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PHASE CHARACTERIZATION AND TRIBOLOGICAL BEHAVIOUR OF NITRIDED STEELS AISI H13, AISI M2 AND AISI D2[1]

Saulo D. Jacobsen[2]
Eduardo Blando[3]
Ruth Hinrichs[4]
Marcos Antonio Zen Vasconcellos[5]

ABSTRACT

Plasma nitriding has been used to improve hardness of different tool steels, like AISI H13, AISI D2, and AISI M2. Nitriding also enhances tribological properties and increases tool life, reducing overall costs due to reduction of replacement time. The characterization of the changes induced in the uppermost layers of the nitrided steels is essential to understand tribological and elasto-plastic properties. In this work AISI H13, o AISI D2 e o AISI M2 steel samples were nitrided simultaneously in a homogeneous plasma configuration, at 400ºC and a gas composition of 80% N_2 and 20% H_2. Samples were tested on a pin on disc tribometer, before and after nitriding, to obtain coefficient of friction (COF) and wear parameters. Glancing incidence x-ray diffraction (GIXRD), scanning electron microscopy (SEM), optical microscopy, instrumented hardness tests (IHT), and profilometry were used to detect alterations induced by the nitriding to the tribological and morphological properties. GIXRD with different incidence angles revealed the formation of several iron nitrides in different depths on the sample surfaces. The phase composition was correlated to the tribological properties obtained with the pin-on-disc test. SEM and optical analysis revealed morphological changes due to nitriding procedures and the frictional load in the tribometer.
Keywords: AISI H13; AISI D2; AISI M2; Plasma nitriding; Pin on disc; Glow discharge.

CARACTERIZAÇÃO DE FASES E DAS PROPRIEDADES TRIBOLÓGICAS DOS AÇOS AISI H13, AISI M2 AND AISI D2 NITRETADOS

RESUMO

Nitretação a plasma tem sido utilizada para aumentar a dureza de diferentes aços ferramenta, como AISI H13, AISI D2 e AISI M2. Nitretação também melhora as propriedades tribológicas e aumenta a vida útil das ferramentas, reduzindo custos operacionais devidos a substituição das mesmas. A caracterização das mudanças induzidas nas camadas superficiais dos aços nitretados é essencial para a compreensão das propriedades tribológicas e elastoplásticas. Neste trabalho os aços supracitados foram nitretados simultaneamente em um plasma homogêneo a 400ºC com atmosfera composta de 80% N_2 e 20% H_2. As amostras foram ensaiadas em um tribômetro do tipo pino sobre disco antes e depois da nitretação, afim de obter os coeficientes de atrito e os parâmetros de desgaste. As amostras foram caracterizadas antes e depois da nitretação e depois dos testes tribológicos. Difração de Raios X em Ângulo Rasante (GIXRD), Microscopia Eletrônica de Varredura (MEV), microscopia óptica, ensaios instrumentados de dureza (IHT) e perfilometria foram utilizados para detectar alterações induzidas pela nitretação nas propriedades tribológicas e morfológicas. Difratogramas de GIXRD em diferente ângulos de incidência revelaram a formação de vários nitretos de ferro em diferentes profundidades. A distribuição das fases foi correlacionada com as propriedades tribológicas obtidas nos testes “pino sobre disco”. As imagens de MEV mostraram as mudanças de morfologia devidas ao procedimento de nitretação e dos ensaios de atrito.
Palavras-chave: Aços nitretados; Nitretação a plasma; Pino sobre disco; Descarga luminosa.

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[2] *Laboratório de Microanálise, IF-UFRG / Doctoral student, PGCiMat UFRGS, c.p. 15051, 91501-970 Porto Alegre, RS, Brazil*
[3] *PhD,'post-doc, Physics Department, UFRGS, Porto Alegre, Brazil*
[4] *PhD, Associate Professor, Geology Department, UFRGS / Laboratório de Microanálise, IF-UFRGS, Porto Alegre, Brazil,*
[5] PhD, Associate Professor, Physics Department, UFRGS / Laboratório de Microanálise, IF-UFRGS, Porto Alegre, Brazil,

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1 INTRODUCTION

The steels AISI H13, AISI D2 and AISI M2 are employed in industry for different purposes due to their specific mechanical properties. AISI H13 is employed in high temperature applications like die casting and extrusion dies for production of standard aluminum profiles, as well as in molds for high temperature manufacturing of industrial components. AISI D2 steels are used in cutting, pulling, gear, pressurized air equipment, and machine knives. AISI M2 steels are commonly used in punch and die tools for cold forming operations.
Each of these applications would increase hardness and corrosion resistance, with the additional benefit of improved tribological properties, resulting in longer tool life under high wear due to a lower coefficient of friction (COF) and reduced wear.
Plasma nitriding on these steels can increase wear resistance and decrease the friction coefficient, providing better physical and mechanical properties.[1-5] It can be performed at relatively low temperatures, preserving the core properties obtained with a previous heat treatment. Passivating layers can be removed from the steel surface with a plasma etching performed in the same reactor, improving the nitrogen diffusion and nitrided layer thickness.
The present work investigates phase changes induced by specific nitriding conditions on the above mentioned steels and reveals correlations with mechanical properties of the surface layers.

2 MATERIALS AND METHODS

Samples were cut from AISI H13, AISI D2 and AISI M2 steel rods, and machined into discs with 18 mm diameter and 5 mm thickness. The samples were hardened following heat treatments summarized in Table 1. After surface grinding, the samples were mirror polished up to 1 μm diamond paste, and cleaned using ether and acetone.

Table 1: Heat treatment parameters

Steel	Tempering (Austenitizing)			Heat treatment		Hardness [HRC]
	Temperature [ºC]	Time [h]	Quenching	Temperature [ºC]	Cooling	
H13	1020	1.0	Oil	600	Air	48
D2	1020	1.0	Oil	300 / 540	Air	55
M2	1190	2.0	Oil	540 / 540 / 550	Air	65

Nitriding was carried out in a laboratory plasma chamber using a d.c. power supply (Figure 1a). Three fitting slots were cut into the sample holder (Figure 1b) with the purpose to nitride three samples simultaneously and to decrease the edge effect on the sample border, where the plasma usually is more intense. Before nitriding, the samples were submitted to a cathodic cleaning (etching) with argon at 350°C for 30 minutes at 15 Torr. Afterwards they were nitrided at 400°C, for 5 h, using a gas composition of 80 vol% N_2 and 20 vol% H_2 at 6.5 Torr.

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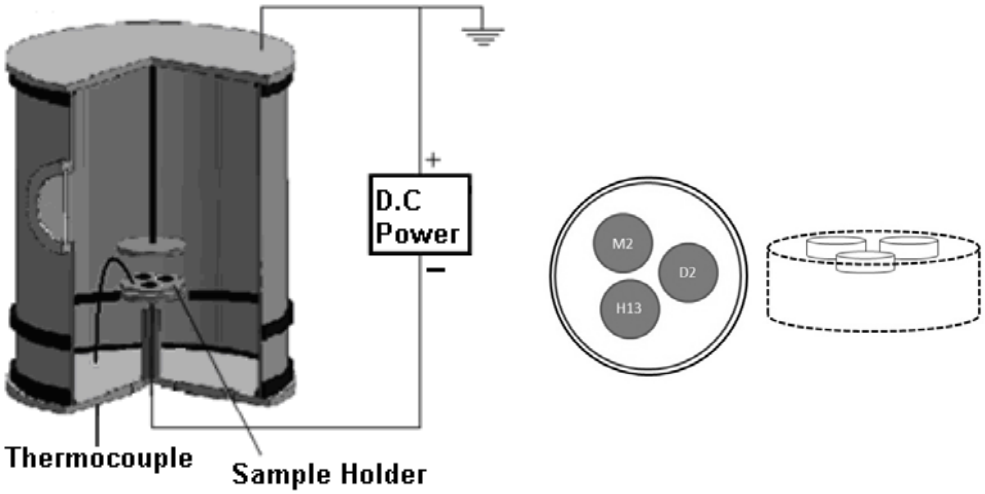

a) b)

Figure 1. Schematic diagram of a) the nitriding chamber[6] and b) the sample holder used to nitride three different steel samples simultaneously.

To evaluate the sample topography electron micrographs were obtained in secondary electron mode (SEI) or backscattered electron mode (BEI) using the scanning electron microscope (SEM) of a JEOL Dual Beam JIB4500. Characteristic x-ray maps were collected with a silicon drifted detector from Thermo Noran.
Surface phases were characterized with glancing incidence x-ray diffraction (GIXRD) in a Shimadzu XRD6000 diffractometer using Cu-Kα radiation. Diffraction patterns with incidence angles 0.5°, 1°, 2°, 4°, 6°, and 8° allowed identifying the phases in different depths of the nitrided layers. With these incidence angles 95% of the total diffracted intensity came from different depths, calculated according to Cullity[7] and shown in Table 2.

Table 2: Diffraction depth

Incidence angle (º)	0.5	1	2	4	6	8
Depth (μm)	0.15	0.30	0.60	1.13	1.64	2.1

To determine preliminary tribological properties of untreated and nitrided sample surfaces, a pin on disc tribometer (PLINT TE 79) was used. Each sample was tested for 30 minutes at 400 RPM on a radius of 5 mm, using a 6 mm alumina ball as a pin, and applying a force of 20 N. The wear was estimated with radial profiles across the wear scar obtained with a profilometer (Ambios Technology XPII). Cross sections of the samples were produced, embedded in resin and polished up to 1 μm diamond paste. Instrumented hardness tests (IHT) were performed on the polished cross sectioned samples using a DUH Shimadzu W-211 equipment, with the application of dynamic load-unload cycles. Depth profile measurements were carried out with a peak load of 100 mN in each cycle, using a Berkovich indenter.[8] Five measurements in each depth (10 μm apart) were considered to obtain mean and standard deviation. Optical micrographs were acquired in a Zeiss microscope using a CCD camera (Delta pix) after 2 seconds of nital etching.

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3 RESULTS AND DISCUSSION

The pristine steel samples were analyzed in a SEM as shown in Figure 2. The samples were observed with adequate magnification to visualize the major inclusions. The BEI micrographs show the presence of inclusions and metal carbides, however do not allow differentiating among them. The corresponding characteristic x-ray maps identified the silicon oxide inclusions (silicon is shown in cyan), the vanadium (green), chromium (magenta), tungsten (red), and molybdenum (yellow) carbides. In the D2 composite element map V and Cr are almost perfectly superimposed on the large inclusions and additional V (carbide) is dispersed in very small particles. In M2 the composite element map shows that Mo (yellow) superimposed to W (red) results in a salmon color and do not overlap with V (in the BEI micrograph, Mo and W corresponds to the white grains, while V corresponds to the black grains).

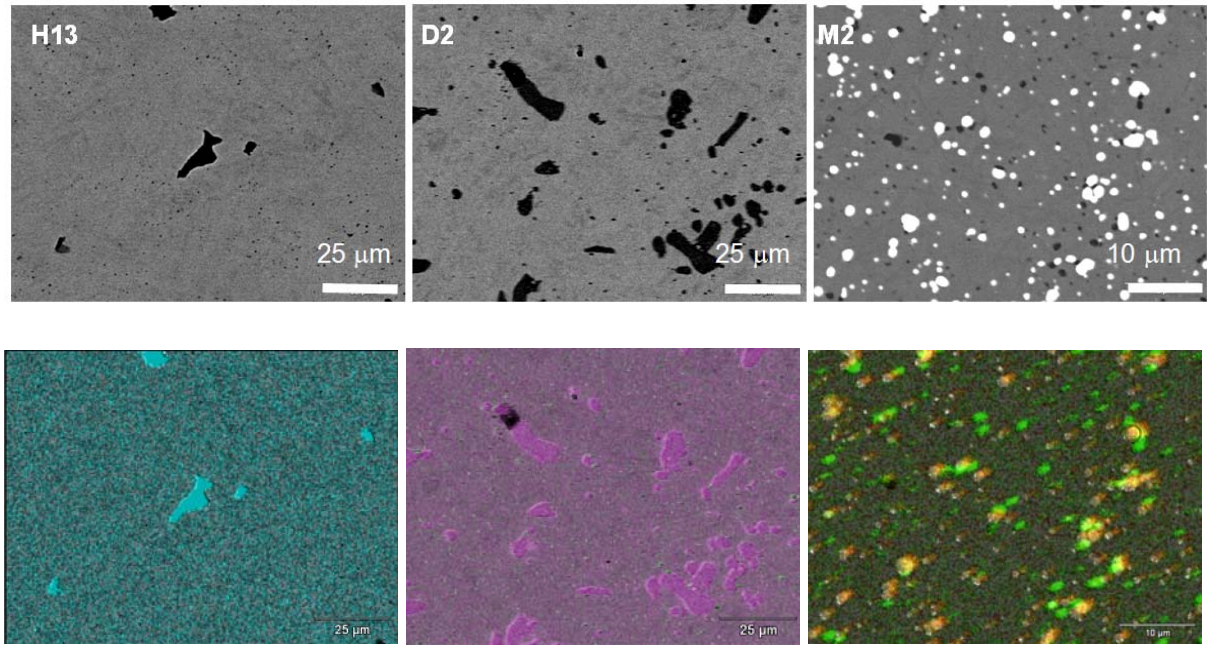

Figure 2. (a) BEI micrographs from AISI H13, AISI D2 and AISI M2 steels. (b) Characteristic x-ray element maps identifying some of the elements that form the inclusions (Si cyan) and carbides (V green, Cr magenta, Mo yellow, W red) on the respective images above.

The samples were analyzed with 8º GIXRD prior to nitriding to establish the pristine phase composition. The diffraction patterns revealed only α-iron in the AISI H13 and AISI D2, while M2 showed the presence of M_6C and VC [9] besides the iron peaks (Figure 3, black curves). After the nitriding procedure at 400 ºC novel phases covered the surface in a compound layer thick enough to obstruct the iron diffraction peaks, including the expanded austenite phases expected from the nitriding experiment. The newly formed top layer was mainly composed of stoichiometric iron nitrides (Fe_4N and FeN), chromium nitride, molybdenum nitride and tungsten nitrides (Figure 3, red curves).

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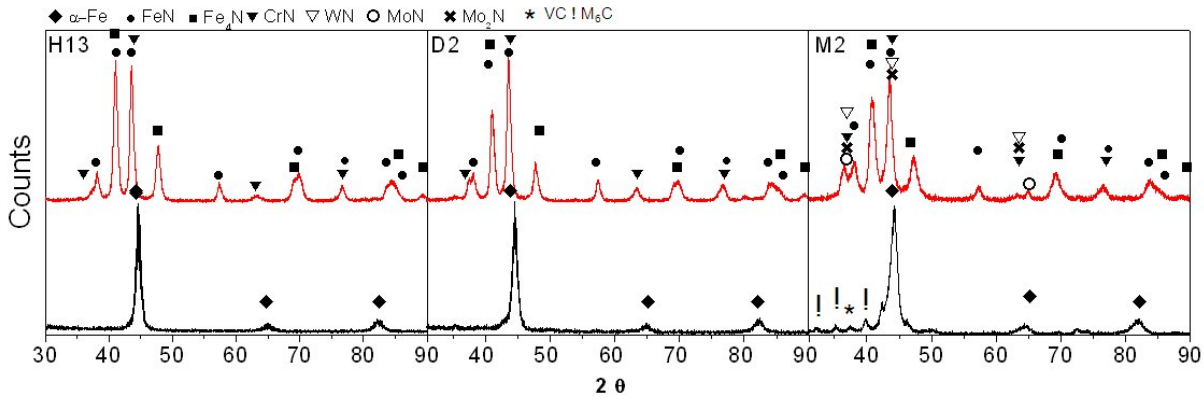

Figure 3. GIXRD with 8º incidence of AISI H13, AISI D2 and AISI M2 steels, before (black) and after nitriding (red).

On Figure 4 patterns taken with 0.5º, 1º, 2º, 4º 6º and 8º of only one nitrided steel (AISI H13) were compared. Observing the patterns obtained with different incidence angles on the same sample, it is possible to establish a depth profile of the phase distribution. If one could assume that the phase abundance was constant, the peak intensity should grow continuously due to increase of the sampled volume. When this does not happen, the depth distribution of this phase is not homogeneous, but the GIXRD has surpassed this phase's layer thickness and is probing the deeper layers simultaneously with the top one.

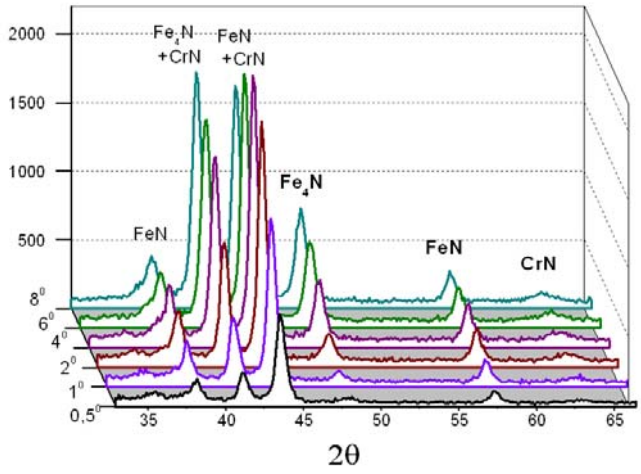

Figure 4. GIXRD with different incidence angles of AISI H13 after nitriding at 400ºC.

The most intense peaks of the diffractograms show significant overlap. Therefore peaks with less intensity but without overlap were used to determine peak intensity evolution due to deeper probing, intending to establish a qualitative depth profile of each phase. The curves in Figure 5 show the different evolution of Fe_4N, FeN and CrN in the three nitrided steels. In all samples the Fe_4N peaks grew monotonically in the whole measured range, revealing a homogeneously distributed phase. In all samples the FeN peaks, richer in nitrogen, are abundant at the surface, but decrease after the 4º incidence. This reveals that this phase was reduced in depths greater than 1.13 μm. The observed presence of FeN nearer to the surface, while Fe_4N occurred also in deeper regions was considered consistent with a N diffusion profile in the iron matrix. CrN seems to enrich at the surface, but less evidently. In AISI D2,

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with much higher chromium content, the increase of CrN is monotonic, showing that the chromium is nitrided in the whole probed depth (2.1 μm).

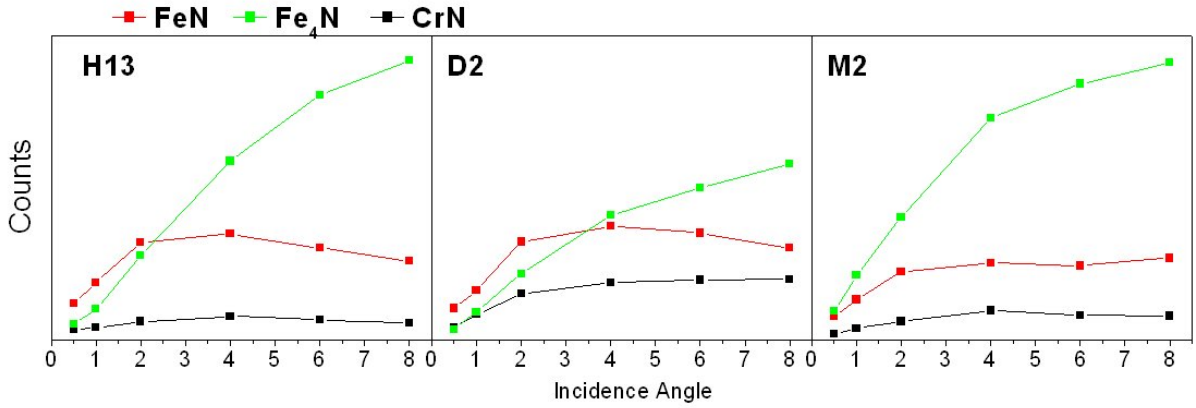

Figure 5. Peak height evolution of Fe_4N, FeN, and CrN with incidence angle in the GIXRD of AISI H13, AISI D2 and AISI M2 (same ordinate scale).

Optical micrographs (figure 6 a) show the thickness of the altered layers on top of the nitrided steels in darker shades of grey. On H13 a light grey surface compound layer can be seen. On D2 and M2 this compound layer cannot be identified with visual means.

Hardness measurements of the cross sectioned samples (Figure 6 b) show a hardness increase next to the surface. The AISI H13 steel shows a surface layer of around 50 μm with a moderate increase, followed by an additional 50 μm layer with a further increase up to 1150 HBN. Afterwards the hardness value falls to bulk values, established by the previous heat treatment. The other steels show increased hardness on a 70 μm upper layer, followed by the bulk value, also established by previous treatments. The uppermost compound layer was too thin (around 5 μm) to allow hardness measurements with our equipment, only the diffusion layers were probed.

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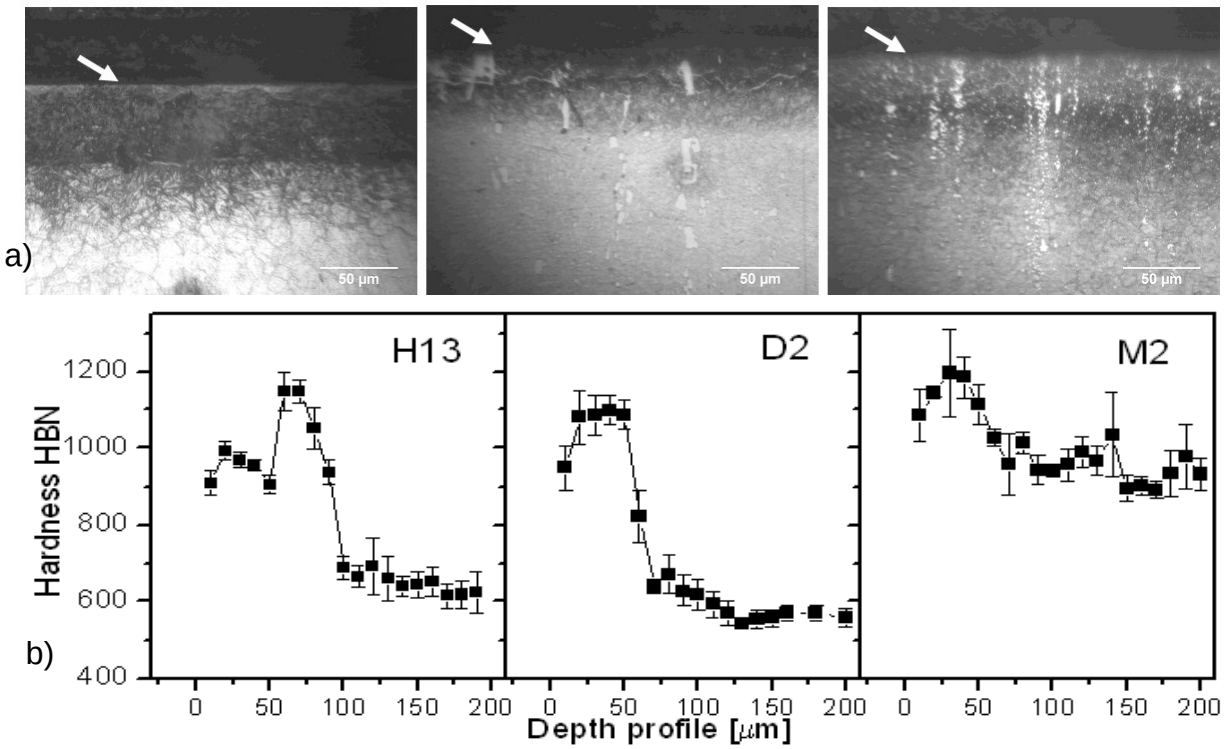

Figure 6. a) Cross section optical micrographs (surfaces indicated with white arrows) and b) hardness depth profiles of the nitrided AISI H13, AISI D2, and AISI M2 steels.

The coefficients of friction (COFs) obtained during the pin on disc experiment are presented on figure 7 for samples before (grey scale) and after nitriding (color coded). Before nitriding the COF stabilized after approximately 100 seconds on all samples and showed a mean of 0.66 on H13, 0.78 on D2 and 0.67 on M2.
After nitriding H13 showed almost no change except during the first few seconds when the initial high value did not appear. On D2 and M2 the first stages were markedly different than the following ones. The COF started around 0.5 and was less erratic. The trend of the COF was to rise in the first and second stages, stabilizing afterwards at a lower value than on the non-nitride samples.

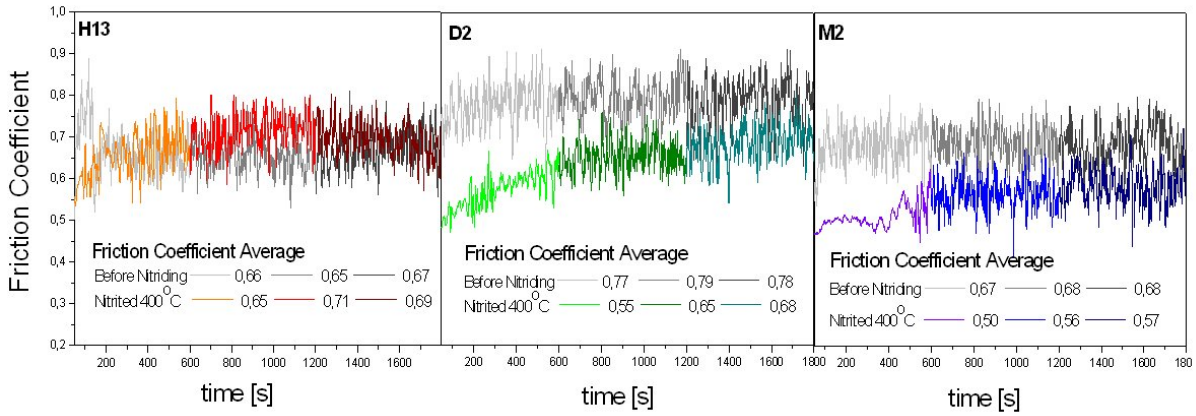

Figure 7. COF versus time (in seconds) before (grey scale coded) and after nitriding (color coded) of the steel samples. Mean values of each stage are inset.

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On Figure 8 the wear scars of the pristine and nitrided samples are shown. Only one set of experiments has been performed so far. It can be noted that the wear scares on the pristine steels all show dug out material next to their borders. The depth of the scars is around 3 μm, less on the M2 steel that was heat treated to higher hardness.
After nitriding AISI D2 showed less wear, while AISI H13 and AISI M2 performed worse. It can be seen, that until the end of this wear test the uppermost compound layer had worn off completely, while the nitrided layer, that is more than 50 μm thick lasts to the end of the experiment.

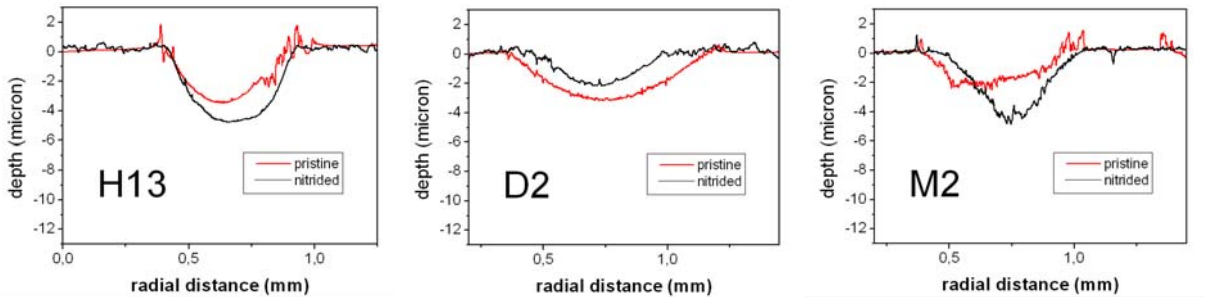

Figure 8. Wear profiles of the steels, before and after nitriding

Comparing the COF graphs with the wear profiles of figure 8, it seems reasonable to affirm that in the first third of the experiment the uppermost compound (white) layer wore away. The nitrided layer below, in this case, seems not to affect the wear significantly

4 CONCLUSIONS

Fe_4N, FeN and CrN were the most important phases generated on the nitrided surfaces of the plasma treated steels.
Fe_4N had a similar depth distribution in AISI H13 and AISI M2, but its presence was much less pronounced in AISI D2, which, due to its high Cr content, has less iron available to form the iron nitride phases. The depth distribution of FeN was very similar in the three steels. CrN in AISI H13 showed a slight near surface augmentation and a decrease after ~1 μm depth. CrN in AISI M2 was present in all probed depths. CrN increased throughout the sampling depths, showing a homogeneous distribution in the probed volume.
The COF remained almost stable for AISI H13, and decreased for AISI D2 and AISI M2 after plasma nitriding, showing a more stable behavior while the compound layer was intact. Afterwards COF increased, and became more erratic, but still remained lower than the COF of the untreated samples. Considering the improvement in wear and COF, AISI D2 seems to benefit from plasma nitriding. AISI M2 has only slight improvement in COF.
The wear tests show no significant alterations on the wear of the nitrided steels
This study is to be extended to a broader range of plasma parameters, in order to establish further correlations between nitride phases on steels and their tribo-mechanical behavior.

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