Boride Coating on Titanium Alloys as Biomaterial in Wear and Fretting Applications

Boride coating on titanium alloys as biomaterial in wear and fretting applications

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Abstract. The issue taken into account is the lifespan and potential toxicity of arthroprostheses with a focus on metal-polyethylene coupling.

The gold standard for hip prostheses is a femoral component made of Ti6Al4V alloy, a head made of CoCrMo alloy and an insert made of UHMWPE while for knee prostheses the gold standard is a tibial component made of CoCrMo alloy, a femoral component made of Ti6Al4V and an insert made of UHMWPE. Open issues are wear of UHMWPE, toxicity of Co alloys and low fretting/wear resistance of Ti alloys.

The aim of this research is to focus on the most biocompatible material (Ti6Al4V alloy) in order to improve its bio-tribological characteristics.

A ceramic surface conversion by thermal treatment was used to obtain a borided coating on the titanium alloy surface in order to combine high hardness, good wettability and lubricant behavior of ceramics with good mechanical properties of Ti metal alloys.

The coatings were characterized by means of optical microscope observation, FESEM analysis, XRD analysis, microindentation, scratch, friction and wear tests in order to identify the thermal treatment most suitable to obtain a coating with the required properties (thickness, hardness, roughness, wear resistance, friction coefficient and scratch resistance, surface lubrication ability in contact with human fluids) without significant modification of the microstructure of the substrate.

Keywords: Titanium Alloy, Boriding, Wear.

1 Introduction

Hip arthroplasties are commonly composed of a femoral component (stem), a head, an insert and an acetabular cup. Tribocorrosion and wear mainly occur at the head-insert or head-acetabolum interface; tribocorrosion can also be an issue at the head-stem junction and at the stem-cement interface. In the first case, it is due to the prosthesis design and aggressive physiological environment, while in the second case it depends on several factors such as micromotions of stem, structure and chemical composition of the cement [1, 2].

For the head-insert or head-acetabolum interface, several different material combinations were developed during the last decades. The most common ones are metal on polyethylene (MoP), ceramic on polyethylene (CoP), ceramic on ceramic (CoC) and metal on metal (MoM), while ceramic on metal (CoM) was clinically tested without success for a short while.

Orthopaedic annual reports indicate that MoP is the most widely used material combination since 2003. In 2017, about 60% of primary hip surgery was carried out using MoP coupling [3]. Due to wear of UHMWPE, a too short lifespan (about 10-15 years) is the main issue of this king of coupling.

MoM implants have a lower wear rate than MoP implants, but their clinical failure is associated to adverse reaction to metal debris, due to wear and tribocorrosion of the metal surface [4].

The most wear resistant implants are CoC, which are also associated to high wettability by natural lubricant, but, in this case, open issues are squeaking during walking, brittleness and need of very accurate positioning and handling during the surgical process [5, 6].

Ceramic conversion surface treatment of a Ti alloy substrate is used in this research to face these issues and to try to increase wear resistance and prosthesis lifespan, as a consequence, of bearing surfaces and to reduce adverse reactions to metal ions release, associated mainly to the use of CoCrMo alloys.

The idea comes from steel boronizing, a well-defined process in literature for increasing wear resistance of cutting tools [7]. Boronizing of commercially pure Ti and Ti alloy has already been studied in literature as a way to increase hardness and wear/fretting resistance [8, 9, 10], but in-depth studies are needed for using borided coating for biomedical applications.

The aim of this work is to perform a borided coating and carry out a preliminary characterization in terms of structure, microstructure, thickness, hardness, adhesion, friction coefficient and wear resistance.

The titanium borided coating was obtained on a Ti6Al4V substrate by means of a solid state diffusion during a thermal treatment, with the advantage of a low cost treatment. Further analyses will be necessary to define the appropriate thermal treatment to simultaneously obtain the suitable coating properties and substrate microstructure.

2 Materials and Methods

The substrate used in this research is titanium alloy grade 5 (Ti6Al4V alloy-composition: N 0.05 wt%, C 0.08 wt%, H 0.015 wt%, Fe 0.40 wt%, O 0.20 wt%, Al 6.75 wt% and V 4.5 wt%, remaining Ti). Disks of 2 mm in thickness are obtained by cutting a bar 10 mm in diameter. The samples were manually ground by SiC grinding papers from 120 to 4000 grit surface finish. The samples were cleaned 5 min in acetone and twice in double-distilled water for 10 min by using an ultrasonic bath. Before the boronizing treatment, a weak acidic solution (HF 5 M) was used to deoxidize the surface of same samples, that then were washed for 2 min.

The boriding powder mixture consisting of B 50 wt%, Na2B4O7 15 wt% and C 35wt% was selected according to previous works [8, 9, 11] on boriding of commercially pure Ti. The powder was milled in a WC ball milling for 6h in air. Inside an Ar filled gloves box, the samples were put in a graphite crucible and embedded in the mix of salts. The protocol followed for the thermal treatment was similar to the one reported in literature [5, 6] carried out on commercially pure Ti. The maximum ttemperature of the heat treatment was set at 1050°C and holding time at 4.5h. The process was carried out in Ar atmosphere in a tubular furnace to avoid oxidation of samples. At the end of the treatment, samples were let to cool at room temperature in the furnace and then they were cleaned twice with ultra-pure distilled water in an ultrasonic bath.

After being borided, same samples were submitted to a post thermal treatment at 1050°C for 4.5h. The post thermal treatment was performed to evaluate if it is useful for increasing the boron diffusion.

Reicher-Jung MeF3 optical microscope and Zeiss supra 40 GEMINI field emission scanning electron microscopy (FESEM) were used to examine the substrate microstructure, coating thickness and morphology of sectioned, metallographically polished and etched samples.

X-ray diffraction analysis was carried out to evaluate the structure of the samples. PANalytical X'Pert Pro PW 3040160 Philips with Cu Kα incident radiation was used in the Bragg–Brentano camera geometry and for grazing angle measurements with incident angle fixed at 1° and 3°.

The roughness of the samples was evaluated by means of Contact Profiler Talysurf 120, three measure for each samples were carried out for a statistic evaluation.

Leitz Durimet microdurometer was employed to measure the hardness of the samples by means of Knoop microindentations. Standard UNI EN ISO 4516 was followed and a normal load of 50gf was applied for 20s.

Revetest Scratch Tester Each with a Rockwell C diamond stylus 200 μm in radius was used to test the adhesion of the coating. Three test were performed on each samples with a line scratch of 4.9 mm, under a normal load increasing 100N/min from 1N to 50N and a speed of 10 mm/min.

Wear tests were performed using Docum Biotribometer with multidirectional motion (Ducom Instruments Europe, B.V., Netherlands).

Hard on Hard contact and Soft on Hard contact were taken into account: in the first case borided Ti alloy disks were put in contact with borided Ti alloy pins, using a constant normal load of 400N, while in the second case borided Ti alloy disks were put in contact with UHMWPE pins, using a constant normal load of 100N. As reference a disk and a pin of CoCrMo alloy were used. A 8 shape path was executed by pins on stationary disks, with a speed of 31.4 mm/s for 1h. The tests were carried out in lubricant condition at 37°C, using FBS as lubricant. During the tests wear was measured by means of Linear Variable Differential Transformer (LVDT). After the tests Phenom XL Scanning Electron Microscope was employed to observe wear tracks on samples.

3 Results and Discussion

3.1 Microstructure

The microstructure of the untreated Ti alloy sample and borided samples was compared in Figure 1. Due to the thermal treatment above the beta transus temperature of the Ti alloy, the microstructure of the borided samples changes after the heat treatment [12]. The untreated sample has a microstructure composed of small acicular grains, while the treated samples have a Widmanstätten microstructure. Maintenance of the initial microstructure is important in order to not modify the mechanical properties of the Ti alloy substrate and future work is in progress in order to optimize this aspect.

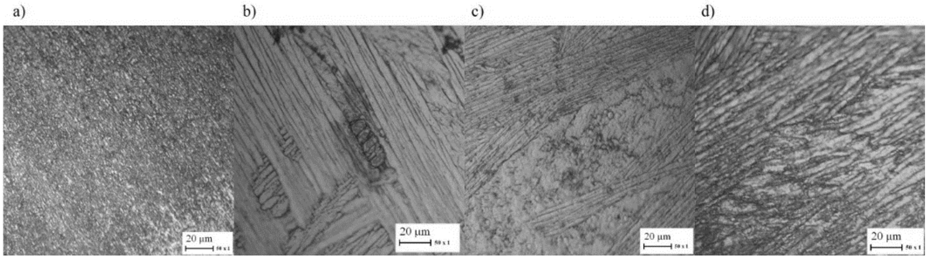

Fig. 1. Optical microscope micrographs of the substrate of a) the untreated Ti alloy sample, b) the borided samples without deoxidized surface, c) the borided samples with deoxidized surface and d) the borided samples subjected to post thermal treatment.

3.2 Morphology and Thickness

Figure 2 shows the cross-sectional micrographs of the treated samples. The cross-section of the coatings is similar for all the samples: the coating consists of whiskers penetrating the substrate and an upper monolithic layer.

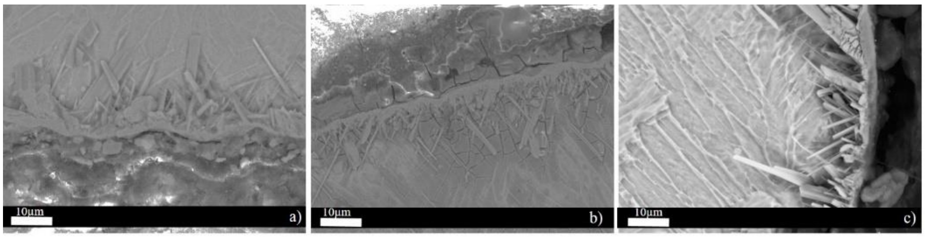

Fig. 2. FESEM images of coatings of a) borided samples without deoxidized surface, b) borided samples with deoxidized surface and c) borided samples subjected to post thermal treatment.

The thickness of the monolithic layer is in the range between 4 µm and 6 µm for all the treated samples, while the penetration depth of whiskers is 19 µm for the borided samples without post thermal treatment and 43 µm for the borided samples subjected to post thermal treatment (Figure 3). The coating thickness reached with the boronizing process on the Ti alloy samples is near to the one obtained by K.S. Ravi Chandran et al. [3, 4] on Ti c.p.

It is possible to observe that the removal of the native oxide layer by the deoxidation pre-treatment does not allow to increase boron diffusion, while the post thermal treatment does. As Figure 3 shows, the thickness of the monolithic layer of the samples with deoxidized surface is a bit thinner than the others, while the post thermal treatment is effective in increasing the penetration depth of whiskers.

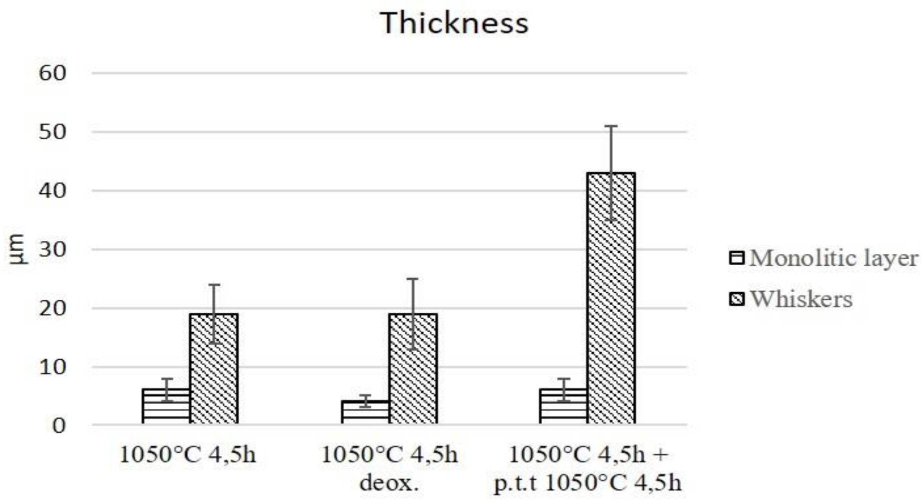

Fig. 3. Thickness of the borided samples.

3.3 Phase Composition

In the case of the borided Ti alloy, X-Ray patterns obtained with Brag-Brentano geometry show well evident TiB and TiB_2 peaks (Figure 4). This suggests that a uniform coating is on surface. In addition, grazing angle measurements at 1° and 3° evidence that the upper layer is mainly composed of TiB_2 while the inner part of the coating, at the interface with the substrate and in correspondence with whiskers, consists of TiB. The patterns of the borided sample with deoxidized surface were not reported in Figure 4, because there is not any difference with respect to the patterns of the borided sample without pre-treatment. The patterns of the borided samples with and without post thermal treatment are compared. The comparison highlights that, during the post thermal treatment, part of the TiB_2 reacted to form TiB, the more stable borided phase. The X-Ray patterns of borided Ti c.p. from literature [8] analogously show a relevant presence of TiB peaks, with an intensity dependent on the amount of whiskers in the coating and small peaks of TiB_2 coming from the monolithic upper layer.

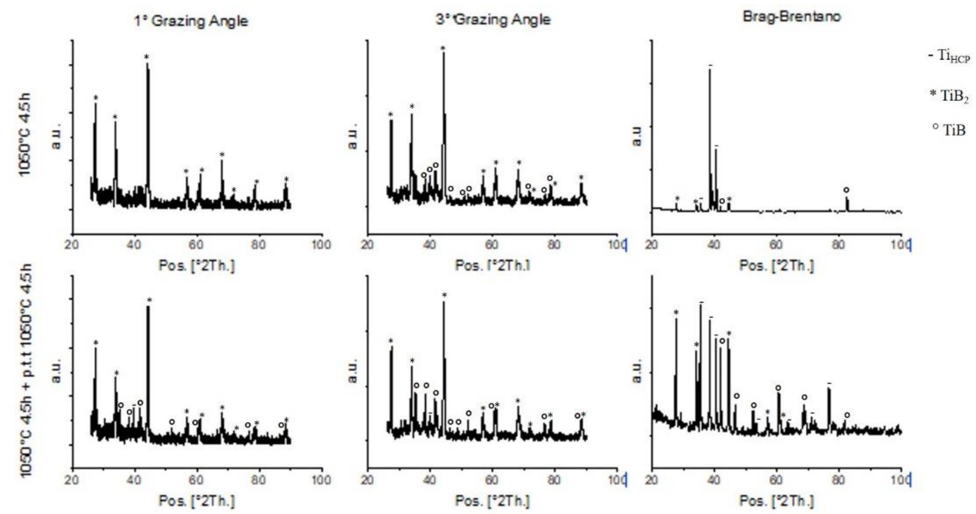

Fig. 4. XRD patterns of the borided sample without deoxidizing surface and of the borided sample subjected to a post thermal treatment.

3.4 Hardness

The boronizing process causes a significant increase of hardness as it can be seen on Figure 5. The boronizing process on the samples without any pre and post treatments allows to obtain hardness of 90±6GPa. The samples with a pre or post treatment (deoxidation process or thermal treatment at 1050°C for 4.5h) respectively have hardness of 68±6GPa and 66±6GPa. The decrease of hardness can be due to reduced thickness of the monolithic coating layer in the case of the samples with pre deoxidizing treatment. In the case of the samples with post thermal treatment, this can depend on the conversion of TiB_2 phase into TiB phase.

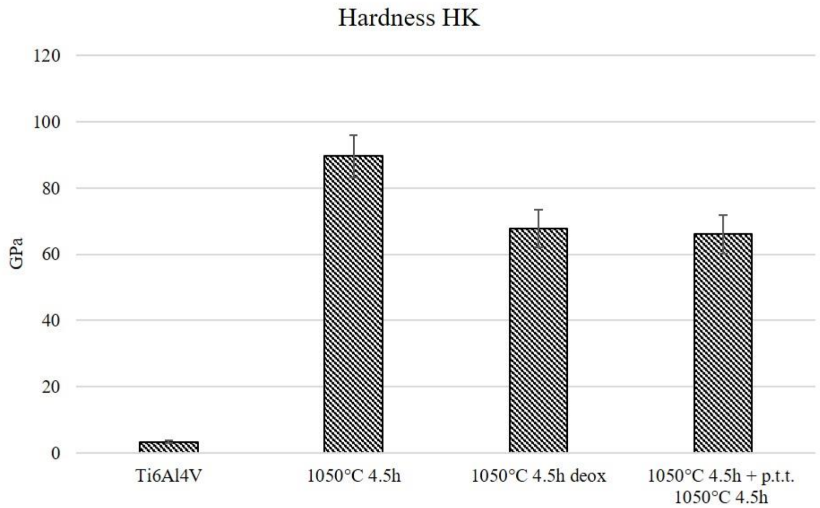

Fig. 5. Knoop hardness of the untreated Ti6Al4V sample and the borided samples.

3.5 Adhesion

Adhesion of the coatings was evaluated by means of scratch test; a first evaluation of friction coefficient (COF) was also performed by this test. COF data of the untreated and borided samples are shown in Figure 6. Scratch test on the untreated Ti alloy was used as reference to define the friction coefficient (COF) of the substrate and to have a COF value suitable as a reference to define the point of detachment of the coatings by observing the friction curves. As reference of gold standard materials used in arthroprosthesis under wear condition, Co-Cr-Mo alloy and alumina were used. COF of the uncoated Ti alloy results to be 0.4, the borided samples have COF between 0.2-0.3 and Co-Cr-Mo alloy and alumina respectively have COF 0.2 and 0.1. It can be concluded that the borided samples have lower COF then the uncoated Ti alloy and it is not far from that of gold standard materials.

From the friction curves, it appears that COF starts to increase respectively at a load of 30 N in the case of the borided sample without any pre or post treatment, while it increases from 45 N in the case of the pre-treated sample and it is constant at 0.2 in the case of the post-treated sample. In the case of the first sample, COF gradually increases and it is slightly lower than 0.4 at the end of the test according to a progressive detachment of the coating. In the case of the second sample, COF abruptly increases at 45 N reaching the value of 0.4 and this behavior could be related to a sudden detachment of the coating. In the last case, no detachment seems to occur up to 50 N according to the friction curve.

Figure 7 shows the appearance of the scratch track and its chemical composition in the case of the borided sample (without any pre or post treatment). EDS analysis detects presence of B till the end of the track even if it is reduced in amount and it shows that there is not a complete decohesion between the coating and substrate during the test; actually, they plastically deform together under the stylus of the instrument and the coating become thinner.

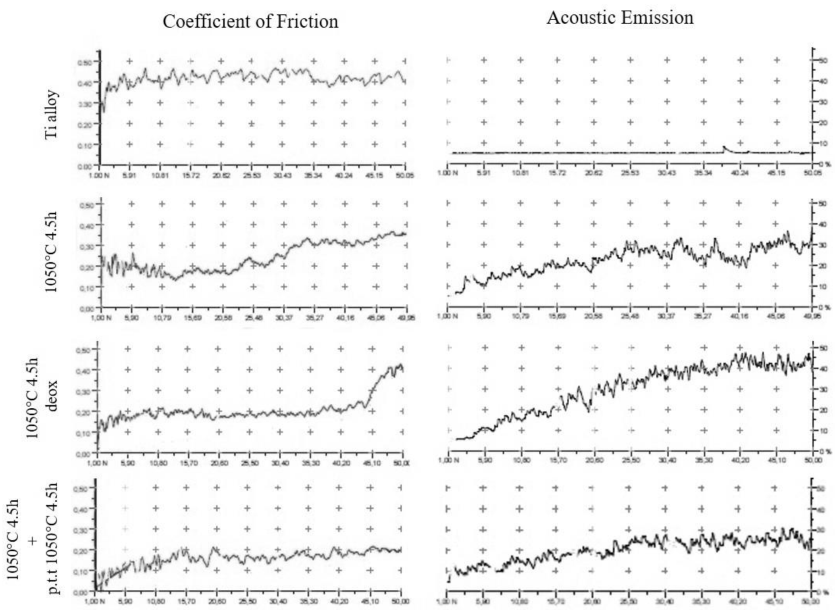

Fig. 6. COF and AE of the Ti alloy and the borided samples.

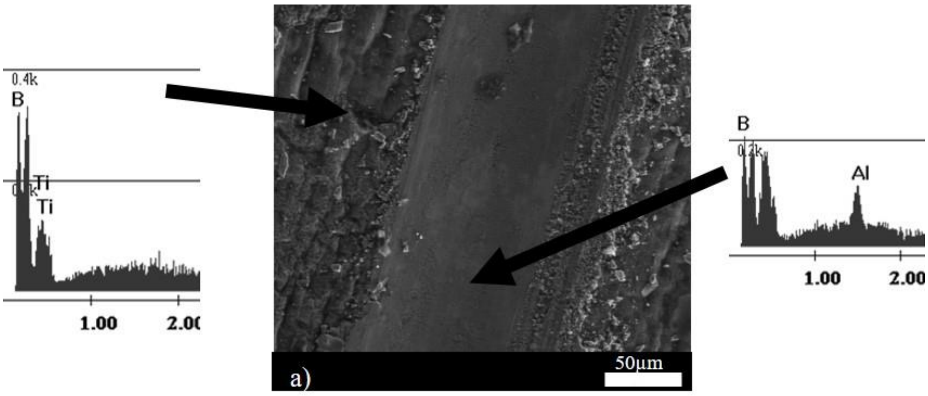

Fig. 7. FESM image and EDS pattern of the end of a scratch tracks of the borided sample without surface deoxidation.

3.6 Wear

COF of the borided samples and Co-Cr-Mo alloy samples (used as reference) in contact with themselves (hard on hard contact) or with a counterpart made of UHMWPE (soft on hard contact) are reported in Figure 8.

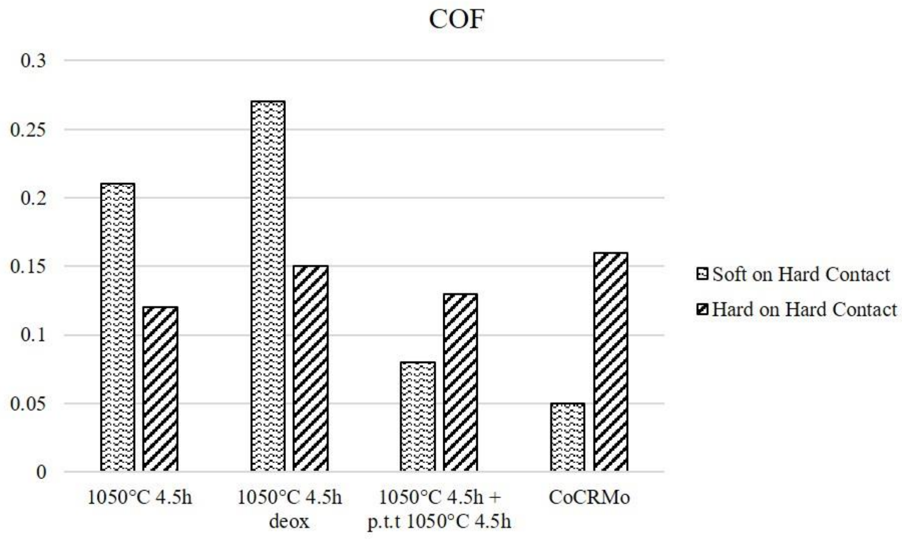

Fig. 8. COF of the borided samples and CoCrMo samples in soft on hard contact and hard on hard contact.

In soft on hard condition, the borided sample with post thermal treatment results to have the lowest COF, closed to the one of the reference material: 0.08 and 0.05, respectively. The highest COF corresponds to the borided sample with a deoxidized surface: 0.27. In hard on hard condition, the borided samples have a COF value very close to that of the CoCrMo reference sample.

In conclusion, borided samples subjected to a post thermal treatment are of interest because they have COF close to the Co-Cr-Mo alloy, both in soft on hard and in hard on hard conditions, but contrary to the last one they are biocompatible materials.

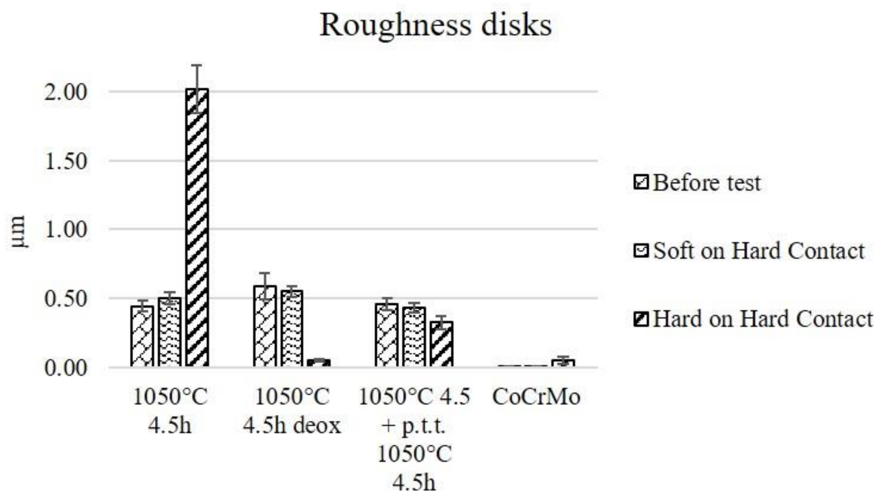

Fig. 9. Roughness of the borided samples and CoCrMo sample before and after wear test in soft on hard and hard on hard condition.

Figure 9 shows the roughness data of the disks employed during the wear tests both before and after the tests. Roughness before the test is comparable on all the borided samples, even if it is slightly higher in the case of the pre-treated sample. On the contrary, roughness of the reference Co-Cr-Mo alloy is significantly lower. Different COFs, mainly in soft on hard condition, depend also on different roughness of the samples and this issue could result in a worst behavior of the borided surfaces with respect to the capabilities of the borided coating. Further work will be performed in order to optimize surface polishing of the borided samples.

Hard on hard contact causes surface polishing in the case of the borided disks pre or post treated, while roughness of the borided disk without pre or post treatments and CoCrMo disk increases after the test (Figure 9): this difference can be related to a different wear mechanism as discussed below.

Figures 10 and 11 show the effect of wear on the pins after the tests. SEM observations on the disks did not reveal any evident track of the PE pins after the tests (Figure 10). There is a surface polishing in the case of the contact of the PE pin with the borided Ti alloy disks, while surface roughness of PE pin increases in the case of the contact with Co-Cr-Mo alloy. Polishing effect can be related to abrasive wear while roughening can be due to adhesive wear.

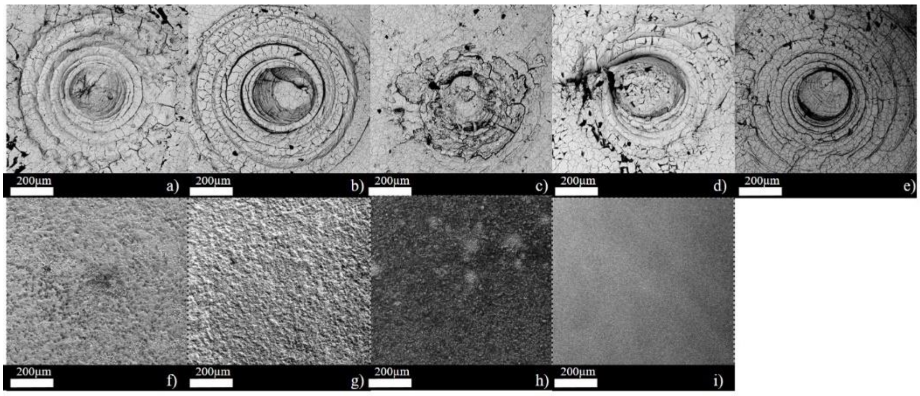

Fig. 10. SEM images of the pins and disks after the wear tests with soft on hard contact: the borided disk (1050°C- 4.5h) and corresponding PE pin are reported in (f) and (a), the pre-treated borided disk (deoxidation of the surface-1050°C- 4.5h) and corresponding PE pin are reported in (g) and (b), the post-treated borided disk (treated twice at 1050°- 4.5h) and corresponding PE pin are reported in (h) and (c), the Co-Cr-Mo disk and corresponding PE pin are reported in (i) and (d). In (e) the SEM image of an unworn PE pin is reported

In the case of hard on hard contact, the disks show on the surface a visible track due to the contact with the pins. In the case of the borided material without any pre or post treatment and of the CoCrMo alloy, there is an evident damage of both the surfaces with an increase of roughness. On the contrary, the borided disks and pins with pre or post treatments show a significant surface polishing (Figure 11).

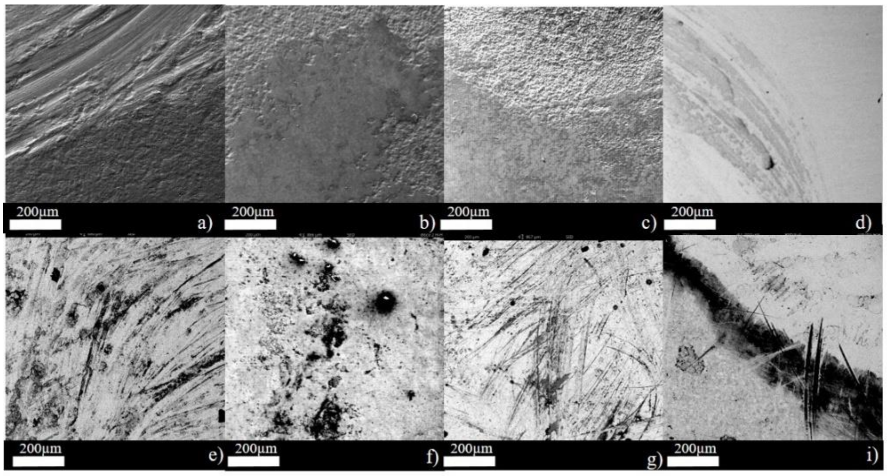

Fig. 11. SEM images of the pins and disks after the wear tests with hard on hard contact: the borided disk (1050°C- 4.5h) and corresponding pin are reported in (e) and (a), the pre-treated borided disk (deoxidation of the surface-1050°C- 4.5h) and corresponding pin are reported in (f) and (b), the post-treated borided disk (treated twice at 1050°- 4.5h) and corresponding pin are reported in (g) and (c), the Co-Cr-Mo disk and corresponding pin are reported in (i) and (d).

Figure 12 shows the linear wear of the samples measured by means of LVDT. In the soft on hard contact, wear increases, it reaches a sort of plateau and then it still slowly and continuously increases on all the samples. The borided disk subjected to post thermal treatment has the lowest wear with respect to the Ti coated samples and behavior similar to the reference Co-Cr-Mo alloy. In the hard on hard contact, the borided samples without any pre or post treatment has the worst behavior: LVDT curves has a slope higher than the others samples and there is a change of slope around the sliding distance of 100 m, that could suggest a detachment of the coating from the surface. FESEM images (Figure 10) show that in any case the surfaces of the pins are more damaged than the disks.

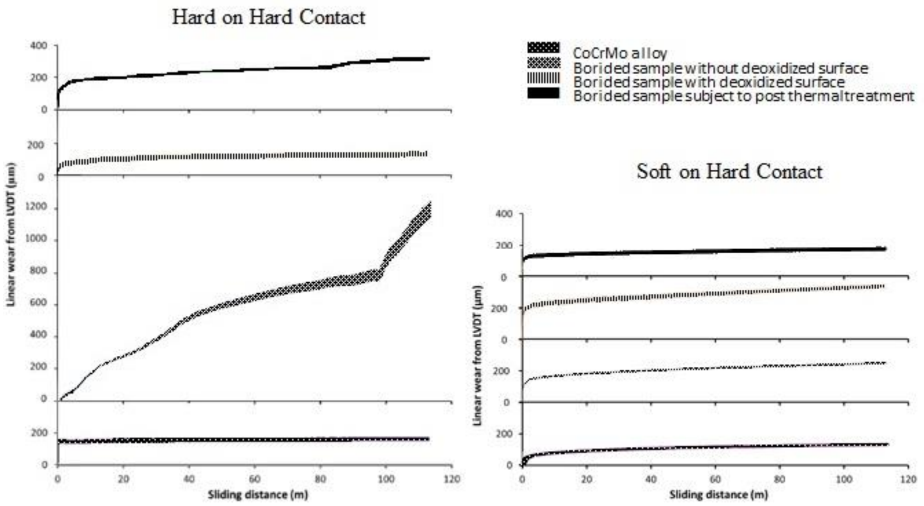

Fig. 12. Linear wear from LVDT.

4 Conclusions

Boronizing process, carried out at 1050°C for 4.5 h, allows to obtain a borided coating on a Ti alloy substrate. The coating consists of a monolithic layer of TiB_2 with a thickness of about 4-6 µm and whiskers composed of TiB with a penetration depth of about 19 µm. Boron diffusion does not increase by performing a deoxidizing surface treatment before the boronizing process, while a post thermal treatment allows to increase the penetration depth of whiskers. A penetration depth of 43 µm is reached in the last case. Boronizing treatment at 1050°C causes a significant change of microstructure, that could influence the mechanical properties of the substrate.

The borided samples have higher hardness and lower COF than the untreated Ti alloy. COF of the treated samples results to be closed to the one of gold standard reference materials both during scratch tests and pin on disk tests in hard on hard contact. Scratch tests show that there is no delamination between the coating and substrate up to 50N in the case of the post treated borided sample; the others borided samples showed a progressive or sudden detachment al lower load.

During pin on disk tests, the borided samples subjected to post thermal treatment show the lowest wear both in soft on hard and hard on hard condition.

Future analyses will be focused on some open issues, such as optimization of the polishing procedure of the coating (factor that could increase wear resistance and lower COF) and of the thermal treatment steps in order to obtain an almost unchanged microstructure. ICP analyses are also scheduled in order to evaluate the ions release during wear tests.

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