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On the Nitrogen Diffusion in a Duplex Stainless Steel

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Duplex Stainless Steels (DSS) have excellent corrosion resistance properties and poor wear resistance. Plasma nitriding is used to increase the surface hardness, by nitrogen diffusion into the crystal lattice, and to improve wear resistance. In this study, DSS samples were plasma nitrided at temperatures between 350 °C and 500 °C for 240 minutes under an atmosphere of 75% N2 + 25% H2 . Aparent diffusion coefficients, activation energy and pre-exponential constant were calculates using the first law of Fick for each material phase, austenite and ferrite. Nitrogen diffusion in both phases appears to be similar. The layer thickness on the alpha phase is greater than in the gama phase. Nevertheless, the difference on the layer thickness in both of the phases is small. From these results, it was proposed a model of nitrogen diffusion into a two-phase stainless steel to explain the morphology of the interface between the layer and the substrate.

Keywords: *plasma nitriding, duplex stainless steel, nitrogen diffusion, expanded austenite*

1. Introduction

Duplex stainless steels (DSS) are used in applications where they must have good wear resistance properties, having a good resistance to corrosion. To accomplish this, DSS are submitted to thermochemical treatments as plasma nitriding to increase the surface hardness[1,2], wear resistance[3] and fatigue properties[4]. Nitriding is done at low temperatures to prevent nitrides formation, which reduces corrosion resistance[5]. Hardening is given by the nitrogen diffusion into the crystal lattice. Although the mechanism of diffusion of nitrogen in austenitic stainless steels (ASS) has been extensively studied[6–8]. In the case of DSS there are studies where nitrided layer properties are evaluated[5,9,10], but the mechanism of formation and the morphology of the layer have not been deeply studied[11,12]. This study aims to study the kinetics of nitrided layer formation on DSS and its morphology.

2. Material and Methods

The material used in this study was a duplex stainless steel with 0.01% C 3.06 Mo 5.82% Ni 21.89% Cr Fe in balance chemical composition. Specimens of 20×10×5 mm were cut, plasma nitrided and characterized by Scanning Electron Microscopy (SEM). Before nitriding, perpendicular to lamination direction face of the specimens was mechanically ground and polished with diamond paste down to 1 µm.

Passive film was removed through a sputtering step of pure Argonium plasma at 350 °C for 1 hour. Specimens were DC-plasma nitrided on the perpendicular to lamination direction face at 350, 400, 450 and 500 °C for 240 minutes in a 75% N2 + 25% H2.

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Nitrided layers, obtain for each temperature, were measured on the micrographs using a conversion of the rule present on the photographs and the real distance on them.

3. Results and Discussion

Microstructures of nitride layers, for each temperature, are present on Figures 1 to 4.

Table 1 shows that temperature increase leads to formation of thicker nitrided layers.

Diffusion coefficients were calculated as function of layer thickness obtained for each treatment temperature, using the Equation 1

$$d=(Dt)\hat{}(1/2) \quad (1)$$

where "d" is the thickness layer, "D" is the diffusion coefficient for nitrogen and "t" is the treatment time. In addition, shown on Table 2.

Calculated diffusion coefficients for austenite and for ferrita are apparent for nitrogen diffusion in each phase. In theory, coefficients of ferrite phase should have around two orders of greatness rather than coefficients for nitrogen in austenitic phase. This is because the nitrogen diffusion in this system is not completely explained by Fick's first law (solid state diffusion)[13]. There are other associated mechanisms, which will be explained later.

It was not possible to find any study in literature that report diffusion coefficients values, for nitrogen in a duplex stainless steels for nitriding at low temperature. By comparing the values of the coefficients of Table 2 and those reported in literature for austenitic stainless steel, it can be seen that the diffusion coefficients found in this study to austenite even with different microstructure are similar to those found in the literature[8,13–15], they are of the same order of magnitude.

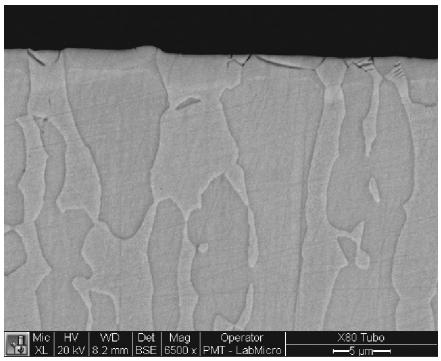

Figure 1. Nitrided layer obtain at 350 °C.

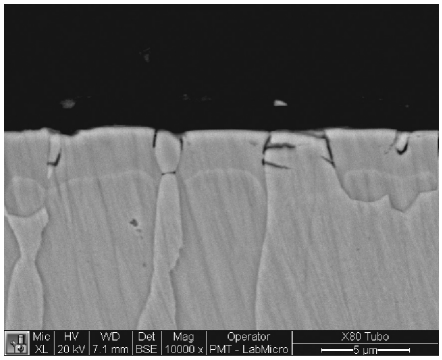

Figure 2. Nitrided layer obtain at 400 °C.

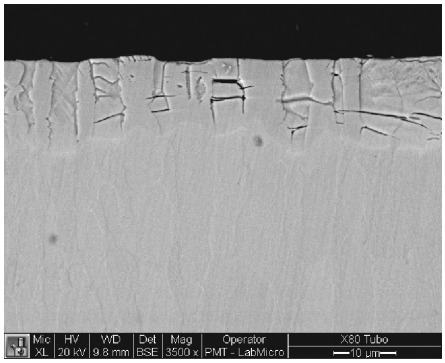

Figure 3. Nitrided layer obtain at 450 °C.

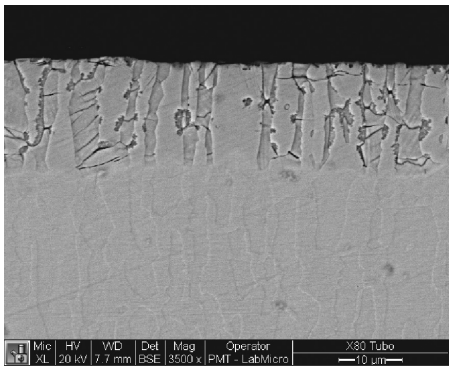

Figure 4. Nitrided layer obtain at 500 °C.

Table 1. Layer thickness obtained for each plasma nitriding treatment for austenite and ferrite phases.

Temperature °C	Experimental Thickness (µm)	
	Austenite	Ferrite
350	2.0	2.4
400	2.3	3.3
450	11.6	13.4
500	19.6	20.6

Table 2. Calulated diffusion coeficients for each phase and nitriding temperature form the experimental layer thickness

Temperature °C	D (m2/s)	
	Austenite	Ferrite
350	2.73386E-16	4.06908E-16
400	3.769E-16	7.45612E-16
450	9.32314E-15	1.24172E-14
500	2.6668E-14	2.9348E-14

Furthermore, when comparing the values of the coefficients found for austenitic stainless steels is noticed that are not equal, even though it has the same crystal structure. These results show that nitrogen diffusion into the crystalline lattice of stainless steel depends on microstructure of the material, alloying elements present[8,16], and crystallographic orientation (texture)[13,17]. In the specific case of single crystal (111)[17], the estimated coefficient is very close to that found in this work for the austenitic phase.

From the curve ln D vs. 1 / T in Figure 5, it is possible to determinate the activation energy and pre-exponential constant.

Some authors calculated the diffusion coefficients from mathematical models that describe the diffusion process of nitrogen in austenitic stainless steel. Moskalioviene[13] calculated that the value of the pre-exponential constant was 8.37 E-6 m2 / s and Parascandola[18] assumed for their calculations of nitrogen diffusion profiles a pre-exponential constant of E-7 m2 / s. For the activation energy, both Parascandola[18] and Möller[19] assumed to his calculations the value of 1.1 eV. Comparing the activation energy values reported on literature with those calculated for the austenitic phase of the duplex stainless steel in this study, the difference was only 0.18 eV. This suggests that diffusion in the austenitic phase of duplex stainless steel has an energy barrier similar to that found for the diffusion of nitrogen in expanded austenite in austenitic stainless steels. It was also observed that ferrite and austenite have similar activation energies. In the case of pre-exponential constant, by comparing the calculated by Parascandola[18] with the calculated in this work, the difference is about an order of magnitude. However, when comparing with the results found by Moskalioviene[13], the value is very similar to the pre-exponential constant found in this study. This result was expected because the presence of ferrite in the material in some way influences nitrogen diffusion into austenite phase. This is because an interstitial atom can diffuse faster in a body centered cubic structure (ferrite) than in face-centered cubic structure (austenite), as will be discussed later.

4. Morphology of the Nitrided Layer

Under ideal conditions, assuming that nitrogen diffusion into the equilibrium phases (ferrite and austenite) of iron and that the layer formation was entirely controlled by diffusion volume, it is possible to calculate the layer thickness, knowing the diffusion coefficient at each temperature using Equation 1, sendo D=D0exp(-Q/(RT))

Where D0 and Q are the diffusion constants for nitrogen into iron.

In Table 3 are the diffusion coefficients calculated for each theoretical stage, using the theorical values for nitrogen diffusion, D0 as 0.0047 cm2/s for ferrite and 0.0034 cm2/s for austenite and Q as 18300 cal/mol for ferrite and 34600 cal/mol for austenite[20]. Moreover, are listed the theorical layer thickness. Theorical layer morphology is presented in Figure 6.

These results, however, consider only unidirectional diffusion in each phase (austenite and ferrite) of duplex stainless steel. According to the theoretical values of thickness of the layer (d) shown in Table 2, whereas unidirectional diffusion, formation of the nitride layer in the material during the nitriding process can be schematized as shown in Figure 6.

This morphology is explained because there is difference of diffusion of nitrogen in the two phases of the material. The diffusion of an atom there are two properties that directly affect, solubility and diffusivity. The solubility is associated with a number of atoms which can stay within the unit cell in this case CFC (austenite) structure can accommodate many more nitrogen atoms therein than CCC structure (ferrite). The diffusivity is associtated with the facility that an atom has to move within the crystalline lattice, overcoming barriers formed by substitutional atoms in the lattice. The interstitial atoms can move faster within the body-centered cubic structure because the atom packing factor is lower. Therefore, lower atomic density, which is why it is easier to cross it. Already nitrogen diffusion in austenitic structure is much more difficult due to the higher atom packing factor of CFC structure, compared with the ferritic structure CCC. In summary, the diffusivity is greater in CCC than in CFC structure and solubility is greater in CFC than in CCC. This can explain the thickness difference between the phases.

The theoretical morphology as calculated above, shown in Figure 6 does not correspond to the morphology observed in this study, which is shown schematically in Figure 7.

This morphology was also reported by other authors. Bielawski[11] explains that this layer shape demonstrates that diffusion in ferrite and austenite are different. As growth in the ferrite phase is faster than in austenitic phase giving rise to the concavity of the arc formed in the layer. The

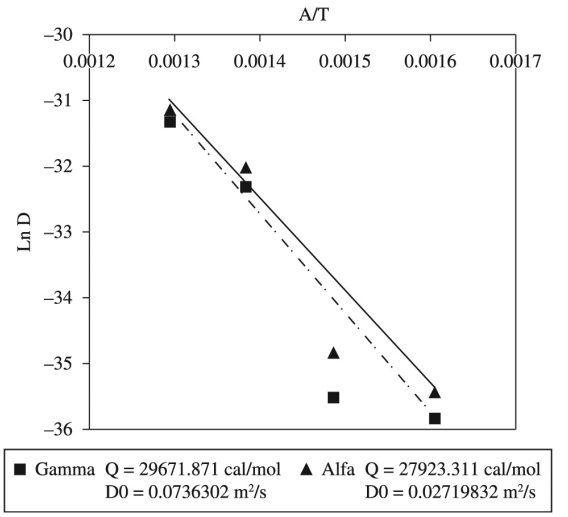

Figure 5. Determination of the activation energy and de preexponencial constant using a linear regression.

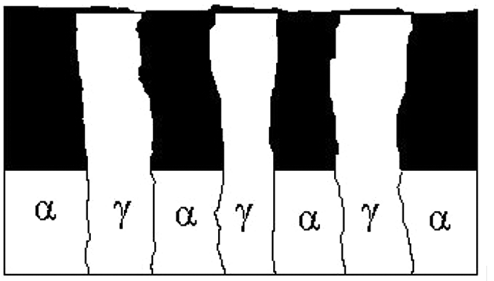

Figure 6. Theorical morphology of the nitrided layer. Only is considered bulk nitrogen diffusion.

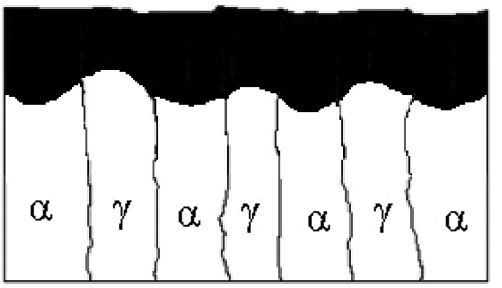

Figure 7. Experimental morphology of the nitrided layer.

Table 3. Theorical values of diffusion coeffients and layer thickness for each phase and temperature

Temperature °C	Theoric diffusion coef (cm2/s)		Theorical layer thickness (um)	
	Austenite	Ferrite	Austenite	Ferrite
350	2.4701E-15	1.78601E-09	0.059640093	50.7134669
400	1.9704E-14	5.35635E-09	0.168445048	87.82449058
450	1.17939E-13	1.38E-08	0.41210728	140.9683075
500	5.60056E-13	3.14573E-08	0.898042436	212.8344084

layer thickness is greater on the ferritic grain and becomes smaller above the austenitic grain. Christiansen[21] explains the difference in thickness grain by grain is due to the effect of the difference in the chemical composition of the austenite and ferrite in solubility and diffusivity of nitrogen in the development of expanded austenite.

By comparing the values of the thicknesses theoretical and experimental, presented in Table 1 and 3, for the ferrite phase, theoretical thickness is much greater than that found experimentally. In the austenitic phase, the experimental thickness is much greater than the theoretical. We conclude that the layer formed in the ferrite decreases and that formed in the austenite increases.

Analyzing this result might be thought that the formation of the layer, the phenomenon of diffusion of nitrogen is not just unidirectional, as assumed by the theoretical model (Figure 6).

Actually, there are four nitrogen fluxes that produce the experimental layer morphology:

1. Flux from the atmosphere into the interior of the material: existing nitrogen plasma atoms enters inside the material to form the nitrided layer. This is the main flux of nitrogen and which expains the growth layer inside the material.
2. Grain boundary diffusion: the nitrogen diffusion occurs not only in the volume of the substrate, but also by the grain boundary. This flux explains that this atom to enter the existing phases between gamma and alpha limits, which makes the resulting interface is formed by recesses (Figure 7) and not by a straight line (Figure 6).
3. Lateral Flow of nitrogen from the ferrite to the austenite: the diffusion of an atom depends not only on the available interstices where can stay and obstacles that exist in the material. The diffusion also depends on the thermodynamic equilibrium that exists between the two crystalline phases: alpha and gamma, i.e. nitrogen in the activity is the same in all phases of the material. Nitrogen will always tend to move from ferrite to austenite to reach equilibrium.
4. Bulk diffusion.

According to the four flows discussed, the formation mechanism of the nitrided layer can be proposed as follows:

This plasma nitriding the nitrogen is in the form of cations. The atoms of this element are attracted to the surface of the sample (cathode). Once the N reaches, the surface begins to spread into the interior of the material as both the grains by their contours. To the extent that the material is enriched in nitrogen, the contours of the regions enriched migrate to the interior of the grain. The extent to which the layer is growing, part of the nitrogen present in the alpha phase diffuses into the austenite, so that trying to reach thermodynamic equilibrium.

5. Conclusion

Nitrogen atoms take four paths to diffuse into de material, which explains the layer morphology. Also is important to conclude that the nitrogen diffusion into DSS is not unidirectional, nitrogen atoms have almost three direction to diffuse into the material, being the flux from ferrite to austenite, which leads the formation of a layer with small differences in thickness layer in both phases.

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