited on titanium alloys at  $600^\circ\text{C}$ .

The friction of diamond-coated Ti-6Al-4V against uncoated Ti-6Al-4V has also been studied. The initial friction coefficient of as-deposited coatings is relatively high, but after a running in period, it decreases to a value of about 0.1 and does not vary with the sliding speed, the contact pressure being, however, very reduced. Some surface smoothing of the diamond coating surface is observed, principally as a result of the titanium transfer, but the faceted diamond coatings with an average roughness of about 80 nm remain too abrasive for uncoated metallic counterfaces. The reduction of the friction and wear of metallic counterparts through the surface modifications of the diamond-coated titanium alloys are therefore being studied more thoroughly.

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