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Development of new duplex treatments on 100Cr6steel combining Thermochemical Treatments, Laser Shock Peening and Physical Vapour Deposition

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Abstract. 100Cr6 steel (AISI 52100) is one of the most used steel grades in the manufacturing of through hardening bearings mainly due to its properties: controlled impurities during steel making process, high hardenability and well known mechanical properties such as wear and fatigue resistance on clean environments. These characteristics play an important role on the performance of a bearing together with the bearing design, loads and environment. However, there is an increasing set of demanding applications where the above mentioned steel does not fulfil the required needs and thus, bearing manufacturers continuously work on the development of technologies to improve the bearing performance.
Nowadays thermochemical treatments (TCT), such as carbonitriding are being applied to this steel in order to enhance the performance of such pieces in contaminated environment, where particles can produce defects on the raceway, increasing the onset of defects that eventually lead to premature fail. These treatments induce the formation of carbides and nitrides which are directly related to the enhancement of the wear resistance and also to increasing the amount of Retained Austenite (RA) in the surface which may have a beneficial effect as it delays the crack propagation on subsurface regions, then increasing bearing fatigue life.
In this work, different TCTs have been applied to 100Cr6 steel flat samples. Using a tribometer (ball-on-disc configuration) and a grinding machine, surface and in-depth wear resistance measurements have been carried out, obtaining wear resistance profiles that have been correlated with the microstructure, microhardness profiles and RA content.
The most promising TCT has been combined either with Laser Shock Peening (LSP) treatments or carbonaceous Physical Vapour Deposition (PVD) coatings with the aim of improving not only the wear resistance but also the CoF of the duplex treated sample.
The results obtained on flat samples are promising; the combination of treatments produces long-lasting low CoF and a reduction of 60% in the wear rate. However, the treatments should be applied on real pieces and tested in a test bench in order to obtain more appropriate data about the lifespan of duplex treated bearings.

1. Introduction

Rolling bearings are one of the most critical components in any mechanical system, especially in automotive and industrial applications where they usually work under high cyclic loads and high speeds requirements, not only in clean but also in contaminated environments where metallic particles are present [1].

Nowadays load bearing capacity requirements for bearings are becoming more demanding, as well as longer service life and higher reliability [2,3]. These requirements are aimed to develop new high-end applications and to reduce maintenance costs.

To meet these demands, tribologists and material experts are exploring new approaches in order to enhance existing materials, such as SAE 52100 steel for bearings, studied in this work [3,4].

Failures in bodies working under rolling or sliding contact, such as bearings, are normally due to Rolling Contact Fatigue (RCF). Cyclic loads lead to crack generation and propagation, what ends in material removal through pitting/delamination of the near-surface area [4,5]. Is therefore clear that surface characteristics have a great influence in RCF resistance [6].

Different material and surface modifications have been analyzed to enhance life performance and wear resistance, as well as friction reduction, by preventing the appearance of RCF.

One of the modifications analyzed are thermochemical treatments, specifically Carbonitriding [7]. It involves the diffusion of C and N into the steel substrate, producing fine carbides and nitrides, compressive surface stress and a higher concentration of Retained Austenite than through hardening treatment. The result is higher hardness and enhanced fatigue life up to 10-15 times longer due to crack propagation reduction [4].

Other modifications include surface treatments such as Laser Peening. It is an industrial surface treatment featuring the formation of shock waves on the surface through laser pulses that produce compressive stress on it [8,9]. For that reason mechanical properties of the material are improved, namely higher hardness, wear and friction reduction under certain conditions, and improved fatigue strength by delaying crack propagation [8,10]. Besides one of the advantages of this technique is that compressive stress from Laser Peening process penetrate deeper than those from Shot Peening [10].

The other surface treatments tested are Diamond-Like Carbon (DLC) coatings. DLC are amorphous materials with different %C (variants: a-C:C) containing significant fractions of sp3 bonds. It is deposited through Physical Vapour Deposition or Plasma Assisted Chemical Vapour Deposition techniques in the form of a sputtered film composed of several layers, and improves coefficient of friction and wear rate by generating compressive stress and high microhardness [11,12]. DLC thickness, which is in the range of 0.75 – 1μm, is a critical factor because is directly related to internal residual stress within the coating. Thick DLC layers are associated to high failure rates in the first steps of RCF [5].

2. Experimental

2.1. Materials

A 100Cr6 steel bar of 50 mm in diameter was cut into slices of 5 mm each. The bar had been previously annealed following this process: 815ºC for 3 hours, 735ºC for 4 hours, 675ºC for 3 hours, slow cool down to 540ºC and finally air cooling down to room temperature.

2.2. Thermochemical treatments (TCT)

The samples were thermally/thermo-chemically treated in an Eros T4 with 2 chambers transfer oven.

The reference samples were heated at 830 ºC in a controlled atmosphere during 1 h and then were oil quenched.

For the TCT, four different temperatures between 800 and 925 ºC were used: T1, T2, T3 and T4. Other parameters set in the TCT were: C potential, NH3 intake and treatment time (see Table I). The samples were oil quenched and split in two groups. The first group was kept in that state and the

second group was subjected to sub-zero (SZ) treatment, performed with the aim of optimizing the retained austenite.

After the different thermal/thermochemical treatments, all the samples were tempered at 180 ºC during 2 h.

Table I: thermal/thermochemical treatment conditions

Sample	Temperature (ºC)	Time (h)	Atmosphere	Sub-zero
Ref	830	1	1% C	No
T1	T1	4	1,1 %C + NH_3	No
T1SZ	T1	4	1,1 %C + NH_3	-45 ºC
T2	T2	4	1,1 %C + NH_3	No
T2SZ	T2	4	1,1 %C + NH_3	-45 ºC
T3	T3	4	1,1 %C + NH_3	No
T3SZ	T3	4	1,1 %C + NH_3	-45 ºC
T4	T4	4	1,1 %C + NH_3	No

2.3. Grinding process

A Chevalier CNC flat grinding machine was used for removing the material for the in-depth wear tests. Borazon extra-fine grinding wheels and low feed rate were used with the aim of minimizing the distortion and phase transformation during this process.

Different thicknesses of material were removed from the samples: 100, 150, 200 and 250 μm. These depths were chosen taking into account the manufacturing process of the bearings and to study wear resistance behaviour of the structure in each layer.

The surface of the samples was polished using cloths and polycrystalline diamond suspension of 9, 3 and 1 μm for the final polishing stage.

2.4. Laser Shock Peening (LSP)

LSP treatments were carried out using a Thales Gaia HP Laser. The configuration used in this work produces pulses of 10 ns and 14 J, with a wavelength of 532 nm, and they are able to produce plastic deformation in the material and induce a compressive layer in the first mm of the surface. Three different configurations were used: LC1, LC2 and LC3.

2.5. Physical Vapour Deposition (PVD)

PVD coatings were deposited using a Metaplas Ionon MZR 323. The equipment has three magnetron sputtering sources, being two of them balanced and one unbalanced.

WC:C coatings of about 1 μm were deposited on the samples.

2.6. Metallography

The treated samples were cut using a Buehler Isomet 4000 precision saw and then hot-mounted in phenolic resin using a Buehler Simplimet 1000 mounting press. The cross sections were first polished using SiC polishing papers (P320, P600, P1200) and then using diamond suspensions of 9, 3 and 1 μm for a final mirror polish. In order to reveal the microstructure of the material and the effect of the TCT, the samples were chemically etched with nital 3 % and Picral.

The optical inspection was carried out using a Leica DMI 5000M metallography microscope. The microstructure, the in-surface depth of the TCT's and the grain size, following the ASTM E112, in the area affected by the TCT were analysed.

2.7. Microhardness

A micrometer Buehler Micromet 2103 was used for determining the hardness profiles of the material. Polished cross sections were tested using a Knoop indenter and a load of 50 gf. Five indents were performed on each studied depth.

2.8. X-Ray Diffraction

Quantitative XRD analysis was used to determine the fraction of retained austenite. For these experiments, samples were polished up to Ra = 10 nm. X-ray diffraction measurements were performed with a Bruker D8 Discover diffractometer equipped with a Co X-ray tube, a Lynx-eye position sensitive detector and Goebel mirror optics to obtain a parallel and monochromatic X-ray beam. A current of 30 mA and a voltage of 40 keV were used. Operational conditions were selected to obtain X-ray diffraction data of sufficiently high quality, e.g., sufficient counting statistics and narrow peak widths. XRD data were collected over a 2θ range of 35 -116º in steps of 0.01º and 0.3 s/step. To minimize the effect of texture, the volume fraction of retained austenite was calculated from the integrated intensities of (111), (200), (220), and (311) austenite peaks and the ferrite (110), (002), (112) planes. For this goal, a calibration curve plotted from the data of three standard reference materials certified by the National Bureau Standards with specific amounts of austenite (5, 15 and 30%) was used.

In-depth residual stress profiles were obtained using the same equipment. The surfaces were measured at different angles and the position of the diffraction peeks was studied, obtaining the surface stress. The measurements were repeated several times after removing layers of material by electropolishing. The results allowed the obtention of the stress profiles.

2.9. Wear tests

The wear tests were performed on a ball-on-disc CSM HT Tribometer with a WC 6 mm in diameter ball as a counterbody, 10 N of normal load and duration of 50.000-100.000 cycles at 10cm/s and track radius from 4 to 8 mm.

The obtained wear tracks were measured by means of an interferometric profilometer Wyko RST 500 TM using the Vertical Scanning Interferometry (VSI) mode. The loss volume was used to determine the wear coefficient of each sample.

3. Results & discussion

3.1. Thermochemical treatments

In the first part of the study, flat samples were treated with the aim of studying the effects of the TCT on the material and discard the treatments that are not suitable to be scaled up to real parts.

3.1.1. Microstructure. Optical microscopy was used to determine the penetration of the TCT. There are two factors affecting the measurement. Firstly, the diffusion of nitrogen and carbon into the material and secondly, the effect of sub-zero quench that changes the susceptibility of the material to be chemically etched, so the thickness of the carbonitrided layer is not clear (See figure 1). Besides, sub-zero treatment transform part of the retained austenite, white and clearly visible in the optical analysis, into martensite, that is similar to the rest of the bulk material. Due to this, the determination of the treated layer by optical methods was not accurate. Results are collected in table II.

3.1.2. Grain size. The optical analysis of the samples allowed the determination of the grain size in the carbonitrided surface. The temperature and time of the TCT are higher than in the conventional quenching process, so the grain size is expected to be bigger (figure 2).

As it can be seen in Table II there are big differences in the depth observed by optical microscopy due to the effect of sub-zero treatment.

The grain size of the material in the area close to the surface has been increased due to the thermochemical treatment (see figure 2). TCT performed at T3 and T4 were dismissed due to the excessive growth of the grain size. It must be considered that the study is focused on the development of treatments intended for bearings, where ASTM grain size number under 9 is not allowed.

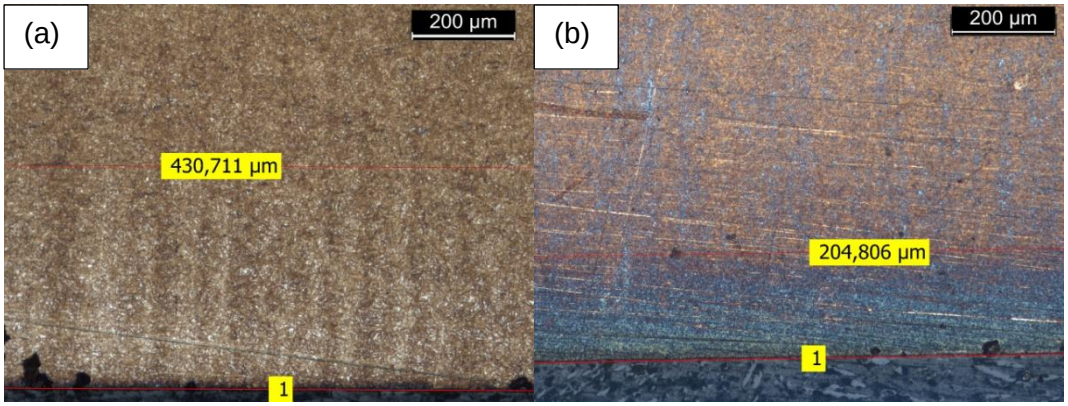

Figure 1: Optical micrographs (100X) of samples T4 (a) and T3SZ (b) after nital etching and estimated treatment depth.

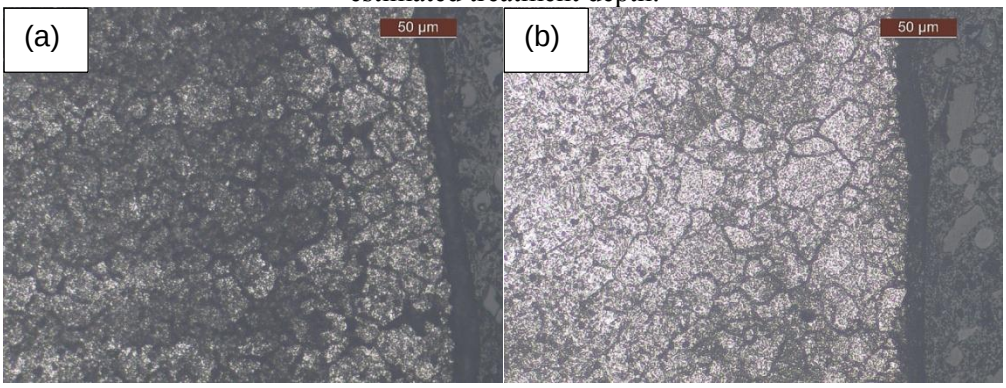

Figure 2: Optical micrographs (200 X) of samples T2 (a) and T3 (b) after Picral etching

Table II: treatment depth, grain size and retained austenite surface content of the different treatments

Sample	Treatment depth (µm)	Surface grain size ASTM	RA content (%)
Ref	---	9-10	7.5
T4	380-450	7	32.6
T3SZ	200-220	7	26.5
T3	300-400	8	29.6
T2SZ	200-220	9	29.7
T2	260-290	9	42.8
T1SZ	180-210	9	22.5
T1	200-220	9	37.0

3.1.3. XRD surface measurements. Surface XRD measurements showed an important increase in the RA content on the surfaces of the treated samples (table II). The RA content of the quenched sample is 7.5 %, but the carbonitriding process increases this amount due to the stabilization effect that nitrogen & carbon induces on austenite.

A drop in the RA due to sub-zero treatment can be observed in all samples. The RA content of sample T3 is lower than expected, which can be ascribed to problems during surface preparation of the sample. Due to this, the difference between the samples T3 and T3SZ is less than 3 %.

Surface RA content higher than 30% is not allowed due to potential distortions during operation in real pieces, so subzero treatments were preferred versus non subzero treatments.

3.2. In-depth measurements

After the first analysis, the number of suitable treatments was reduced to two: T1SZ and T2SZ.
After this first stage of the study, two sets of samples of each treatment were prepared, then grinded at different depths and polished with the aim of evaluating the in-depth properties of the treatments and obtain the information needed for scaling-up the process to be applied on real bearings.

Different characterization analyses were performed on the samples: optical microscopy, RA measurement by XRD and wear resistance measurements by means of Pin-on-disc tribology analysis. The results are gathered on table III.

The microstructure study (figure 3) shows that, at T1, the cementite content of the surface is increased, producing carbide networks. These networks could represent a problem in the manufacturing process of real parts, so must be taken into account.

In addition to this, microhardness profiles were measured in cross sections of samples T1SZ and T2SZ as it can be seen in figure 4.

The analysis of the curves in figure 4 allows determining the depth at which the wear is minimum in light of the tribology results, which is a goal in this study. This point is 200 µm for T1SZ and 150 µm for T2SZ and the obtained value can be considered similar to the wear rate of the quenched (Ref) sample. These points correspond with RA contents of 8.8 % in the treatment at T1 and 22.4 % in the one at T2. This difference could be explained for the different content in nitrides, carbides and carbonitrides, which was not analysed.

Regarding the microhardness, figures 4 and 5 show how a high RA content affects strongly the surface hardness of sample T2SZ, lowering it, especially in the first 100 µm. The lower content of RA observed in sample T1SZ, combined with the presence of cementite, allow the increase of the hardness with respect to the Ref sample. The hardness has been increased in the first 400-500 µm of the material, to decrease later to bulk values.

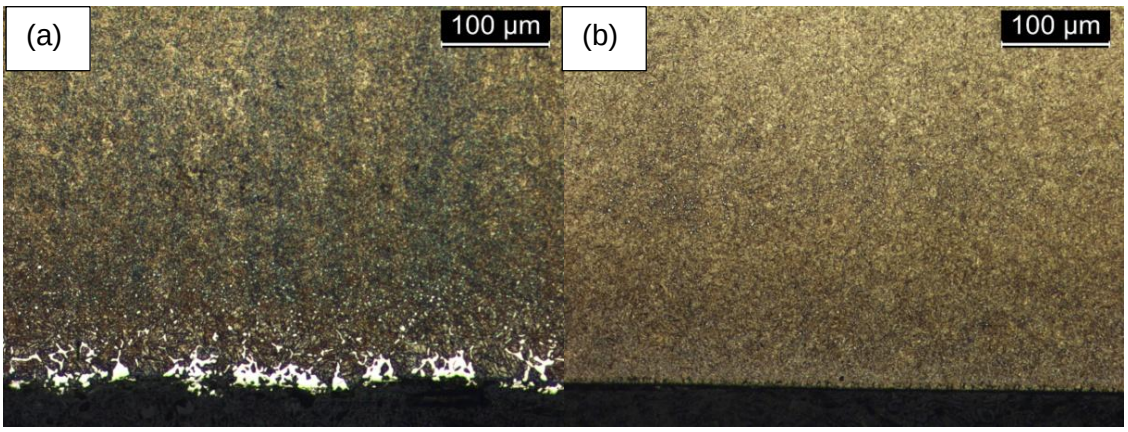

Figure 3: Optical micrographs (200 X) of samples T1SZ (a) and T2SZ (b) after nital etching. Cementite segregates in grain boundary in the first 100 µm of the samples T1SZ

After this stage, T1SZ was selected to be combined with LSP and PVD treatments. Is expected that treatment T1SZ will be able to improve the fatigue resistance of the material without losing surface hardness and wear resistance.

Table III: samples obtained after grinding process and measured properties

Sample	Removed	RA (%)	K wear * E16

	material (µm)		(m3/Nm)
Ref	0	7.5	5.2 ± 3.0
T1SZ	0	22.5	23.2 ± 4.6
T1SZ100	100	15.2	19.9 ± 4.4
T1SZ150	150	13.6	17.4 ± 5.5
T1SZ200	200	8.8	10.1 ± 5.1
T1SZ250	250	8.2	12.8 ± 5.9
T2SZ	0	29.7	26.1 ± 6.9
T2SZ100	100	27.4	17.4 ± 5.0
T2SZ150	150	22.4	9.8 ± 5.6
T2SZ200	200	20.3	13.7 ± 8.8
T2SZ250	250	19.3	18.0 ± 9.6

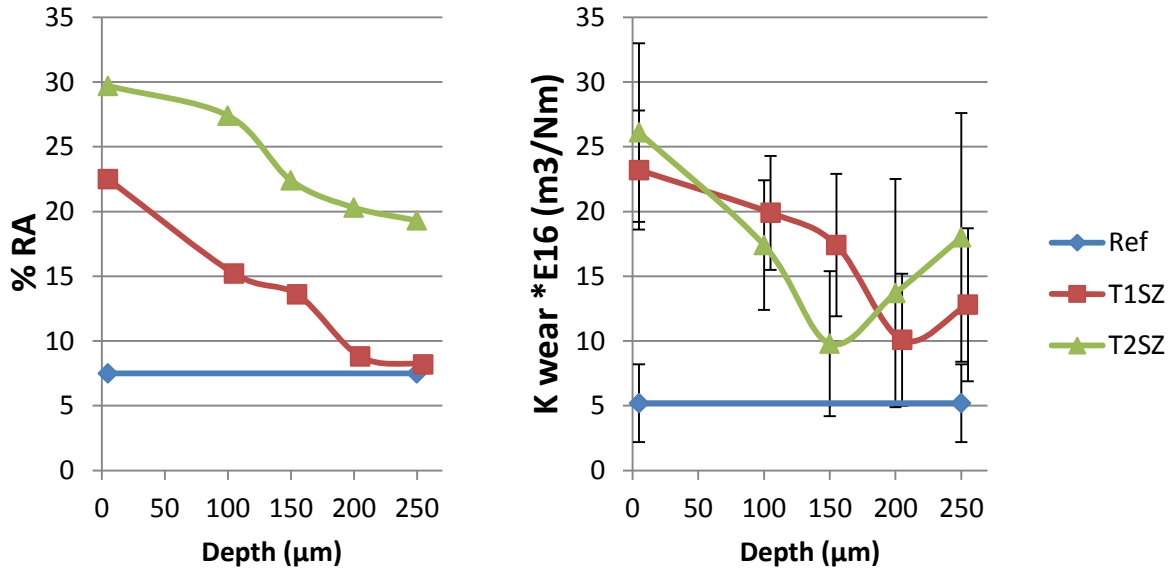

Figure 4: Graphs of RA content and Kwear profiles of Ref, T1SZ and T2SZ

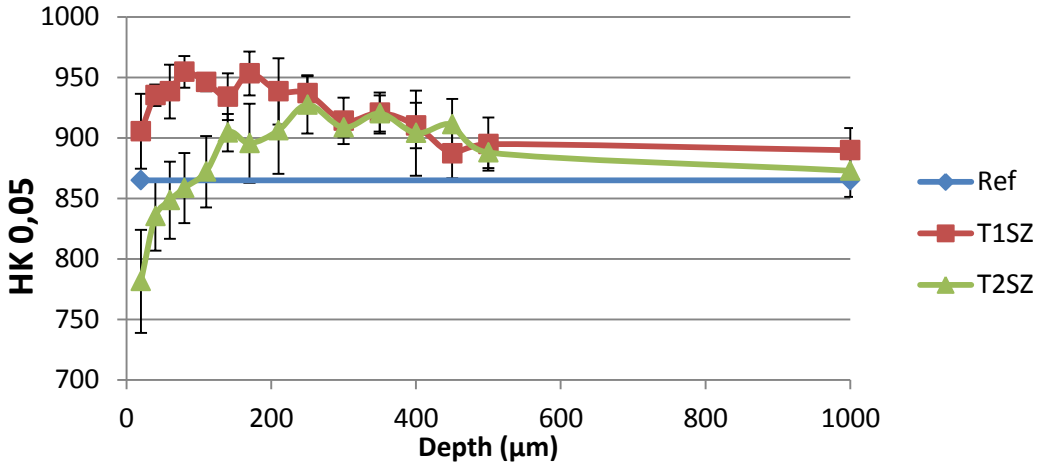

Figure 5: Microhardness profiles of samples Ref, T1SZ and T2SZ

3.3. Laser Shock Peening (LSP)

Stress profiles were studied with the aim of determining the effect of LSP on the 100Cr6 treated samples. Figure 6 shows the profiles obtained after the application of 3 different LSP treatments. All of them induce a compressive layer of about 400 MPa at 50 µm that decreases to 200 MPa at 600 µm of depth.

LSP1 was the best of the treatments taking into account the profile produced and the time consumption.

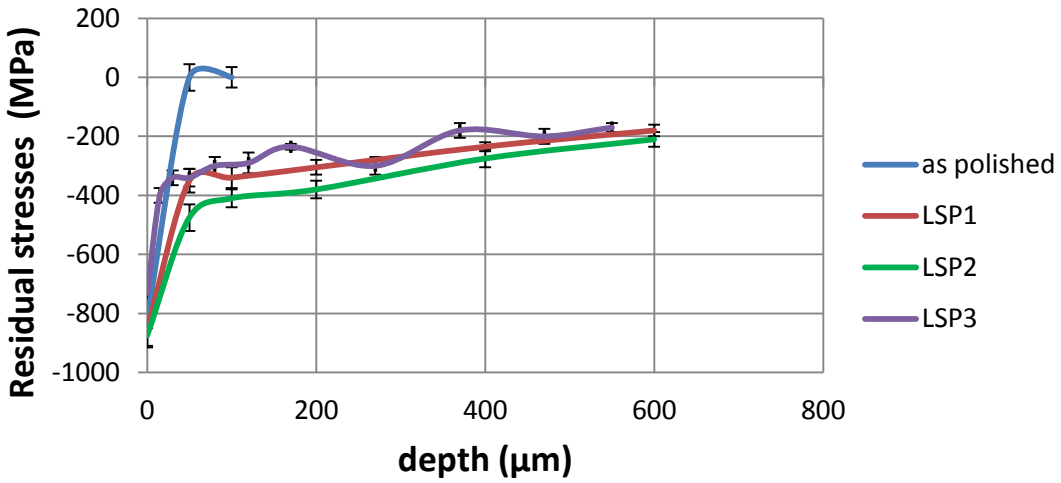

Figure 6: Stress profiles produced by LSP treatments

3.4. Duplex treatments

With the aim of characterizing the duplex treatments, samples with T1SZ treatment were grinded, 200 µm of material were then removed, and finally the samples were treated either by LSP (Treatment LSP1) or by PVD (WC:C coating).

Wear resistance of the duplex treated samples were tested and the results compared with the reference and the single treated sample.

As can be seen in figure 7, PVD coating improves the wear resistance of the sample with respect to the reference, so it is a suitable treatment for the required application. The improvement on the wear resistance of 100Cr6 provided by LSP treatment is not clear and the obtained measured wear rate is higher than the reference one.

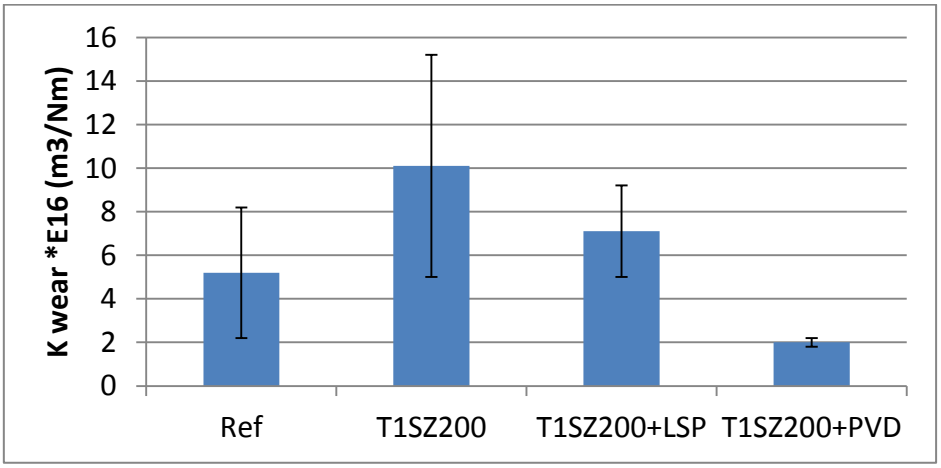

Figure 7: Kwear of the different duplex treatments

Table IV: Kwear of the duplex treated samples

Sample	Removed material (μm)	K wear * E16 (m^3/Nm)
Ref	0	5.2 ± 3.0
T1SZ200	0	10.1 ± 5.1
T1SZ200+LSP	200	7,1 ± 2.1
T1SZ200+PVD	200	2.0 ± 0.2

4. Conclusions

The application of TCT on 100Cr6 intended for improving the performance of bearings must be controlled due to several characteristics of the treatment.

The grain size of the material grows in contrast to the quenched samples due to the temperature of the process, and the longest times at these temperatures (4 h Vs. 1h). Samples treated at temperatures over T2 have suffered an unacceptable growth of its grain size, from 9-10 to 7-8 in ASTM Grain Number.

The diffusion of C and N in the material is hardly observable by optical microscopy due to changes in the chemical etching susceptibility of the material.

The diffusion on N into the steel matrix stabilizes the austenite, increasing the RA content from 7.5 %, present in the quenched sample, to a maximum of 42.8 %, measured in the surface of the sample T2.

At T1 the low diffusion of the C produces enrichment in the cementite content of the surface, generating harmful carbides networks which can affect the machinability of the material. The depth of the affected layer is less than 100 μm.

The in-depth wear resistance of the material is affected by the RA content and the presence of particles of carbonitrides, nitrides and carbides, producing profiles that present a minimum in the wear rate curve. In the studied treatments this minimum was found at 200 μm in the sample T1SZ and at 150 μm in the case of sample T2Z. In both cases this parameter is slightly higher than the one of the quenched sample.

Hardness profiles show that the treatment can produce an increase in the hardness of the first 300-400 μm for the sample T1SZ. The low RA content of this treatment and the presence of cementite in the surface are responsible of this result.

However, the sample T2SZ is affected by the high RA content, so the hardness is lower than the reference in the first 200 μm and slightly higher between 200 and 400 μm.

The combination of TCT and LSP does not produce a clear improvement in the wear resistance of the material. On the contrary, TCT + PVD coating enhance the properties of the surface, reducing up to 60 % the wear rate.

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