EFFECT OF PLASMA NITRIDING ON THE WEAR AND CORROSION PROPERTIES OF HASTELLOY CW2M SUPER-ALLOY[1]

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Abstract

Hastelloy C alloys are widely used in chemical, aerospace and nuclear industries in corrosive environments. The predominant alloying element of these alloys is typically nickel, 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, and a treatment time of 5h. As cast and plasma treated samples were analyzed using scanning electron microscopy, wear and corrosion tests. 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 at 450°C yielded the appearance of chromium and molybdenum nitrides peaks and possibly an expanded phase; and 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.

Key words: Hatelloy C; Plasma nitriding; Wear; Corrosion.

EFFEITO DA NITRETAÇÃO POR PLASMA NO DESGASTE E NA CORROSÃO DE UMA SUPER-LIGA HASTELLOY CW2M

Resumo

Super-ligas do tipo Hastelloy C são amplamente utilizadas na indústria química, aeroespacial, nuclear e em ambientes corrosivos. O elemento predominante nestas ligas é tipicamente o níquel, porém outros elementos podem ser adicionados. A nitretação por plasma é um tratamento de superfície eficaz para aumentar a resistência ao desgaste. O objetivo deste trabalho foi de avaliar a influência do tratamento de nitretação por plasma na resistência ao desgaste e à corrosão da super-liga Hastelloy CW2M. A liga foi nitretada por plasma empregando-se o método de corrente contínua com as seguintes condições: usando-se uma mistura gasosa com 80% H_2 e 20% N_2, em volume, uma pressão de 500Pa, temperaturas de 450 e 500°C e tempo de tratamento de 5h. A liga foi nitretada na condição como fundida e então as amostras analisadas por microscopia eletrônica de varredura e ensaios de desgaste e corrosão. A nitretação por plasma do Hastelloy CW2M produziu uma camada homogênea e com alta dureza. A difração de raios-X revelou a fase γ (CFC) para a liga CW2M não nitretada. A nitretação a 450°C resultou no aparecimento de picos de nitretos de cromo e molibdênio e possivelmente uma fase expandida, e em 500°C, um aumento nos picos de nitretos de cromo e molibdênio foi observado. O desgaste das amostras nitretadas a 450 e 500°C foi quase 10 vezes menor do que o desgaste do substrato, o que indica uma grande melhoria nas propriedades tribológicas. Os parâmetros de corrosão mostraram que, embora o potencial de corrosão aumente com o aumento da temperatura de nitretação, a corrente de corrosão diminui. A nitretação a 450°C promoveu uma boa proteção contra a corrosão, apresentando um baixo valor potencial de circuito aberto e baixo potencial de corrosão.

Palavras chave: Hatelloy C; Nitretação por plasma; Desgaste; Corrosão.

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1 INTRODUCTION

Hastelloy (registered trademark of Haynes International) is applied as the prefix name of a range of different highly corrosion resistant alloys, also called by super-alloys. The predominant alloying element is typically nickel, although other elements are added, such as molybdenum, chromium, cobalt, iron, copper and others. There are several Hastelloy's families for specific applications. The C family Hastelloy's are widely used in chemical, aerospace 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 provides an attractive process to improve 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. The expanded austenite is a metastable phase with a super-saturation of nitrogen which remains in solid solution.[6-8] This layer possesses a good combination of mechanical, tribological and corrosion properties.[8] Nitriding at lower temperature means lower cost, less distortion and less surface roughening.[9]

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 was melted 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, and time period of 5h.

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*

Vickers micro-hardness measures were performed on a digital Buehler equipment with load of 50gf and application time of 10s. Electron microscopy was performed using

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a scanning electron microscope (SEM), LEO 440 model with a tungsten filament. 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. 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 volume (V) of each wear crater were calculated according to the literature.[10,11]

The electrochemical cell used to obtain the potentiodynamic polarization curves utilized 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. For monitoring the potential and current, an Autolab model VGSTAT-302 potentiostate was used. 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

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 (2) 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 thickness, due to the increase on nitrogen diffusivity at higher temperatures.

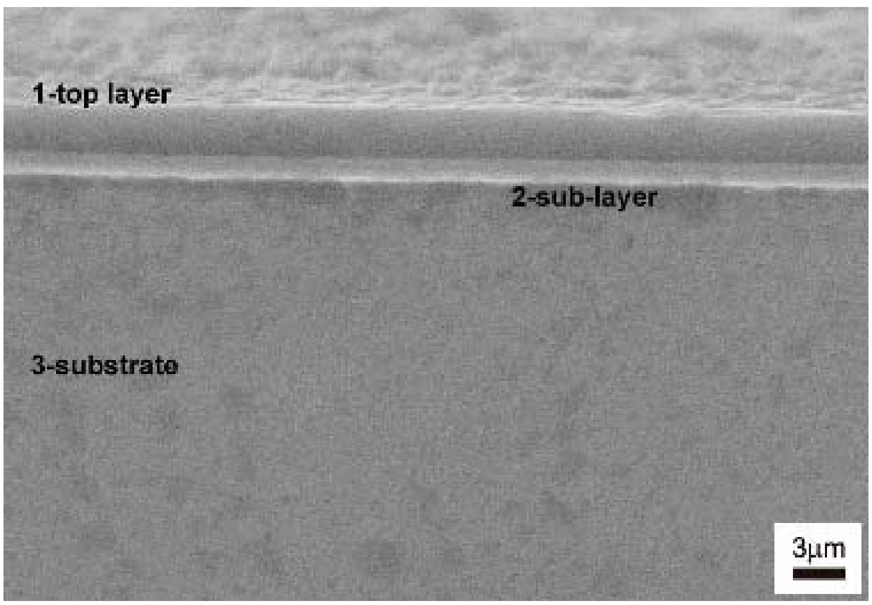

Figure 1. Cross section electron micrograph of the plasma nitrided CW2M at 500ºC.

The 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. The sub-layer (2) on Figure 1 is probably a nitrogen expanded phase and the top layer (1) is composed by chromium and other nitrides.

Figure 2 presents the X-ray diffraction patterns of the nitrided (at 450 and 500°C) and un-nitrided CW2M samples.

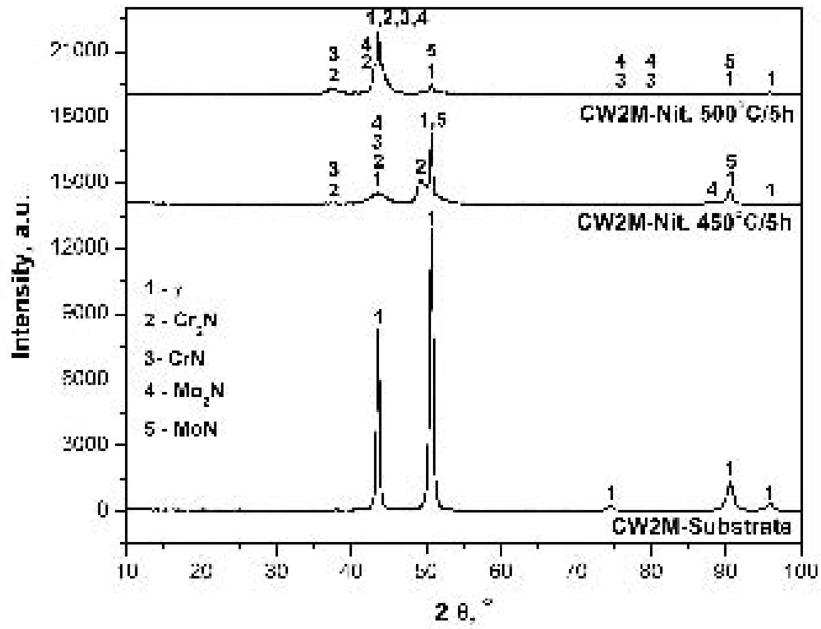

Figure 2. X-ray diffraction patterns of the un-nitrided and nitrided CW2M samples.

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 patter confirms the fcc structure type. The samples plasma nitrided at 450 and 500°C showed a considerable decrease on diffraction peaks intensities.

Sample treated at 450°C yielded the appearance of a peak shifted to the left at around 50 degrees, which can indicate 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.

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, indicating clearly the precipitation of these nitrides. Although the CW2M super alloy is a nickel based alloy, nickel nitrides were not observed.

The diffraction patterns indicates that at 450°C the nitrides precipitation is smaller and possibly the formation of a nitrogen expanded phase, which is also observed on electron microscopy; and at 500°C the layer thickness increases (Tab. 2) diminishing the substrate diffraction and the nitride precipitation takes place.

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.

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

The surface micro-hardness of the nitrided samples increased as temperature was increased.

3.1 Wear Characterization

The worn volume curves of the substrate itself and plasma nitrided samples are shown in Figure 3. In Figure 3a 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. Figure 3b presents only the worn volume of the plasma nitrided samples.

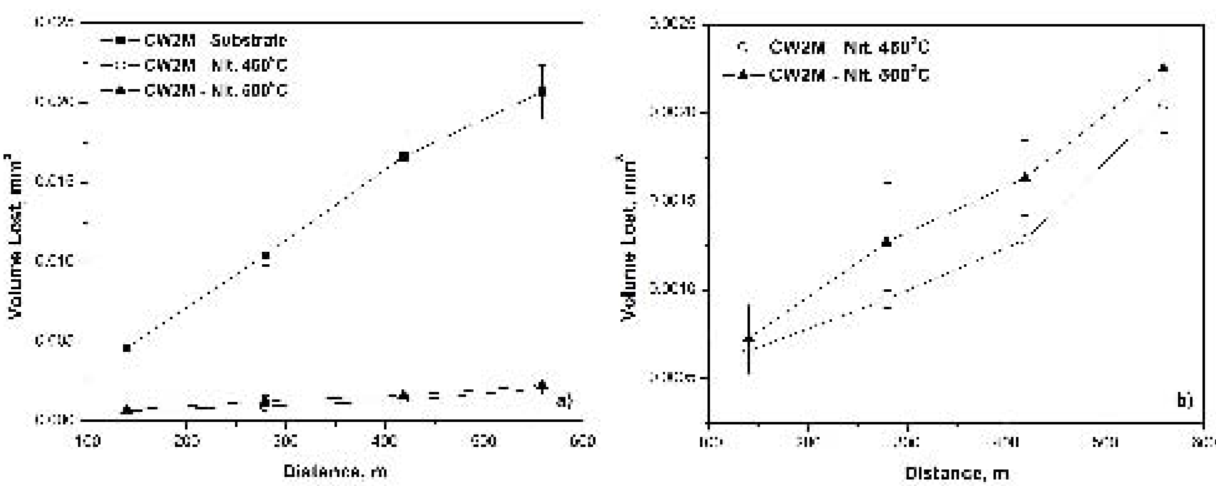

Figure 3. Worn volume curves of the plasma nitrided CW2M alloy: (a) with the substrate and (b) without the substrate.

The wear volume of the sample nitrided at 450°C, on Figure 2b, 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.[12] The massive precipitation of chromium and molybdenum nitrides at 500°C shown by X-ray diffraction (Fig. 2), creates a harder layer, although brittle.

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3.2 Potentiodynamic Polarization

Potentiodynamic polarization curves for different nitriding temperatures (450 and 500°C) and the un-nitrided CW2M alloy are shown in Figure 4.

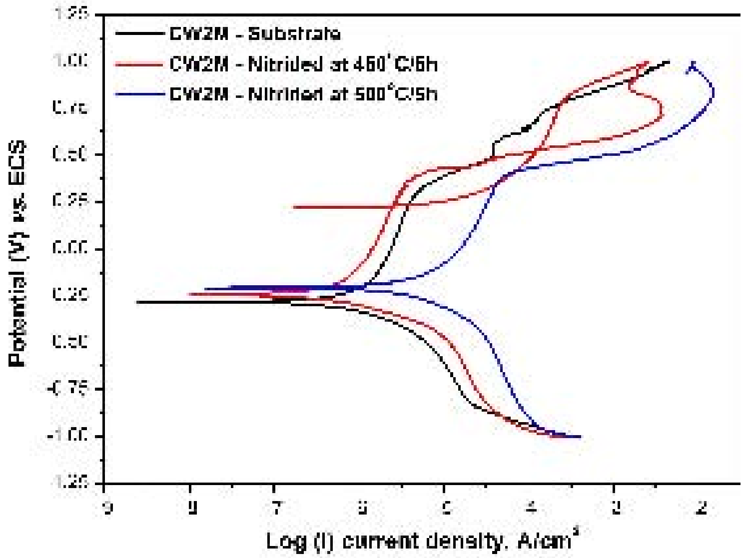

Figure 4. Potentiodynamic polarization curves of the untreated and plasma nitrided CW2M samples.

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.

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

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.

X-ray diffraction patterns of plasma nitrided samples indicates the possibly production 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 super-alloy.

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