REVISTA MEXICANA DE FÍSICA **45 SUPLEMENTO 1**, 138–140 JUNIO 1999

Hardness, mechanical and morphological properties of iron nitride thin films

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Recibido el 27 de febrero de 1998; aceptado el 25 de mayo de 1998

A study of mechanical properties, hardness and morphology of iron samples (99.9%), as a function of nitrogen content, is presented. An increase up to ~ 300% in hardness was obtained. Nitriding of iron substrates were performed in an ECR microwave plasma source with a high-density regimen of ionized particles (5×10^{11} cm^{-3}) under a pressure of 4.0×10^{-4} Torr. Working atmosphere was a H_2 / N_2 gas mixture, 100% / 0%, 90% / 10%, 85% / 15%, 80% / 20% and 0% / 100%. The pressure of working gas; the microwave power, 300 W; the processing time, 20 min and the substrate temperature were all kept constant during the nitriding processes. Sample characterization was carried out by X-ray diffraction, scanning electron microscopy and microhardness; mechanical properties were determined with an Instron equipment.

Keywords: Iron nitride; ECR plasma treatment; microstructure; hardness

En este trabajo se presenta el estudio de las propiedades mecánicas, dureza y morfología de películas de hierro (99.9%) nitruradas. Para estas películas se obtuvo un aumento en la dureza hasta en un ~ 300%. La nitruración de los substratos se realizó mediante una fuente de plasma de microondas por resonancia ciclotrónica de los electrones (ECR) con un régimen de alta densidad de partículas ionizadas (5×10^{11} cm^{-3}) bajo una presión de 4.0×10^{-4} Torr. La atmósfera de trabajo fue una mezcla de gases H_2 / N_2 en diferentes proporciones: 100% / 0%, 90% / 10%, 85% / 15%, 80% / 20% y 0% / 100%. Durante el depósito la presión del gas, la potencia de la fuente de microondas, 300 W, el tiempo de proceso, 20 min, y la temperatura del substrato se mantuvieron constantes. La caracterización de las muestras se llevó a cabo mediante difracción de rayos X, microscopía electrónica de barrido y microdureza; las pruebas mecánicas se realizaron con una máquina Instron.

Descriptores: Hierro nitrurado; plasma ECR; microestrura; dureza

PACS: 81.15; 68.55

1. Introduction

For the last decades, the iron-nitrogen system has been studied due to its mechanical and magnetic properties. Initially the interest in this system arose from the nitriding of steels to improve the abrasive strength by surface hardening [1]. The surface hardness allows these thin films to be used as ultra-hard coating materials, tools and abrasives.

Several methods have been carried out to prepare iron nitride, such as iron metal nitriding, sputtering, ion plating, molecular beam epitaxy, ion beam deposition and ion implantation [2–5]. In this work we include the electron cyclotron resonance (ECR) microwave plasma technique, which seems promising to prepare FeN and FeN-H thin films. Structure, morphology, hardness and mechanical properties of the samples were determined by X-ray diffraction, SEM, Vicker micro-indenter and Instron equipment.

2. Experimental

Fe substrates (99.9%) prepared under the ASTM steel norm were mirror polished and characterized by micro-hardness measurements using a Matzusawa MXT30-UL tester. Nitriding of iron samples were performed in an ECR microwave plasma source [6]. Prior to nitriding, the chamber was evacuated to 1.07×10^{-3} Pa by means of a 200 l/s diffusion pump, then high purity nitrogen gas was introduced into the deposition chamber to give a working pressure of 5.33×10^{-2} Pa, this resulted in the highest value of plasma density 4×10^{11}cm^{-3} and an electron energy of 7 eV. The pressure of working gas; the microwave power, 300 W, the processing time, 25 min and the substrate temperature, 300°C were all kept constant during the nitriding process. The working atmospheres were factory supplied H_2 / N_2 gas mixtures: 0% / 100%, 90% / 10%, 85% / 15%, 80% / 20%, and 100% / 0%. Crystalline phase characterization was performed using a Siemens D-5000 X-ray diffractometer. The microstructure was determined by a scanning electron microscope (Leica-Cambridge 440). The hardness was determined by Vickers micro-indenter measurements and the mechanical characterization was carried out with an Instron machine.

3. Results and discussion

3.1. Crystalline phases and structure

The XRD patterns for FeN and FeN-H films, which were obtained for different H_2 / N_2 mixtures, are shown in Fig. 1,

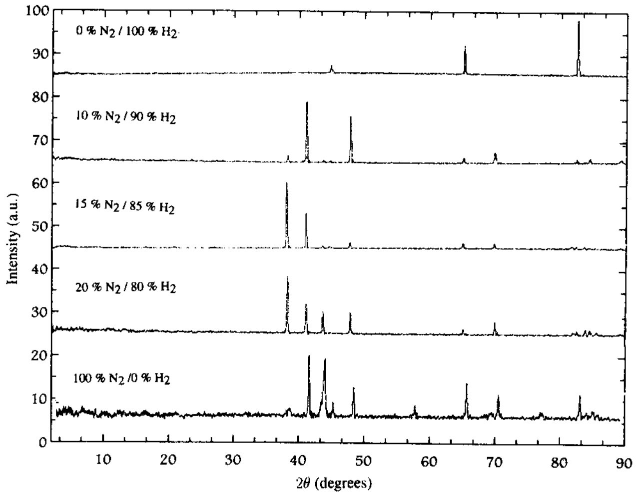


FIGURE 1. XRD patterns of the samples obtained by ECR technique under different working atmospheres N_2 / H_2.

where systematic structural variations can be observed. Sample P1, obtained under 100% N_2, is a single phase Fe_3N product with a hexagonal structure, JCPDS card 3-925. For 20%/80%, and 15%/85% N_2 / H_2 working atmospheres, samples P2 and P3 show a mixture of phases Fe_3N-Fe_4N, although P3 contains a minimal amount of the Fe_4N phase. Sample P4, 10% N_2 / 90% H_2, is a single phase product, Fe_4N, with a cubic structure; JCPDS number 6-627. For P5, with a 100% H_2 working atmosphere, a pure Fe phase was observed.

3.2. Microstructure

SEM images showed that the grain size of the samples is reduced as the nitrogen content increases in the working atmosphere; for 100% N_2, the grain size is 50 nm. Two SEM photographs are shown in Fig. 2, a) for a layer nitrided under 20%/80%, and b) 10%/90%, N_2 / H_2 ratio in the working atmosphere.

Cross-sectional SEM studies of FeN-FeN:H samples indicated that the nitrided layer has a thickness between 2.5 and 6 μm. Within the experimental errors, the chemical analysis (EDS) along the plane and cross plane section-in the surface/interface region- demonstrated that the nitride layer has a constant iron and nitrogen content. These studies also revealed that the 10% of oxygen present at the interface FeN/substrate in all samples is probably caused by an oxide film on the iron surface which was not totally removed during processing.

3.3. Mechanical properties

Mechanical properties of the samples were improved as the N_2 content in the working atmosphere increased; for single phase samples, a small deformation was observed: $\varepsilon_R = 0.02024$ for Fe_3N and $\varepsilon_R = 0.05495$ for Fe_4N. Strain-stress

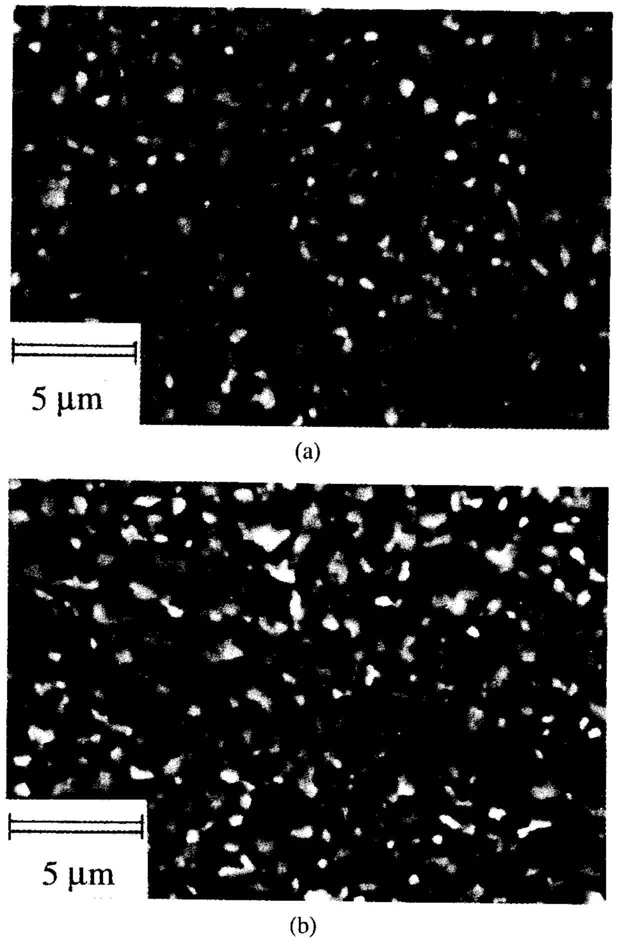


FIGURE 2. SEM images of the microstructure for thin films obtained under: (a) 10%/90% N_2 / H_2 and (b) 20%/80% N_2 / H_2, working atmospheres.

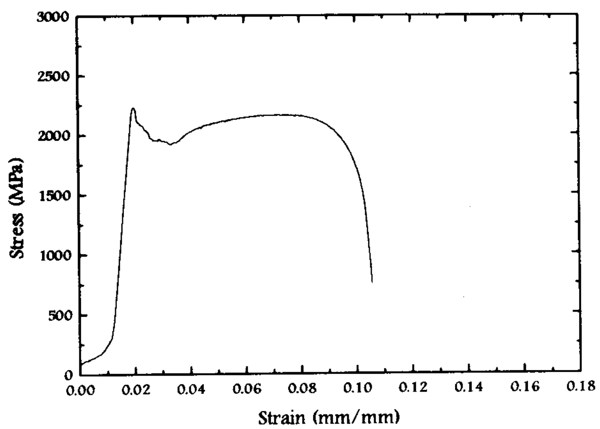
TABLE I. Hardness as a function of the N_2 / H_2 ratio in the working atmosphere.

Sample	Gas mixture N_2%	Gas mixture H_2%	Hardness Vickers
P1	100	0	404.0
P2	20	80	340.7
P3	15	85	335.1
P4	10	90	312.0
P5	0	100	60.9

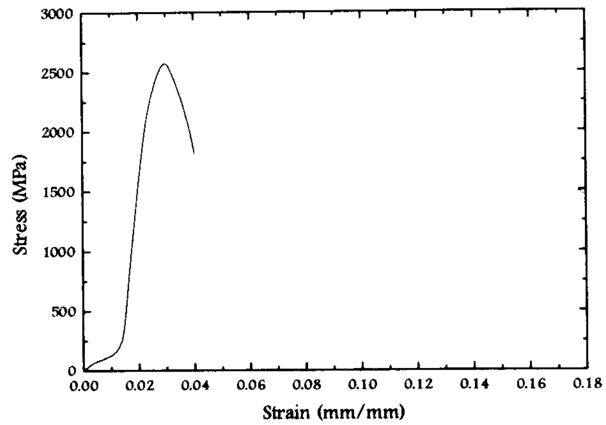
diagrams for a sample nitrided under a working atmosphere of 100% N_2 and for a pure iron sample are shown in Fig. 3.

Results indicated that the presence of nitrogen in the working atmosphere increases the hardness of the nitrided films; for 100% N_2 the film is almost 300% harder than that of a pure iron substrate, Table I. Finally, after few months, no corrosion was observed in the nitrided samples.

ECR microwave plasma technique is a new low-pressure nitriding approach which provides an attractive process to im-



(a)



(b)

FIGURA 3. Strain-stress diagrams: a) sample nitrided under a working atnosphere of 100% N_2 and b) pure iron sample.

prove the wear resistance and the corrosion properties of the iron. In a similar way, it has been shown that plasma nitriding treatment of stainless steel improves the surface hardness without affecting its corrosion properties [7]. With the ECR microwave plasma technique, the ease of formation of the iron nitrided thin film was improved by the addition of H_2 in the working atmosphere, the same fact to that reported by Lo *et al.* [8] who obtained rf-sputtered Fe-N compounds. The grain size of the products, which were obtained by ECR, was comparable to that reported by Panda and Gajbhiye [2], who obtained nitride particles by chemical reduction.

4. Conclusions

Iron nitride thin films have been prepared using a high density ECR plasma. Results showed that the H_2 / N_2 ratio affects the incorporation of nitrogen in the iron substrate and therefore the structure and the properties of the nitrided samples. XRD patterns showed the presence of two single phase FexN compounds for a high or low % N_2 content in the working atmosphere (100%, 10% and 0) and two mixed phase materials for intermediate cases. Single phase compounds show a bilayer growth with a constant nitrogen composition. Cross-sectional SEM studies indicated that the nitrided layer has a thickness between 2.5 and 6 μm. Mechanical properties of the samples were improved with an increase of %N_2 in the working atmosphere; for 100% N_2 the film is almost 300% harder than that of pure iron substrate. Superior chemical stability was observed in these samples; after few months, no corrosion was observed in the nitrided films. The increase in hardness and the abrasive strength observed in the samples indicate that these films may be used for tools or like anticorrosive layers.

Acknowledgments

We want to acknowledge L. Baños, J. Guzmán, A. Caballero, E. Martínez, and M. Hipólito for their technical assistance. This work was partially supported by CONACyT-México under Grant No. 3325PA.

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