PLASMA NITRIDING OF HIGH-ALLOY STEELS

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ABSTRACT

Plasma nitriding is in many cases one of the few ways to increase the wear resistance of a surface in high alloy steels. These are hot-rolled steels and high-speed steels, but they are mainly a whole group of stainless steels with a chromium content of over 12%, where in addition to the requirement to increase surface hardness, there is also a requirement to ensure sufficient corrosion resistance. The thesis describes some aspects of this process, the influence of process parameters, and ways that allow these processes to lead safely to the desired results.

1. Introduction

Nitriding is the process of saturating the steel surface with nitrogen. In order for this nitrogen diffusion process to be realized, it is necessary to create its atomic form. In gas nitriding processes, its formation is linked to the thermal cracking of ammonia and for this reason these types of processes are not well controllable for high-alloy steels. The size of the nitriding number **Kn** is related to the degree of dissociation of NH_3 and for the necessary reduction of its value below **Kn = 1** it is necessary to use high nitriding temperatures of the order of over 550 ° C. In general, these types of steels cannot be optimally nitrided in gas below 480 ° C because the degree of dissociation of NH_3 is low, but at the same time **Kn** is high. High temperatures can then have a negative impact on other properties of high chromium content, such as corrosion resistance, even when **Kn** decreases.

$$Kn = p_{NH3}/(p_{H2})^{3/2}$$

Another situation is in nitriding in plasma, where atomic nitrogen is obtained by the cracking of a nitrogen molecule in glow discharge. This process is tied exclusively to the electrical parameters of the discharge, its relationship to temperature is secondary and minor. For this reason, the plasma nitriding process is applicable from low temperatures, with the lowest practical ones being around 350 ° C. The plasma nitriding process is completely feasible in a mixture of pure N_2/H_2 gases in the absence of NH_3 and the value of nitrogen activity is completely independent of NH_3 dissociation.

$$x = k * \sqrt[2]{Do * e^{(-Q/RT)} * t}$$

However, the problem of low temperatures is in the diffusion equation, where there is an exponential dependence of the diffusion depth on the nitriding temperature, diffusion constants and activation energy. The process times to reach an acceptable diffusion depth are extended to unbearable times at low temperatures, which means that the process is economically unusable or changes in perspective.

This problem of time economy is all the more significant the more nitride-forming alloying elements in steel are contained. Although the solubility of nitrogen in **α-Fe** increases with increasing number of alloying elements, the diffusion coefficient decreases significantly and the activation energy required to ensure the movement of the nitrogen atom in the matrix increases.

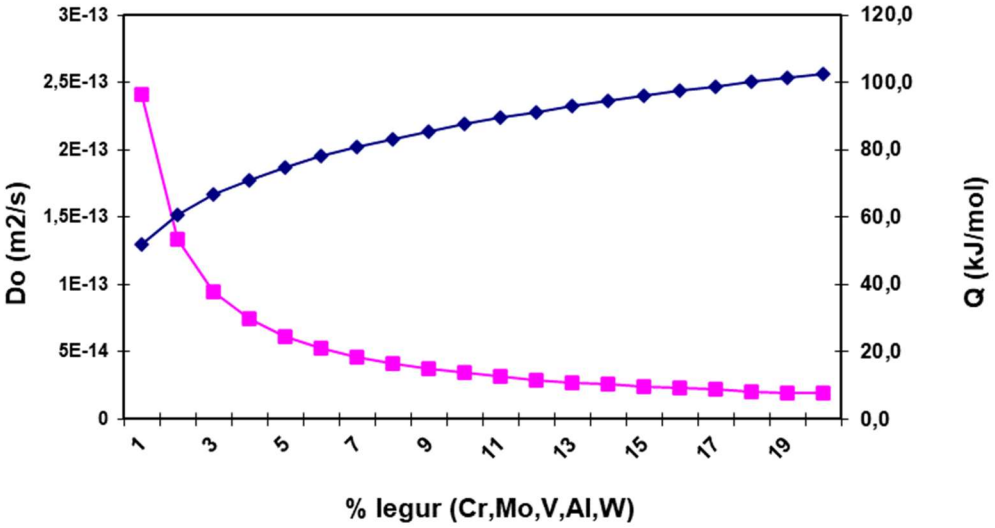

Fig. 1 *Diffusion coefficient **Do** and activation energy **Q** values versus the number of nitride-forming alloying elements.*

2. Stress in layers

The accompanying phenomenon of nitriding are compressive stresses arising from the filling of interstitial free positions in iron **α-Fe**, resp. in austenite **γ-Fe**. The macroscopic manifestation of these compressive stresses is the change in the lattice parameter measured by X-ray analysis,

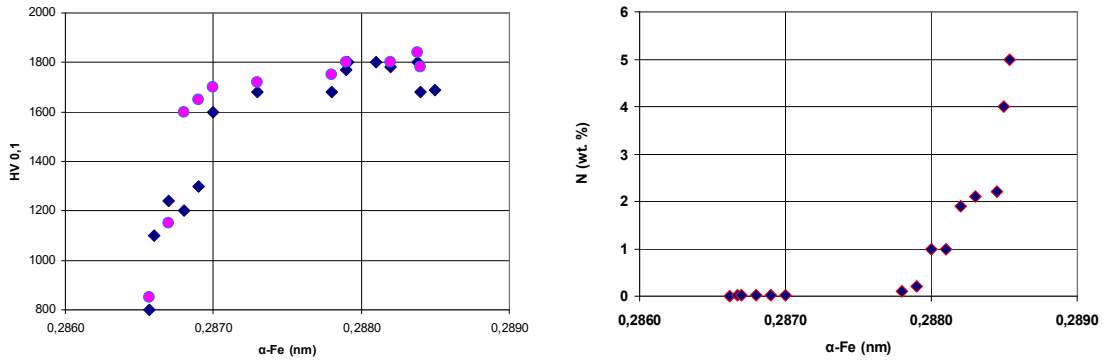

Fig. 2 *– Layer microhardness **α´-Fe(N)** as a function of the lattice parameter value in **HSS 19830** (1.3343) steel, and nitrogen content as a function of the lattice parameter in the same steel.*

the external manifestation is then the hardness of the layer. In the case of steel type HSS 19830 (1.3343), these stresses were measured with a magnitude of up to 3-4 GPa, while microhardness above 1000 HV is achieved already with an **N** content above **1 wt.%.** Therefore, in order for such stresses not to lead to the formation and propagation of cracks due to insufficient strength of the base material, sufficient strength and toughness of the layer, resp. base material is needed.

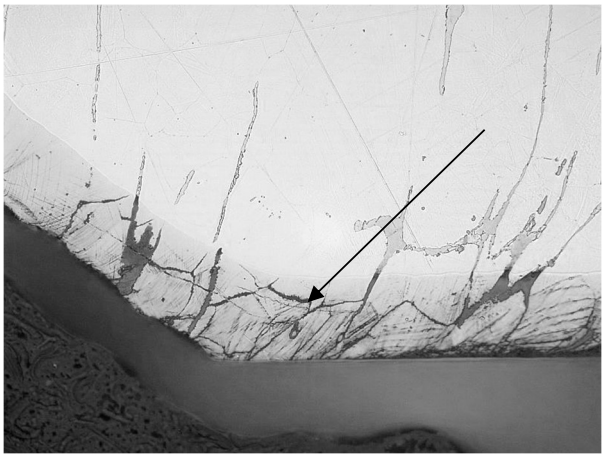

Fig. 3 *– Layer microstructure in 1.4922 steel with typical horizontal cracks (magnified 500x)*

In the process of plasma nitriding of materials 1.4922, 1.4571, cracks were found in the layer, laid horizontally at a depth of 10 - 30 μm. During the X-ray analysis of the crack layer in the material 1.4922, compressive stresses up to 420 MPa were found, ie stresses which cannot directly result in layer failure, also precisely because it is still a solid solution of nitrogen in **α-Fe**, without any compound layer. However, since the same stresses were found in both the radial and tangential directions, it can be hypothesized that on this type of material, which is characterized by a high density of dislocations, the layer will slip due to these tangential stresses, in a plane parallel to the surface. material. Cracks also release the stress in the layer and therefore the amount of stress is lower than would be expected.

3. Resistance to corrosion

Most high chromium steels are expected to have increased corrosion resistance at both low and high temperatures. However, as a result of nitriding, the **Cr-O** bond, which provides this corrosion resistance, is replaced by a **Cr-N** bond. This reduces corrosion resistance and is an undesirable phenomenon in most applications.

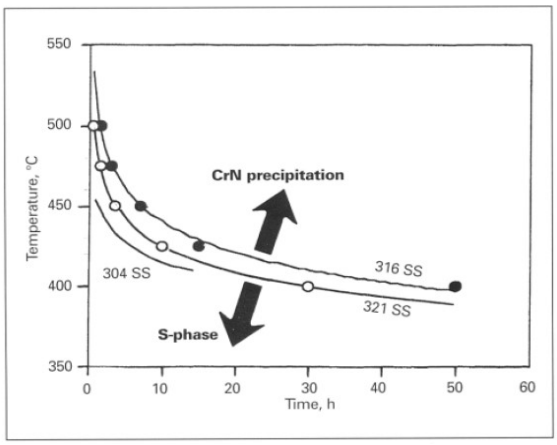

Fig. 4 *– A diagram that shows boundary between* ***CrN*** *development and* ***S-phase****, oversaturated nitrogen austenite*

Therefore, in order to eliminate this negative phenomenon, nitriding should take place at low temperatures of 400-450 °C, at which chromium nitride precipitation does not occur, or only to a minimal extent. However, these low temperatures also determine the method of nitriding and the possibilities of this process with regard to the combination of a very low diffusion rate due to the high alloying of the steel, and a low nitriding temperature. For these reasons, gas nitriding processes can almost be ruled out.

4. Experiment

Samples of steels 1.4922 and 1.4923 were nitrided at 525 °C, time 16 h, atmosphere **N_2/H_2 = 1/10.** Samples before nitriding were vacuum hardened from 1040 °C/2h to oil, and tempered to 720 °C/2h and 580 °C/2h to a final strength of 280, respectively. 350-370 HB10/3000. The measured diffusion depth was 90 - 100 μm.

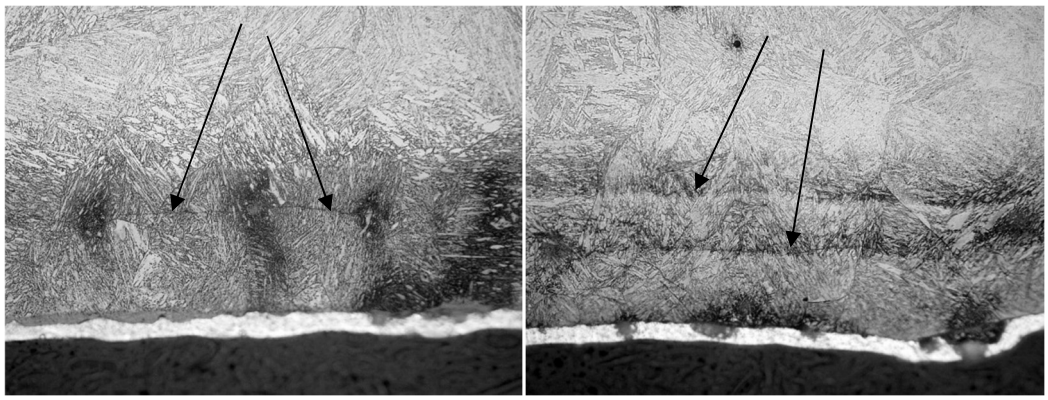

Fig. 5 a, 5b *– Metallography of layer 1.4922, 720/2h, 400x and 1.4922, 580/2h, 400x with cracks*

Cracks in a plane parallel to the surface were found in both cases and in both materials.

In another experiment, samples from the mat. 1.4923, 1. 4571 and 17240 nitrided at 450 °C, 8h, **N_2/H_2 = 1/20**. The aim was to reduce the stress in the layer as much as possible by reducing the diffusion depth. Some samples were additionally annealed at 620 °C/4h after the nitriding

process, the time between the nitriding and annealing process was 6 hours. The resulting microhardness measured HV0.3 is in the following table:

sample	material	avr	HV0,3			
1	W.Nr. 1.4923	**1434**	1433	1405	1478	1419
1	W.Nr. 1.4571	**1221**	1261	1181	1274	1168
1	CSN 17240	**1265**	1298	1250	1274	1238
2	W.Nr. 1.4923	**771**	786	769	775	752
2	W.Nr. 1.4571	**1055**	1089	1070	1025	1034
2	CSN 17240	**1160**	1181	1181	1160	1119

In all cases, even at 1/20 atmosphere, the expected microhardness of the layer was achieved, and this microhardness was maintained except for steel 1.4923 where there was a significant decrease in hardness to 752-786 HV0.3.

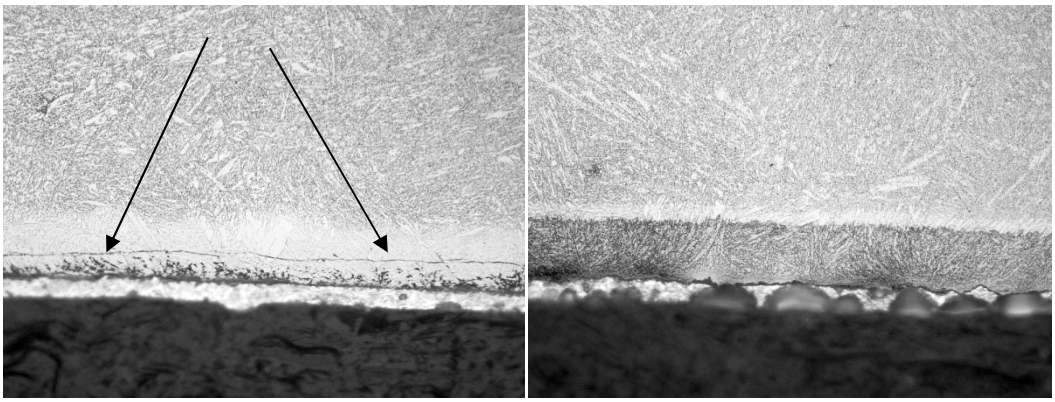

Fig. 6 a 6b *– Metallography of layer in steel 1.4923; layer after nitriding only and with cracks on the left, after nitriding and annealing and with no cracks on the right*

Even at a reduced diffusion depth to a level of approx. 30 µm, cracking of the layer was not prevented. The layer still shows horizontal cracks, the formation of which is not easy to explain. In contrast, all layers that have undergone additional annealing after nitriding show a nitriding layer without cracks and damage. The diffusion layer after etching is very even and homogeneous.

5. Conclusions

Nitriding of high-alloy materials with a chromium content of more than 12% while maintaining sufficient corrosion resistance is proving to be a complex problem. The compressive stresses in the layer reach considerable values, although this could not be proven radiographically. However, the X-ray method is a cross-sectional method and cannot unambiguously affect the stress in the individual layers. However, due to the high values of microhardness, these stresses exist. It is probable that the tangential component of the compressive stresses leads to the slippage of the layer on the dislocations in a plane parallel to the surface. However, despite attempts to reduce these stresses by reducing the diffusion depth or increasing the nitriding

temperature, the desired effect has not been achieved. Only by including the annealing process at 620 °C/4 h after nitriding, the behavior of the layer was significantly improved. For 1.4923, the hardness has dropped to 750 HV0.3, but even these values are acceptable for use in applications with increased mechanical wear resistance at high temperatures. The difference in the behavior of steels 1.4923 and 1.4571 and 17 240 is due to the fact that steel 1.4923 (1.4922) is of the martensitic type, steels 1.4571 and 17240 are purely austenitic, with an even higher chromium content of 17 to 18%.