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Tribo-mechanical features of nitride coatings and diffusion layers produced by cathodic cage technique on martensitic and supermartensitic stainless steels

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ABSTRACT

The mechanical and tribological properties of martensitic AISI 420 (MSS) and supermartensitic HP13Cr (SMSS) stainless steels plasma nitrided using the cathodic cage design were investigated. Nitride compounds were produced in the plasma from the cage´s sputtered ions, which eventually deposited on the electrically isolated sample. Prior to nitriding, samples were austenitized and oil quenched in order to attain a fully martensitc microstructure. Nitriding was carried out at different temperatures (350-450 °C) for 6 h. Mechanical properties and scratch resistance were characterized by instrumented indentation and nanoscratch, and were correlated with morphological and microstructural changes by using atomic force microscopy, scanning electron microscopy, X-ray diffraction and profilometry. Both nitrided MSS and SMSS comprised two distinct regions: (i) an outermost nitride layer (300-800 nm thick) containing deposited ε-Fe$_{2-3}$N and γ´-Fe$_4$N nitrides and (ii) a diffusion zone composed of N-expanded martensite phase α_N. At 450 °C, diffusion zones thicknesses were 4 μm (MSS) and 6 μm (SMSS). Nitride layers presented intense brittleness under normal and tangential loadings. Critical loads for nitride layer detachment were 49 mN and 127 mN for MSS and SMSS, respectively. However, after removal of the thin nitride layers, the toughened diffusion zones were revealed, being uniformly distributed through the entire sample area. Its hardness was 11 GPa. Such value corresponds to a twofold and threefold increase from the hardness of MSS and SMSS substrates, respectively, which are comparable with other plasma nitrided steels at similar temperature conditions.

1. Introduction

The cathodic cage plasma nitriding (CC) is a deposition method derived from the active screen plasma nitriding [1,2]. It has been investigated in the last years in different classes of materials such as steels and titanium alloys [3–5]. Differently from the conventional plasma nitriding (PN), ionic species do not interact directly with the surface under treatment. The sample is electrically isolated from the chamber and remains under a floating potential, settled over a ceramic plate at the bottom of a cathodically polarized conduction cage. As described by Daudt et al. [5], an effect of multiple hollow cathodes takes place at the walls of the cage. In such a high potential field, the sputtering of the cage walls and interaction with the nitriding atmosphere produce compounds and/or metallic species, which eventually deposit on the sample´s surface. The desorption and diffusion of nitrogen from the nitride compounds at the specimen surface are also considered to contribute with the CC surface treatment [2]. The thermal energy arriving at the treated surface is provided by irradiation from the sputtered walls [1]. It is important to stress that cage´s composition rules the coating nature, which generally comprises of crystalline phases such as ε-Fe$_{2-3}$N and γ´-Fe$_4$N if iron-based materials are used and δ-TiN in the case of titanium-based cathodes [3–5].

CC coatings are especially attractive because of the thickness uniformity, structural and excellent mechanical properties throughout the surface area, eliminating the so-called edge effect, typical of plasma nitriding when the sample is directly polarized [1,5]. Such property draws attention to the use in special materials subjected to mechanical and abrasion environments, as the martensitic and supermartensitic stainless steels. *Martensitic* alloys such as the AISI 420 retain the martensitic microstructure at the working temperatures, maintaining also smaller amounts of ferrite and carbides depending on the annealing conditions. They are applied in molds, cutting tools and structural parts of automotive and biomedical

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devices. However, their corrosion performance is lower than other stainless steels due to the carbon (~0,1 wt%) and relatively low chromium (~13 wt%) contents [6,7]. For the *supermartensitic* alloys such as HP13Cr steel, corrosion and weldability are improved by reducing carbon concentration (~0.01 wt%) and adding Mo (~2 wt%) and Ni (~6 wt%) to the composition, whereas the chromium content is maintained the same as in martensitic steels. In welds, the heat affected zone remains martensitic, which enables attaining strengthened junctions without previous heating [8–11]. Because of the lower production costs, supermartensitic stainless steels are possible substitutes to duplex steels as raw materials for oil and gas pipelines, where components are subjected to corrosive agents in the presence of high temperature and pressure conditions [12,13]. However, certain applications demand improvements on the surface properties of both martensitic and supermartensitic steels. For instance, petroleum dragged from petroleum wells situated under the oceanic platforms usually generate severe abrasion, because of the mixed oil and sand going through pipelines and other metallic components in contact (the devices and parts of "subsea trees").

In a previous work, de Sousa et al. [14] prepared martensitic steels AISI 420 using CC nitriding in the temperature range 350 °C – 500 °C using a cage made of AISI 316 stainless steel. Thick coatings were produced, with several micrometers, presenting iron nitrides and the expanded martensite phase (the nitrogen in solid solution in the matrix). The layer hardness was about 11 GPa, similar to other values reported for AISI 420 submitted to PN [7,15]. Concerning supermartensitic stainless steels, our research group recently observed that HP13Cr, submitted to PN in the temperature range 350 – 450 °C, also produced modified layers (15-60 μm) plus diffusion coatings thicker than that observed in austenitic steels. Those results were attributed to the enhanced nitrogen diffusion in the martensitic microstructure. Hardness of the modified surfaces increased about threefold, whereas scratch resistance were also significantly improved [16].

This work aims at contribute further with the understanding of plasma nitriding in the HP13Cr supermartensitic stainless steel (SMSS) and the AISI 420 martensitic stainless steel (MSS), using the cathodic cage (CC) method. Structure and morphology of MSS treated by CC were previously analyzed [14], and here we investigate further additional features of the modified surfaces. In general, analyzes concentrate on cross-sectioned regions of the nitrided specimens [1,3,14]. Because loads at working conditions act normally and/or tangentially to the material´s surface, a different approach was employed, where microstructure and tribo-mechanical investigations were carried out directly at the outermost surface. Consequently, the results in this article disclosed significant evidences of the nitriding mechanism originated from the CC method, which produced two coatings, a nitride and a nitrogen-diffusion layers, with distinct properties on both steels. For the sake of clarity, in this report the analyses initially concentrated on general aspects of the treated MSS and SMSS, namely the substrate preparation and the crystalline structure of the as-nitrided surface; morphology and tribo-mechanical features were treated separately for the nitride region and the interface with the diffusion layer.

2. Materials and methods

2.1. Samples preparation

Samples with 15 x 15 x 2 mm were cut from blocks presenting the following composition (in wt %):

- AISI 420 (MSS): 12.5 Cr, 1 Mn, 1 Si, 0.15 C, 0.03 S, balance Fe.
- HP13Cr (SMSS): 13Cr, 5 Ni, 0.45 Mn, 2 Mo, 0.025 C, balance Fe.

Initially, the samples were subjected to quenching from austenitizing temperatures, in order to attain a fully martensitic microstructure at the starting material. This step aims at ruling out spurious effects on the surface mechanical response from the substrate beneath, resulted from the several microstructure compositions which can be found in these materials (ferrite plus carbides in MSS, and mixtures of martensite and austenite in SMSS) [7,11,17].

In a previous work [16], the heat treatment conditions for SMSS were systematically studied, in which temperatures ranged from 975 to 1100 °C, whereas the cooling media were water or mineral oil. As found at that study, likewise employed here, the treatment conditions for SMSS that allowed converting the austenite fraction into martensite, with no formation of carbides, were as follows.: (i) austenitizing into a preheated furnace at 1100°C, during 30 min in air; (ii) quenching in a bath of mineral oil at 20 °C, contained in a 1 L beaker; (iii) tempering concomitant with the nitriding process in the plasma chamber. The MSS alloy was submitted to a similar protocol, but using a different austenitizing temperature. Previous results by Pinedo and Monteiro [7] and Scheuer at al. [18], employed here, indicated that optimized conditions for martensitizing of AISI 420 steels are attained by heating at 1050 °C during 30 min with subsequent oil quenching at 20 °C. Tempering was concomitant with the nitriding process.

The untreated reference SMSS and MSS samples were austenitized and oil quenched, as aforementioned, and subsequently tempered

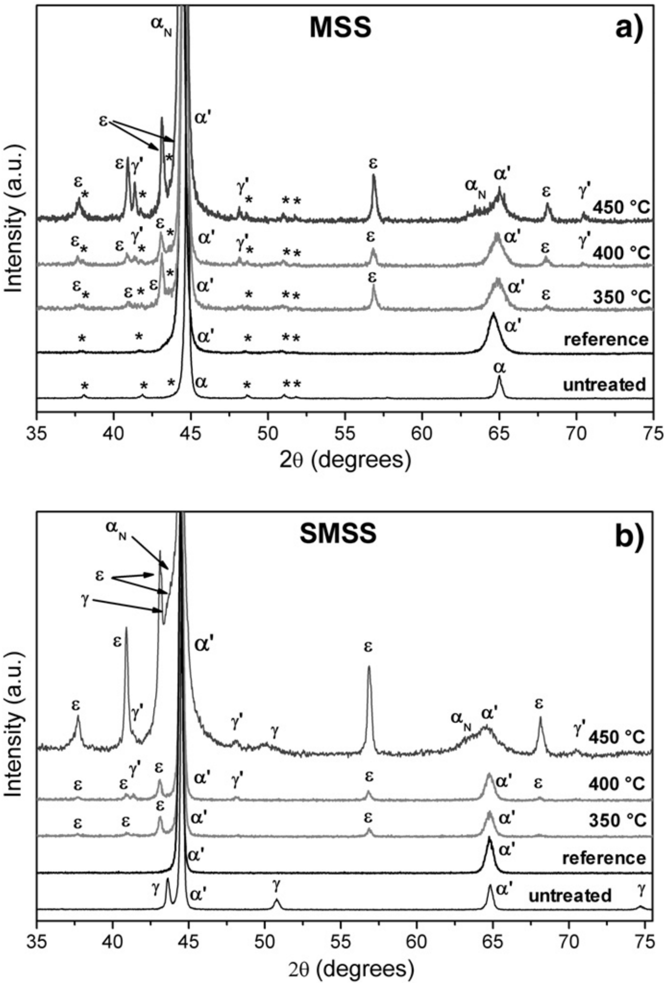

Fig. 1. X-ray diffractograms of (a) MSS and (b) SMSS samples: as received (labelled as "untreated"); oil quenched from 1100 °C (austenitizing temperature), with subsequent tempering in Argon (labelled as "reference"); and the quenched ones submitted to the cathodic cage nitriding at the indicated temperatures. γ = austenite (face-centered cubic); α = ferrite (body-centered cubic); α´ = martensite (body-centered tetragonal); α_N = expanded martensite; ε = $Fe_{2\text{-}3}N$; γ´ = Fe_4N. The asterisk (*) indicates carbides ($M_{23}C_6$, M_7C_3, and M_3C, where M corresponds to a metal atom).