Evaluation of the Effect of Cooling Speed on the Layer Formation on Stainless Steel by Plasma Carbonitriding

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Abstract

Plasma carbonitriding has been used to improve the tribological and mechanical properties of materials, specially iron-based alloys. The Pulsed Glow Discharge (PGD) technique was used for carbonitriding steel in order to investigate the effect of the cooling conditions on the properties of the formed layers. This method is more economical than others because it provides for faster nitrogen and carbon diffusion, which in turn allows for lower processing temperatures and/or shorter treatment times with satisfactory results. Two sample sets were carbonitrided in a gas mixture of 2 vol % CH_4, 20 vol % N_2, 78 vol % H_2 under a pressure of 400 Pa, discharge frequency of 9 kHz, temperature of 580 °C, during 90 minutes. The first sample set was cooled under vacuum and the second set was quickly removed from the furnace and then quenched in oil. The two sets were characterized by optical microscopy (OM), X-ray diffraction (XRD), and microhardness. Our results showed that it is possible to change the microestrutural profile of the carbonitrided steel by using different cooling modes. For the sample slowly cooled inside the chamber, the compound layer consists of ε-$Fe_{2-3}N$, γ'-Fe_4N, Fe_3C, γ-$FeN_{0.095}$, and CrN phases. The ε-$Fe_{2-3}N$ and γ'-Fe_4N phases of the nitrided layer are not detected for the sample cooled in oil. Also the α-Fe and $FeFe_2O_4$ phases where detected at the surface of the sample quenched in oil.

Keywords: steel, carbonitriding, plasma, compound layer, characterization.

Introduction

Carbonitriding of iron and steels has been used to improve both the mechanical and chemical properties of their surfaces. This technique is used to modify the substrate material surface in order to improve its mechanical properties. The new properties acquired by the substrate/coating system can be widely applied. Efforts have been made to develop plasma carbonitriding techniques for industrial applications [1,2].

Our recent studies [3,4] have shown that significant improvements can be achieved in the ion nitriding and/or carbonitriding processes and in the microstructure of the produced layers by different cooling conditions. In these studies, the Pulsed Glow Discharge (PGD) technique was used for nitriding and nitrocarburizing pure iron in order to investigate the effect of the cooling conditions on the characteristics of the formed layers.

The use of plasma for surface modification of stainless steels leads to a dramatic modification in tribological behavior [5–7] and enhanced corrosion resistance [8]. For austenitic (FCC) Fe–Cr–Ni alloys such as AISI 304, the mechanism for this improvement was attributed to an unusually thick layer of supersaturated N solid-solution FCC phase. The degradation was associated to the presence of CrN, formation of the σ-phase, and decrease of the chromium content [8]. The same surface layer was obtained by various techniques, such as beam implantation, plasma ion implantation, ion nitriding, and gas nitriding. Systematic studies of the energy, flux, and temperature dependence of the modified layer have been carried out [9]. However, few attempts have been made to understand the cooling conditions on the surface properties.

In this work, the Pulsed Glow Discharge (PGD) technique was used for nitriding steel in order to

investigate the effect of the cooling conditions on the characteristics of the formed layers. Two different cooling conditions were employed. In the first one, the samples were cooled inside of a vacuum chamber. In the second condition, the samples were cooled in oil. Differences in surface composition and morphology were investigated by optical microscopy (OM), X-ray diffraction (XRD), and microhardness.

Materials and Methods

Two sample sets with a rectangular shape (15 mm X 10 mm X 3 mm) were produced. The samples were ground and polished with chromium oxide (15 μm), and ultrasonically cleaned in alcohol. The plasma apparatus used for nitrocarburizing is similar to that described by Alves et al. [10]. It consists basically of a main chamber, a vacuum system, a gas system, a power source, and a data acquisition system. Two samples of AISI 304 stainless steel were carbonitrided in a gas mixture of 2 % vol CH_4, 78 % vol H_2, and 20 % vol N_2, under a pressure of 400 Pa, discharge frequency of 9 kHz, temperature of 580 °C, during 90 minutes. One sample was cooled in vacuum and the other was quickly removed from the furnace and quenched in oil. The microstructure was revealed using 2 % nital (2 % HNO_3 – 98 % CH_3CH_2OH) and was examined by a Zeiss Axiotech optical microscope. OM profiles were employed to determine the thickness of the nitride layer and transformed layer. Microhardness measurements were carried out on a Buehler 1660-6300 Knoop tester using a load of 25-50 g. Ten indentations were done in different locations on each sample surface. X-ray diffraction patterns were taken by using a Siemens D5000 diffractometer, with a Co Kα source ($\lambda = 0.17889$ nm) operated at 40 kV and 40 mA. The XRD measurements were performed with a 2θ scan step of 2° per minute in the range of 24°-114°.

Results and Discussion

Figures 1 and 2 show two cross-sectional OM micrographs of plasma carbonitrided samples cooled inside the vacuum chamber (Fig. 1) and in oil (Fig. 2). The compound layer of the sample cooled under vacuum is thicker than the one cooled in oil. For the sample cooled in oil, the γ-phase is present, and a thin compound layer is observed. It can be observed the changes in the surface morphology and in the layer thickness due to the different cooling conditions. For the samples cooled inside the chamber, it occurs only a compound layer with a thickness value of approximately 35 μm. For the samples cooled in oil, the first two layers thinned down significantly, with an irregular thickness value of approximately 5 μm for the compound layer, and 20 μm for the transformation zone.

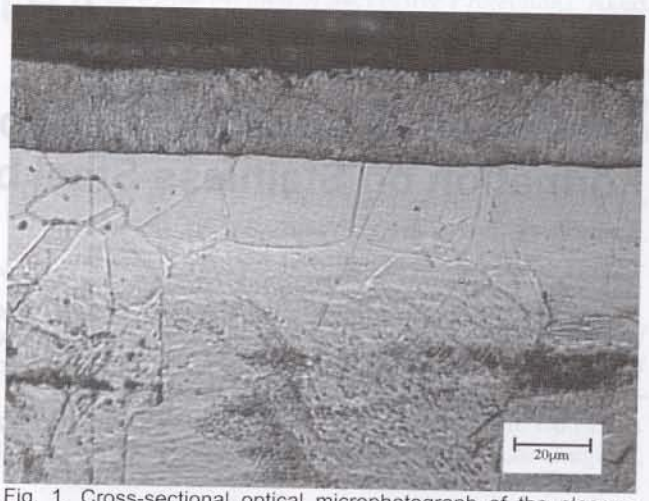

Fig. 1. Cross-sectional optical microphotograph of the plasma-carbonitrided steel cooled inside the vacuum chamber.

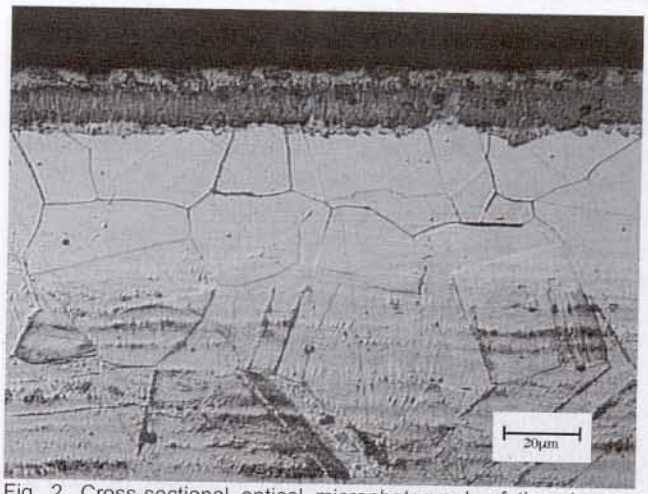

Fig. 2. Cross-sectional optical microphotograph of the plasma-carbonitrided steel cooled outside of the chamber in oil.

Figures 3 and 4 display OM micrographs showing the differences in the surface appearance for the samples cooled inside the vacuum chamber (Fig. 3) and in oil (Fig. 4). Fig. 3 reveals very small particles, of the order of a micrometer size. Pores were formed for the samples cooled under vacuum, increasing the contact area between the gas and the surface. The sample cooled in oil presented fewer surface pores than the samples cooled inside the vacuum chamber, and this is probably due to the formation of an oxide layer on the surface. This fact was confirmed by EDS, which detected some oxygen and no nitrogen for the sample cooled in oil.

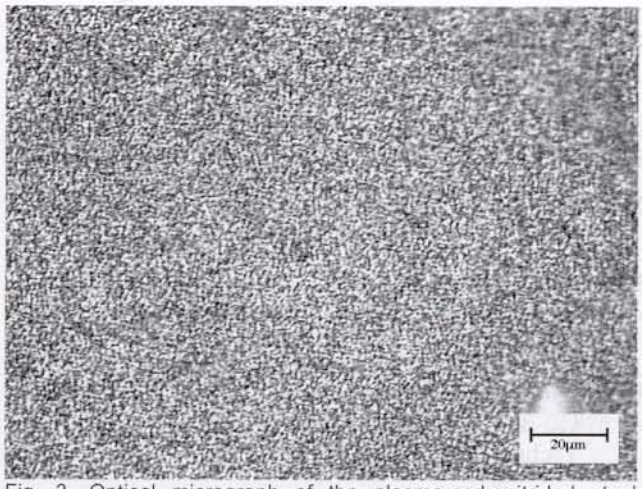

Fig. 3. Optical micrograph of the plasma-carbonitrided steel cooled inside of the vacuum chamber.

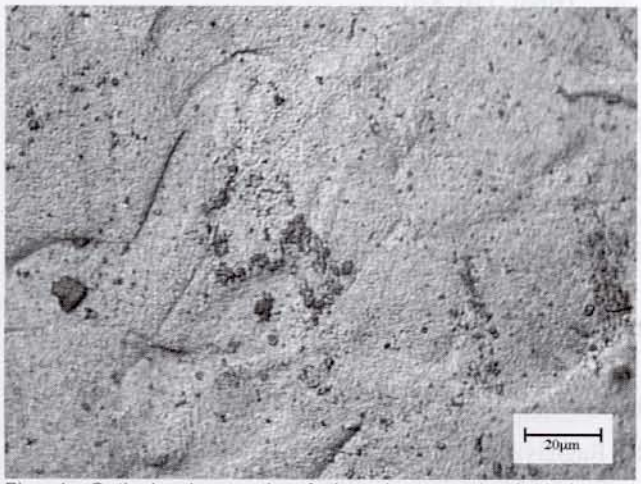

Fig. 4. Optical micrograph of the plasma-carbonitrided steel cooled outside of the chamber in oil.

The presence of the γ phase was observed by several investigators. Metin and Inal [11] reported that the interstitial nitrogen stabilizes the γ phase at temperatures above 590 °C. This γ phase transforms into γ' and α, according to the Fe-N phase diagram [12]. Kurny [13] presented a model explaining the presence of the nitrogen-enriched austenite (γ phase) as follows: the austenite transforms into γ' and α phases under slow cooling after nitriding and/or carbonitriding, and this would lead to its total extinction for long treatment times. For rapid cooling rates, the nitrogen saturation would diminish the temperature of the martensitic transformation and the metastable γ phase would remain. The presence of a transformation layer for the samples cooled in oil, observed in this work, seems to corroborate Kurny's results.

Fig. 5 indicates the presence of ε-$Fe_{2-3}N$, CrN, Fe_3C, and γ'-Fe_4N phases for the sample cooled under vacuum. Fig. 6 reveals that the peaks associated to the ε-$Fe_{2-3}N$ and γ'-Fe_4N phases from the nitride layer almost disappeared for the sample cooled in oil, while α-Fe and Fe_3O_4 phases were detected at the surface. A nitrogen-enriched austenite phase (γ_N) was detected under the nitride layer for both cooling conditions.

Due to the precipitation of CrN, the corrosion resistance of the layer is greatly decreased for the two samples. Xu et al. [14] suggest that the diffusivity of substitutional atoms is greatly increased as the treatment temperature is raised. They mention that the bonding between Cr and N is greater than that of other substituitonal atoms with N, so the CrN can nucleate and grow [14]. The results of the two cooling modes suggest the transformation of the γ-phase in γ'-Fe_4N and ε-$Fe_{2-3}N$.

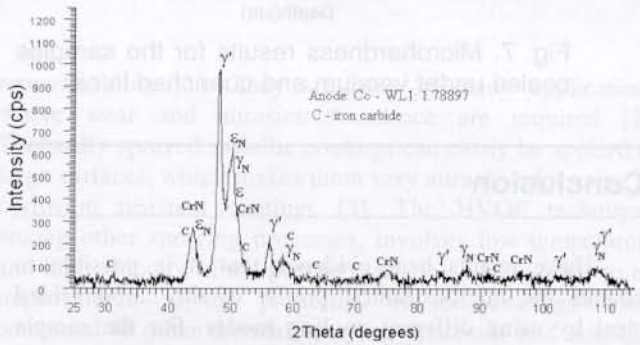

Fig. 5. Diffraction pattern of the plasma-carbonitrided steel cooled inside the vacuum chamber.

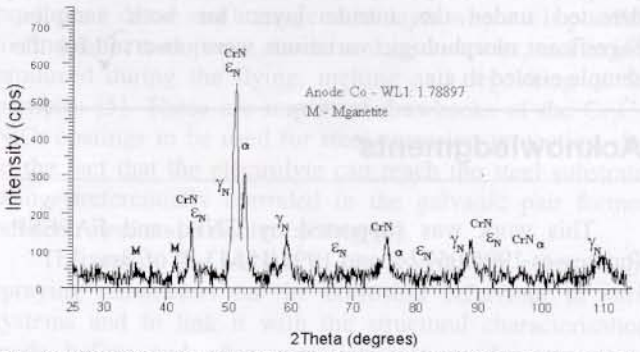

Fig. 6. Diffraction pattern of the plasma-carbonitrided steel cooled in oil.

Figure 7 shows the microhardness test results as a function of depth for the samples cooled under vacuum and in oil. The longer cooling rate used for the sample set cooled under vacuum caused a better diffusion of nitrogen and carbon, which produced the formation of more stable phases, such as γ'-Fe_4N, and a larger growth of the compound layer. In contrast, the samples quenched in oil showed an irregular nitride layer, followed by a well-defined austenite transformation zone. The lack of γ'-Fe_4N phase in these layers can be explained by the rapid cooling rate, which impeded the formation of γ'-Fe_4N, but rendered a solid solution containing nitrogen and carbon. This solid solution presents a microhardness plateau

similar to that occurring for the samples cooled outside the chamber.

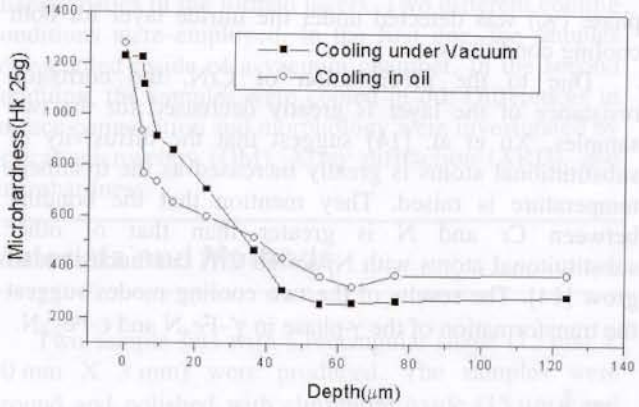

Fig. 7. Microhardness results for the samples cooled under vacuum and quenched in oil

Conclusion

These results bear evidence that it is possible to change the microestrutural profile of the carbonitrided steel by using different cooling modes. For the sample cooled inside of the chamber, the compound layer is formed by ε-$Fe_{2-3}N$, γ'-Fe_4N, Fe_3C, and CrN phases. The presence of a nitrogen-enriched austenite phase (γ_N) was detected under the nitride layer for both samples. Significant morphologic variations were observed for the sample cooled in air.

Acknowledgments

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