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EFFECT OF PLASMA NITRIDING ON THE WEAR AND CORROSION PROPERTIES OF HASTELLOY CW2M ALLOY

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ABSTRACT

Hastelloy C alloys are widely used in chemical and nuclear industries in corrosive environments. The predominant alloying elements of these nickel based alloys are typically chromium and molybdenum, although other elements are added. Plasma nitriding is an efficient surface treatment to increase wear resistance. The objective of this work was to evaluate the influence of nitriding treatment on the wear and corrosion properties of the Hastelloy CW2M super-alloy. Hastelloy CW2M was plasma nitrided using the direct current method with the following conditions: a gas mixture of 80 vol. %H_2 and 20 vol. %N_2, a pressure of 500Pa, temperature of 450 and 500°C during 5h. As cast and plasma treated samples were analyzed using scanning electron microscopy, wear and corrosion tests. EDS line scan performed on the samples cross section indicates that Cr and Mo content are the largest on the layer, with decreasing amounts of Ni and with stable amounts of Fe. Plasma nitriding of Hastelloy CW2M produced a homogeneous layer with high hardness. X-ray diffraction revealed a γ (fcc) phase for the un-nitrided CW2M. The nitriding performed at 450°C yielded chromium and molybdenum nitrides peaks and an expanded phase. At 500°C an increase on the chromium and molybdenum nitrides peaks was observed. The wear of samples nitrided at 450 and 500°C were almost 10 times lower than the substrate's wear, which indicates a great improvement on tribological properties. The corrosion parameters showed that although the corrosion potential goes toward positive potentials, increasing nitriding temperature, the corrosion current moves in the opposite direction. Nitriding at 450°C promoted a good corrosion protection with a low open circuit potential value and low corrosion potential.

Keywords: Hatelloy C; Plasma nitriding; Wear; Corrosion.

1 INTRODUCTION

Hastelloy (registered trademark of Haynes International) is applied as the prefix name of a range of different highly corrosion resistant Nickel base alloys, also called super-alloys. The predominant alloying elements are molybdenum, chromium, cobalt, iron and copper. There are several Hastelloy families for specific applications. The C family Hastelloy is widely used in chemical and nuclear industries because its high corrosion resistance and high strength at elevated temperature [1].

Hastelloy C-4 (or CW2M) alloy is a nickel-chromium-molybdenum alloy with outstanding high-temperature stability, high ductility and corrosion resistance, even after longtime aging at 649 to 1038°C. The alloy also has excellent resistance to stress-corrosion cracking and to oxidizing atmospheres up to 1038°C [2]. However its wear properties are low due to its γ (fcc) phase.

Plasma nitriding treatment is an attractive process allowing improved wear resistance without affecting the corrosion properties [3, 4]. Williamson and co-workers studied the insertion of nitrogen in a Hastelloy-X alloy obtaining a nitrogen rich thin layer [5]. The formation of expanded phases (γ_N) after nitrogen insertion is a common behavior of austenitic steels as well for a nickel fcc alloys [6, 7]. The expanded austenite is a metastable phase with a super-saturation of nitrogen which remains in solid solution [8-10]. This layer possesses a good combination of mechanical, tribological and corrosion properties [10]. Ion nitriding of some austenitic alloys at lower temperatures usually promotes the expanded austenite phase and means lower cost, less distortion and less surface roughening [11].

The objective of this work was to evaluate the possibility of obtaining expanded phases after plasma nitriding of a Hastelloy C-4 and study the wear and corrosion properties of the produced layers.

2 MATERIALS AND METHODS

The CW2M super-alloy melt was performed in an induction furnace and its chemical composition is shown in Table 1. Plasma nitriding was performed in the as cast condition. Samples of CW2M were cut and prepared, according to conventional metallographic techniques and then plasma nitrided. Firstly the samples were cleaned by argon sputtering (on work pressure and temperature of 50°C lesser than the nitriding temperature, for 30min), inside the plasma chamber. The plasma treatment was carried out using the direct current method with the following conditions: a gas mixture of 80 vol. % H_2 and 20 vol. % N_2, a pressure of 500Pa, temperature of 450 and 500°C, during 5h.

Vickers micro-hardness measures were performed on a digital Buehler equipment with load of 50gf and application time of 10s. Electron microscopy was performed on the samples cross sections using a Scanning Electron Microscope (SEM), LEO 440 model with a tungsten filament, coupled with an Energy Dispersive Spectroscopy (EDS) detector.

The X-ray diffraction patterns were obtained on the surface of the samples using a Rigaku Gergerflex equipment with scanning angles ranging from 10 to 100°. The analyses were performed using copper Kα radiation and continuous scanning with a speed of 2°/min.

The wear tests were performed on a micro-wear machine with fixed ball configuration without the use of abrasive at a temperature of about 25°C. As a counter material it was used an AISI 52100 sphere. The diameter of the ball was 25.4mm, with rotational speed of 350rpm and load of 2.45N. Consecutive wear scars with test times of 5, 10, 15 and 20min were produced to obtain the volume loss curve. The removed volumes (V) of each wear crater were calculated according to the literature [12, 13].

The electrochemical cell used to obtain the potentiodynamic polarization curves employs a saturated calomel (SCE) reference electrode and a platinum auxiliary electrode. The electrolyte employed was natural sea water (pH 8.0) collected from a Brazilian beach. The potential and current during the tests were monitored by an Autolab model VGSTAT-302 potentiostate. The polarization curves of the samples were obtained using a scanning speed of 1mV/s from -0.8 to 1.125V. Also, the open circuit potential (OCP) was obtained, before the polarization curves, after the stabilization of the potential.

3 RESULTS AND DISCUSSION

3.1. Microstructural Characterization

The cross section of the sample plasma nitrided at 500°C is shown in Figure 1. The nitrided surface layer presents three distinct regions: a top gray layer (1) a light gray sub-layer (2) and the substrate itself (3). Both nitriding temperatures produced surface layers with the same morphology and two distinct regions, although with different thicknesses, due to the increase on nitrogen diffusivity at higher temperatures.

The two-layer morphology of the nitrided CW2M layer is also found in plasma nitrided AISI 316 steel, where at around 500°C the expanded austenite is replaced by a chromium nitrides layer, leading to a double layer morphology [7, 9]. The nitrogen expanded layer is produced under special conditions where the interstitial diffusion is enhanced creating a nitrogen supersatured zone free of compounds. Furthermore, increasing alloying elements diffusion (e.g. time and/or temperature) nitride precipitation can arise. In our case, the sub-layer (2) on Fig. 1 is probably a nitrogen expanded phase and the top layer (1) is composed by chromium and other nitrides.

On Figure 2 an EDS line scan profile, on the sample nitrided at 500°C, is shown. The profile presents qualitatively the concentration of chromium (Cr), nickel (Ni), molybdenum (Mo) and iron (Fe), from inside of the top nitrided layer (labeled as 1 in Fig. 1) to the substrate (labeled as 3 on Fig. 1), with a total scan length of 9.7µm. The EDS analysis clearly indicates that the top gray layer exhibits a larger Cr and Mo amount. The Ni increases from the top layer to the substrate and the Fe quantity remains constant. The concentration of the analyzed elements on the sub-layer (2) remains constant through the depth as for the substrate.

Figure 3 presents the X-ray diffraction patterns of the nitrided (at 450 and 500°C) and un-nitrided CW2M samples. On the un-nitrided CW2M substrate, peaks with high intensities and only related to the γ phase are found. The CW2M Hastelloy is a nickel based alloy with chromium and molybdenum in solid solution, and the diffraction pattern confirms the fcc structure type.

The samples plasma nitrided at 450 and 500°C showed a considerable peak broadening and a decrease on diffraction peaks intensities. The reflection (200) of the substrate is observed on both nitrided diffraction patterns although with lower intensities, indicating that increasing nitriding temperature (i.e. layer thickness) the reflections are mostly from the layers.

Sample treated at 450°C yielded the appearance of a peak shifted to the left of the γ (200) at 49.28 degrees, which is an indication of the formation of an expanded phase. However this shifted peak also indicates the presence of Cr_2N. Furthermore other compounds are possibly formed, such as CrN, Mo_2N and MoN, which are related to the reflection at 43.5 degrees.

Further increase in nitriding temperature (500°C) almost extinguish the diffraction peaks related to the substrate and more CrN, Cr_2N and Mo_2N peaks are detected, clearly indicating the precipitation of these nitrides.

Although the CW2M alloy is a nickel based alloy, nickel nitrides were not observed on X-ray patterns. Also, the EDS line scan on Fig. 2 indicates that on the region where the nitrides precipitation takes place (top gray layer on Fig. 1) nickel atoms are pushed inward by nitrogen insertion. This fact is explained by the low affinity between nitrogen and nickel [7].

The diffraction patterns indicate that at 450°C the nitrides precipitation is smaller than at 500°C; and possibly the formation of nitrogen expanded phase, which is also observed on electron microscopy (Fig. 1). At 500°C the total layer thickness increases (Tab. 2) diminishing the substrate diffraction and the nitride precipitation takes place. It is difficult to address, based on X-ray diffraction patterns only, what kind of nitrides are formed because many of the reflections overlap.

In Table 2 are shown the surface hardness and layer thickness of the plasma nitrided samples. Plasma nitriding at 500°C produced a total layer thicker than that obtained at 450°C; however the sub-layer is thicker at 450°C in which the chromium nitrides precipitation is smaller. The surface micro-hardness of the nitrided samples increased as temperature was increased.

3.2. Wear Characterization

The worn volume curves of the substrate itself and plasma nitrided CW2M samples are shown in Figure 4. In Fig 4a the volume loss of plasma nitrided samples are compared with the substrate's wear. The wear of nitrided samples at 450 and 500°C are almost 10 times lower than the substrate's wear, which indicates a great improvement on tribological properties after plasma nitriding. Fig. 4b presents only the worn volume of the plasma nitrided samples.

The wear volume of the sample nitrided at 450°C, on Fig. 4b, is slightly inferior to that observed for nitriding at 500°C. At 500°C the layer is harder (Tab. 2) although its wear resistance is lower. This phenomenon is observed for plasma nitriding of austenitic stainless steels, in which wear increases with increasing nitriding temperature from 400 to 500°C and it can be attributed to the increase in layer fragility [14]. The massive precipitation of chromium and molybdenum nitrides at 500°C shown by X-ray diffraction (Fig. 3), creates a harder layer, although brittle.

3.3. Potentiodynamic Polarization

Potentiodynamic polarization curves for different nitriding temperatures (450 and 500°C) and the un-nitrided CW2M alloy are shown in Figure 5.

All polarization curves presented the same general features with a well defined cathodic region (-1.00 to -0.25V) and a passivation region from -0.25 to 0.25V. In higher potentials an increase in current is observed.

Table 3 shows the open circuit potentials, which were obtained before the polarization curves and the corrosion parameters collected from the polarization curves. The parameters from the polarization curves show that although the corrosion potential goes toward positive potentials, increasing nitriding temperature, the corrosion current moves in the opposite direction.

The sample plasma nitrided at 450°C presented the higher OCP value followed by the sample treated at 500°C and the substrate. The sample nitrided at 500°C yielded the higher corrosion potential; however the polarization curve was shifted towards higher currents, when comparing with the un-treated CW2M. Sample nitrided at 450°C was slightly shifted to the left, towards higher currents and potentials. Thus, nitriding at 450°C promoted a good corrosion protection with low OCP value.

4 CONCLUSIONS

Plasma nitriding of CW2M Hastelloy produced thin and homogeneous surface layers for both applied temperatures. These layers showed a two-layer morphology and their thickness increase with the treatment temperature. EDS analyses indicated that Cr and Mo quantity are larger on the top gray layer, Ni increases from the layer to the substrate and Fe remains constant.

X-ray diffraction patterns of plasma nitrided samples presents evidence of a nitrogen expanded phase at 450°C and the initiation of chromium and molybdenum nitrides precipitation; at 500°C the nitrides precipitation is larger.

The wear of samples nitrided at 450 and 500°C are almost 10 times lower than the substrate's wear, which indicates a great improvement on tribological properties. The worn volume of the sample nitrided at 450°C is slightly inferior to that observed for nitriding at 500°C.

The corrosion parameters shows that although the corrosion potential goes toward positive potentials, increasing nitriding temperature, the corrosion current moves in the opposite direction. Nitriding at 450°C promoted a good corrosion protection with low OCP value.

Thus, plasma nitriding at 450°C provides an increase in corrosion and wear resistance of the CW2M alloy.

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Tables:

Table 1: Chemical compositions (weight %) of CW2M alloy.

	Cr	Mo	Ni	Mn	Si	Fe	S	P	W	C
Nominal	15-17.5	15-17.5	Bal.	1.0*	0.8*	2.0*	0.03*	0.03*	1.0*	0.02*
Obtained	16.75	17.10	Bal.	0.81	0.55	-	0.0089	0.0038	-	0.0027

* maximum values

Table 2: Micro-hardness and layer thickness of the plasma nitrided CW2M alloy

	Hardness, HV	Layer thickness, μm	
CW2M-Substrate	429±11	---	
CW2M-Nit. 450°C	606±11	**Total**	2.57±0.09
		Top-layer	1.1±0.1
		Sub-layer	1.45±0.04
CW2M-Nit. 500°C	962±51	**Total**	4.3±0.1
		Top-layer	2.85±0.04
		Sub-layer	1.34±0.04

Table 3: Corrosion parameters values and open circuit potential (OCP).

Sample	Ecorr, mV	Icorr, nA	OCP, mV
CW2M-Substrate	-283	1.22	-150
CW2M-Nit. 450°C	-243	5.19	60
CW2M-Nit. 500°C	-207	7.63	-100

Figure captions:

Figure 1 - Cross section electron micrograph of the plasma nitrided CW2M at 500ºC.

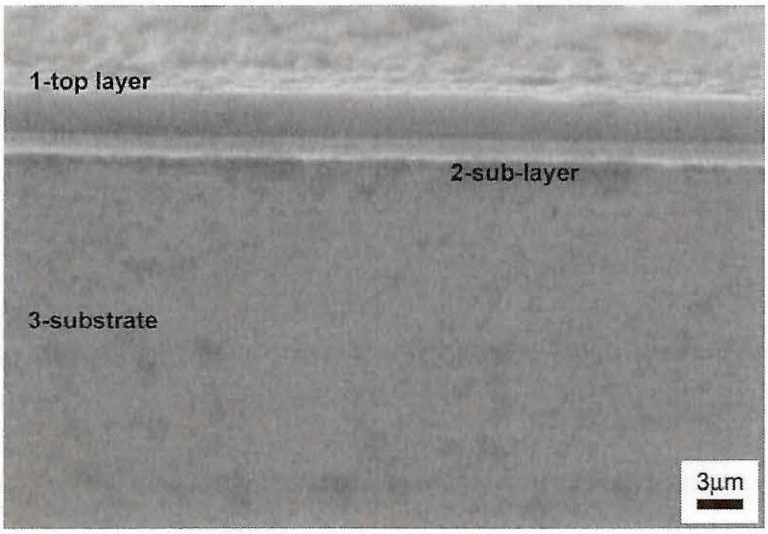
Figure 2 - EDS line scan on the layer produced after nitriding at 500ºC; for chromium, nickel, molybdenum and iron.

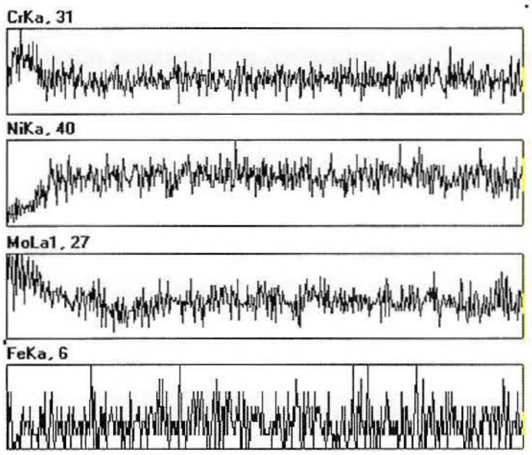
Figure 3 - X-ray diffraction patterns of the un-nitrided and nitrided CW2M samples.

Figure 4 - Worn volume curves of the plasma nitrided CW2M alloy: (a) with the substrate and (b) without the substrate.

Figure 5 - Potentiodynamic polarization curves of the untreated and plasma nitrided CW2M samples.

Figures:


1-top layer
2-sub-layer
3-substrate
3µm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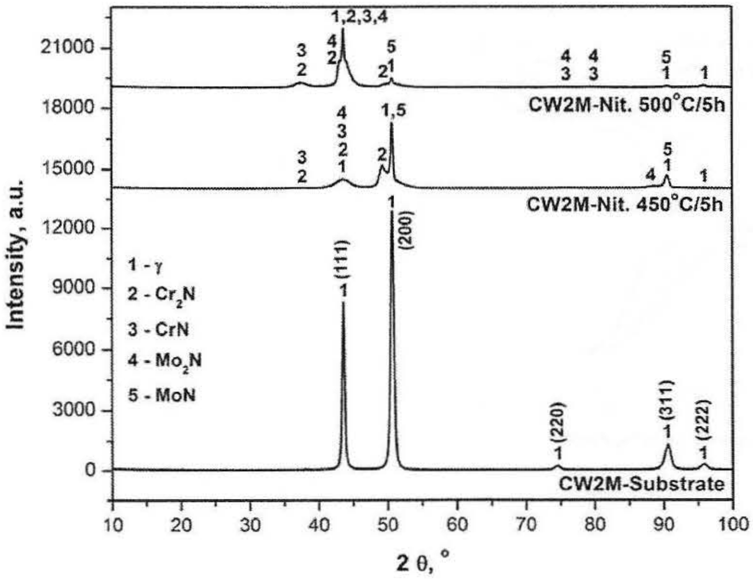
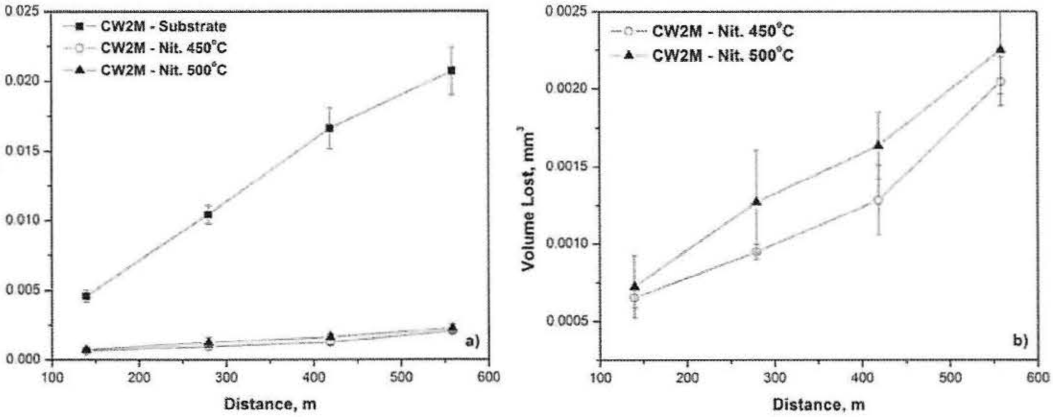
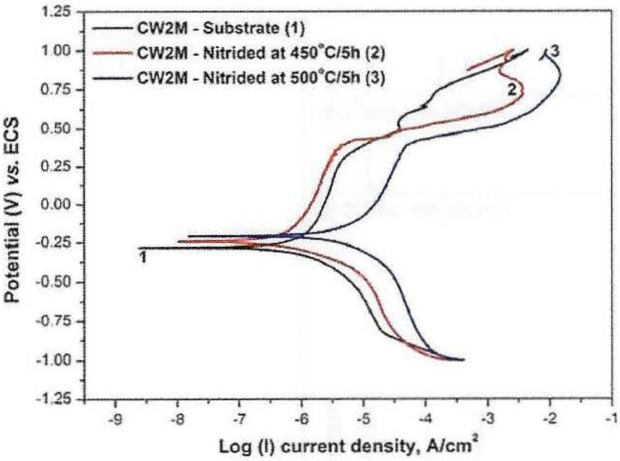
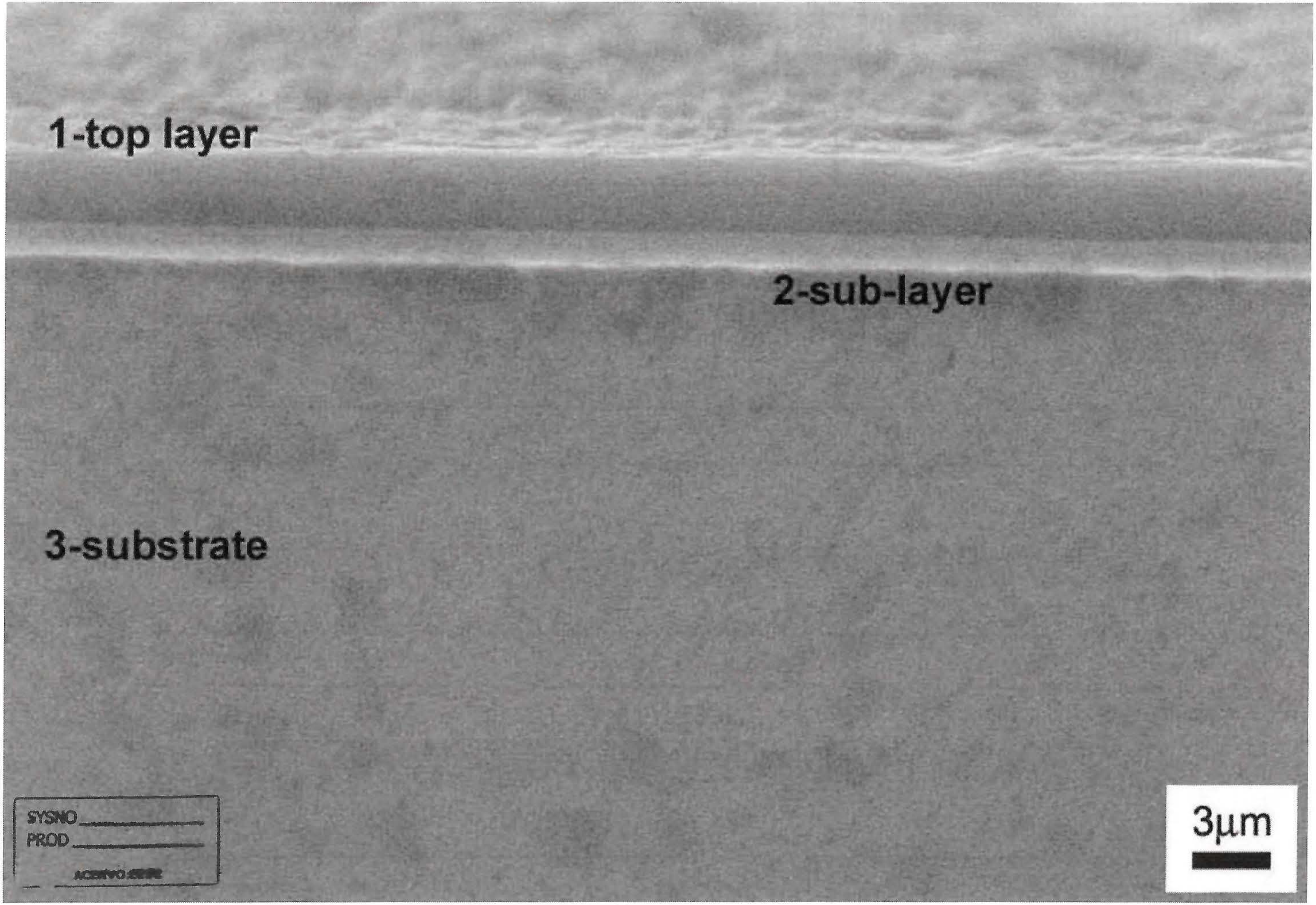
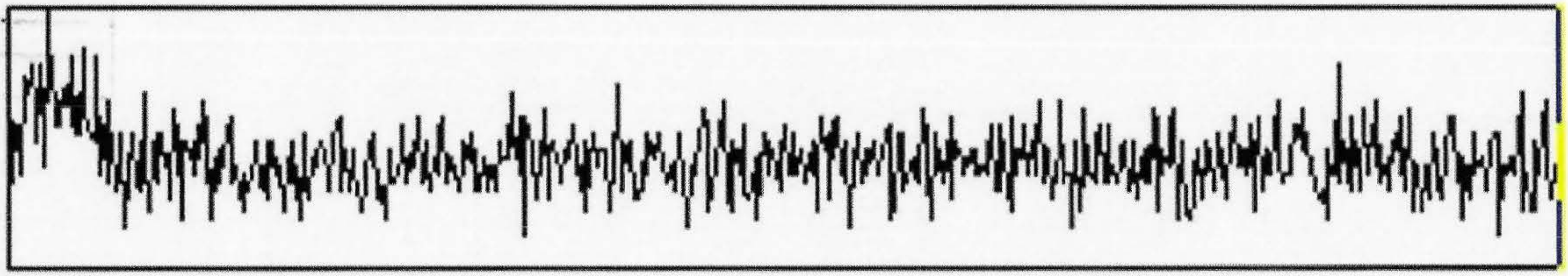
NiKa, 40
MoLa1, 27
FeKa, 6


Intensity, a.u.
2 θ, °
1,2,3,4
CW2M-Nit. 500°C/5h
1,5
CW2M-Nit. 450°C/5h
CW2M-Substrate
(111)
(200)
(220)
(311)
(222)
1 - γ
2 - Cr₂N
3 - CrN
4 - Mo₂N
5 - MoN

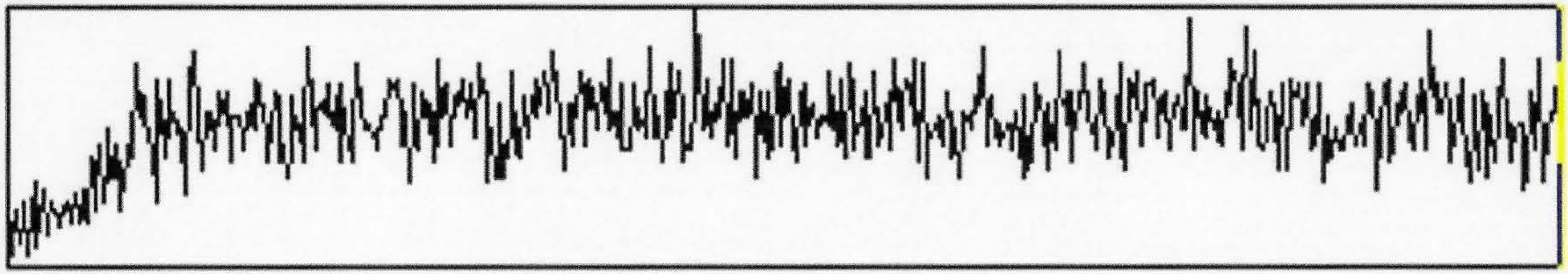

CW2M - Substrate
CW2M - Nit. 450°C
CW2M - Nit. 500°C
Volume Lost, mm³
Distance, m
a)
b)


CW2M - Substrate (1)
CW2M - Nitrided at 450°C/5h (2)
CW2M - Nitrided at 500°C/5h (3)
1
2
3
Potential (V) vs. ECS
1.25
1.00
0.75
0.50
0.25
0.00
-0.25
-0.50
-0.75
-1.00
-1.25
-9
-8
-7
-6
-5
-4
-3
-2
-1
Log (I) current density, A/cm²


1-top layer
2-sub-layer
3-substrate
3μm



CrKa, 31



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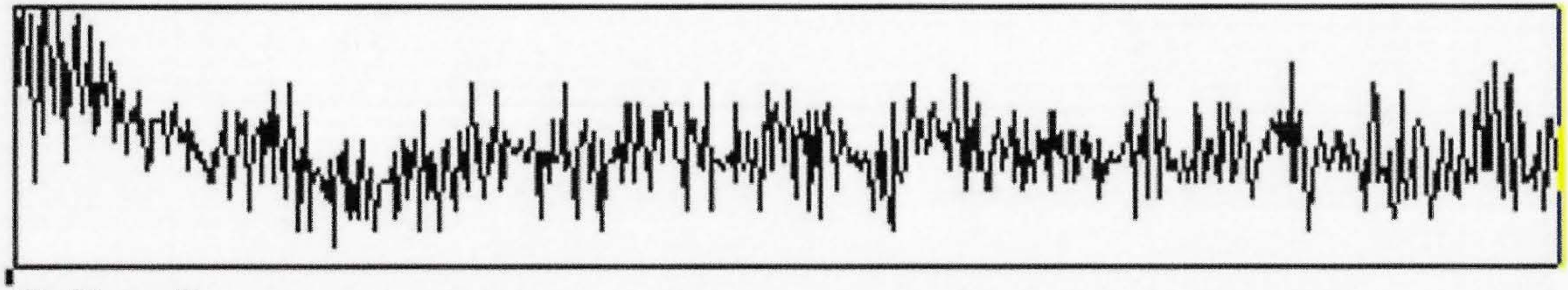
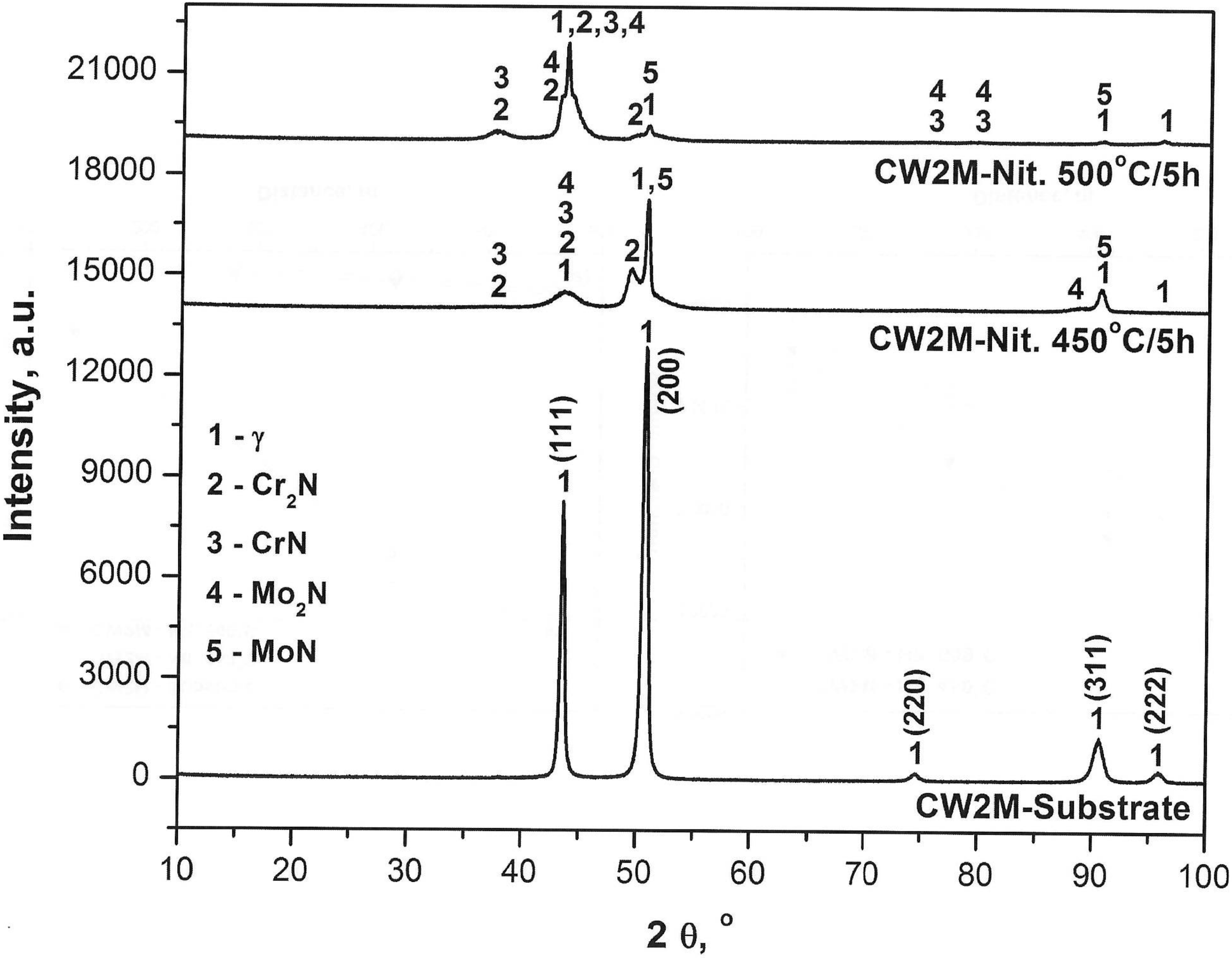
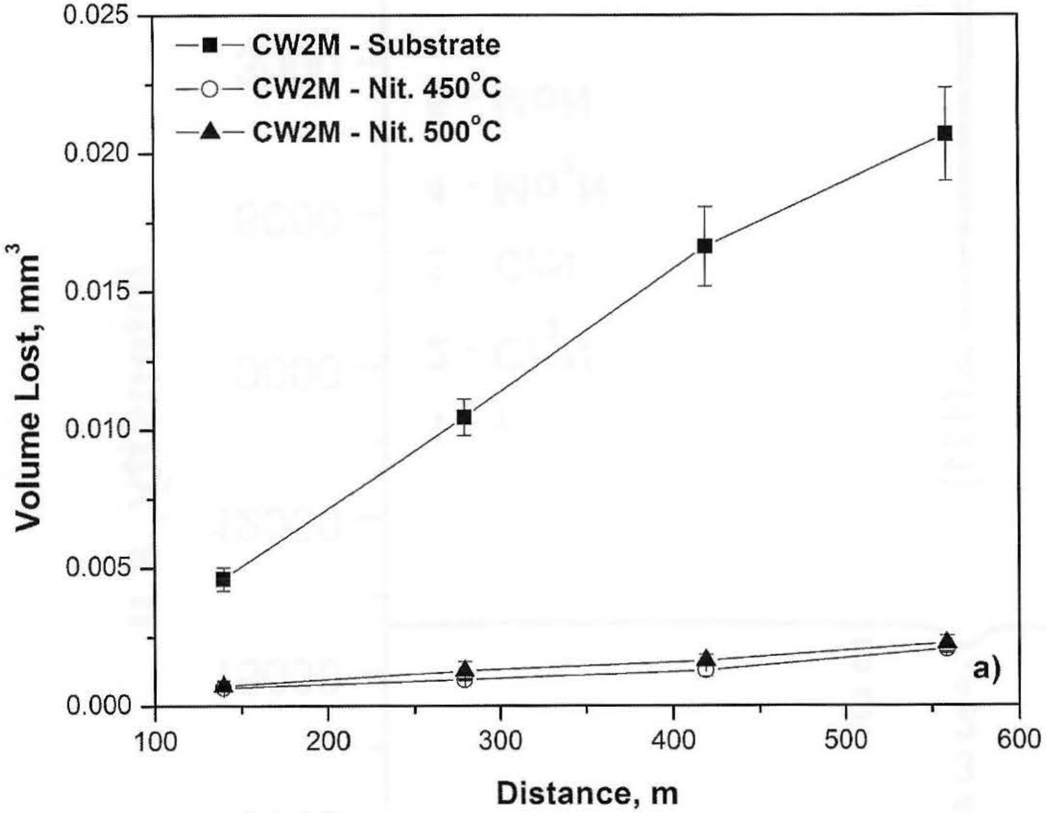
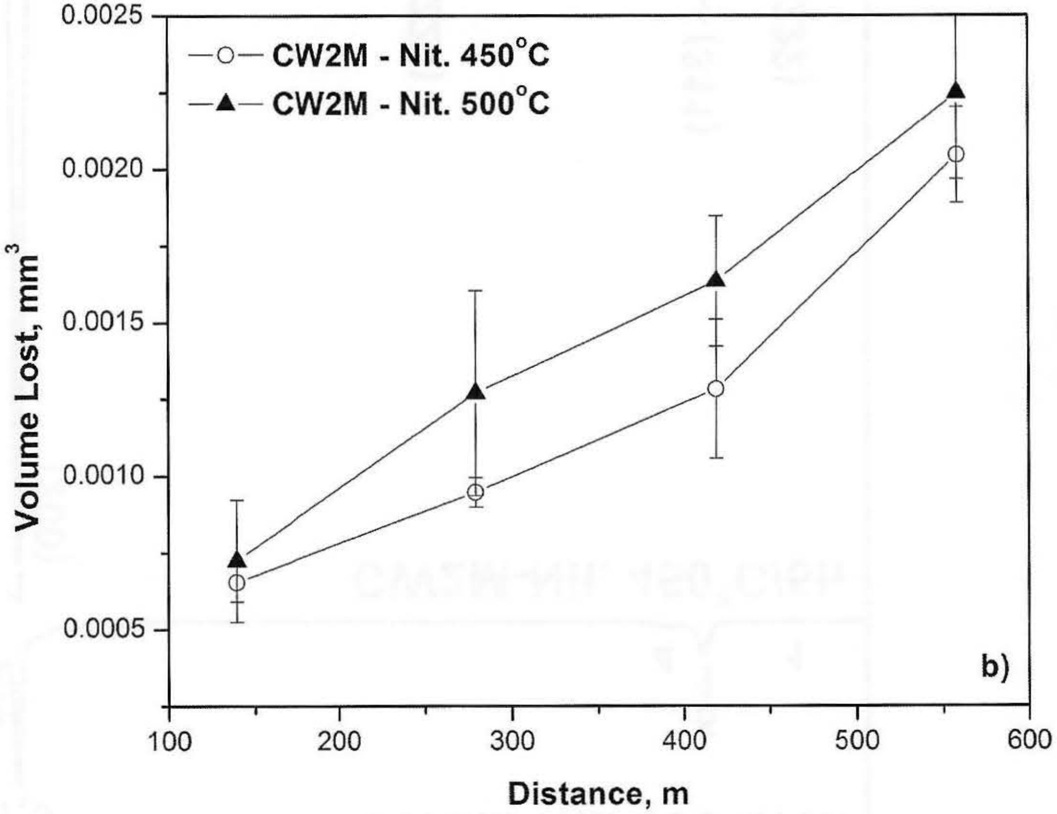


MoLa1, 27

FeKa, 6


Intensity, a.u.
0
3000
6000
9000
12000
15000
18000
21000
10
20
30
40
50
60
70
80
90
100
2 θ, °
1 - γ
2 - Cr2N
3 - CrN
4 - Mo2N
5 - MoN
CW2M-Nit. 500°C/5h
CW2M-Nit. 450°C/5h
CW2M-Substrate
1,2,3,4
1,5
(111)
(200)
(220)
(311)
(222)


CW2M - Substrate
CW2M - Nit. 450°C
CW2M - Nit. 500°C
Volume Lost, mm³
0.025
0.020
0.015
0.010
0.005
0.000
100
200
300
400
500
600
Distance, m
a)


CW2M - Nit. 450°C
CW2M - Nit. 500°C
Volume Lost, mm³
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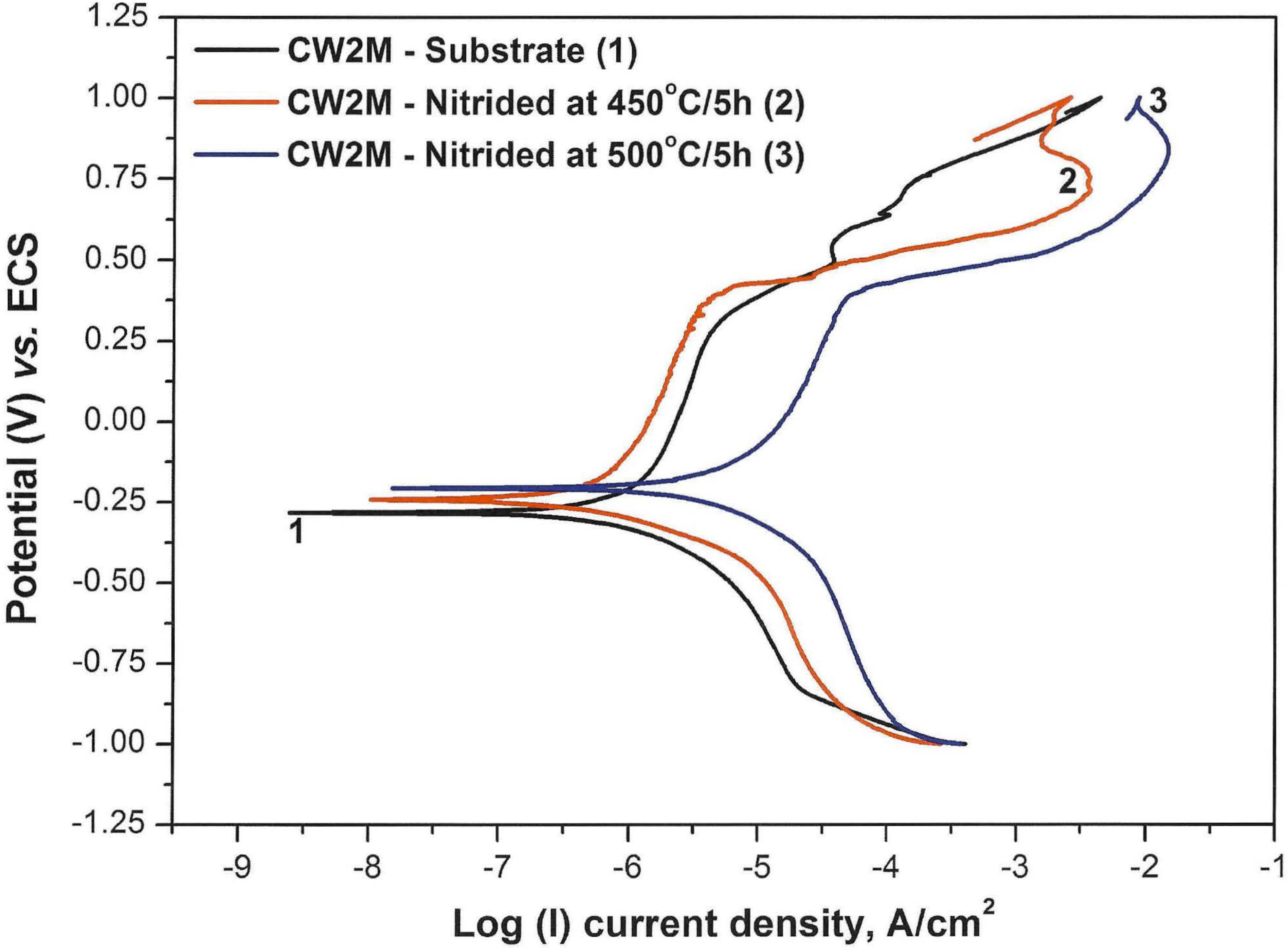
0.0020
0.0015
0.0010
0.0005
100
200
300
400
500
600
Distance, m
b)


CW2M - Substrate (1)
CW2M - Nitrided at 450°C/5h (2)
CW2M - Nitrided at 500°C/5h (3)
1
2
3
1.25
1.00
0.75
0.50
0.25
0.00
-0.25
-0.50
-0.75
-1.00
-1.25
-9
-8
-7
-6
-5
-4
-3
-2
-1
Potential (V) vs. ECS
Log (I) current density, A/cm²