Plasma nitriding for duplex coating on HSS steel

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Abstrakt

The technology of duplex coating is based on combination of nitrided surface and think layer deposited by PVD method. Except unique installation when all is done during one process, the majority of applications are done separately. The nitriding process is made in nitriding furnace and PVD layer in special devices for this technology. PVD technology has a clear definition, the nitriding process not. In this paper is description of some problems related to the selection of nitriding method and the description of correlation between nitrided surface and adhesion of PVD layer,.

1. Introduction

At present, the requirements for the so-called duplex coating, ie the combination of nitriding and PVD technology of thin film deposition such as TiN, TiAlN, etc., are increasing. However, it is known from practice that if the nitriding process is not part of the coating process, there are problems with the adhesion of the layer on the nitrided surface. This is due to low knowledge of the nitriding process, and the influence of the nitrided surface on the adhesion of the layer from the deposition process. This work aims to partially clarify the relationship between the nitrided surface and the TiN layer and to try to find optimal properties for the adhesion of the layer.

2. Theory

It can be seen from the **Fe-N** phase diagram that the nitriding layer can consist of up to 4 different phases depending on the nitrogen concentration in the layer, starting with a solid solution of **α´-Fe (N)** with different nitrogen content, nitrides **γ´-Fe_4N**, **ε-$Fe_{2-3}N$**, up to the **ζ-Fe_2N** phase. The relationship between the TiN layer and the nitrided surface is determined solely and exclusively by the condition of the surface, not the diffusion profile of the nitrided layer.

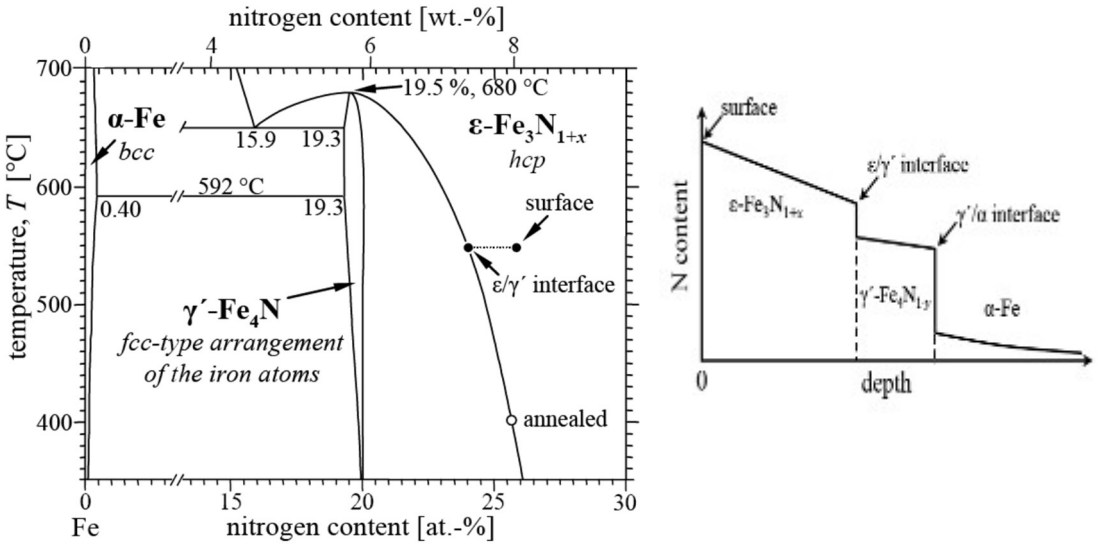

Fig. 1 *- Fe-N phase diagram and theoretical profile of nitrogen concentration in the nitrided layer*

In terms of hardness, the individual phases behave as follows:

HV(α´) > HV(γ´) > HV(ε) > HV(ζ) > HV(α) ~ HV(γ)

The highest hardness is reached by a solid solution of nitrogen in iron **α**, nitride phases with a higher concentration of nitrogen show a lower hardness.

The adhesion of the **TiN** layer on the steel surface is realized only through the covalent bond between the individual atoms. If we consider ideal conditions, then the epitaxial growth of the **TiN** layer on the iron lattice would be optimal. This situation can only occur if the lattice parameters have the same or similar dimensions.

However, it can be seen from Fig. 2 that the basic lattice parameters are not identical. Thus, a variant of epitaxial growth is unlikely, although there is work demonstrating epitaxial growth of the **TiN** layer on **M_6C** or **VC** carbides.

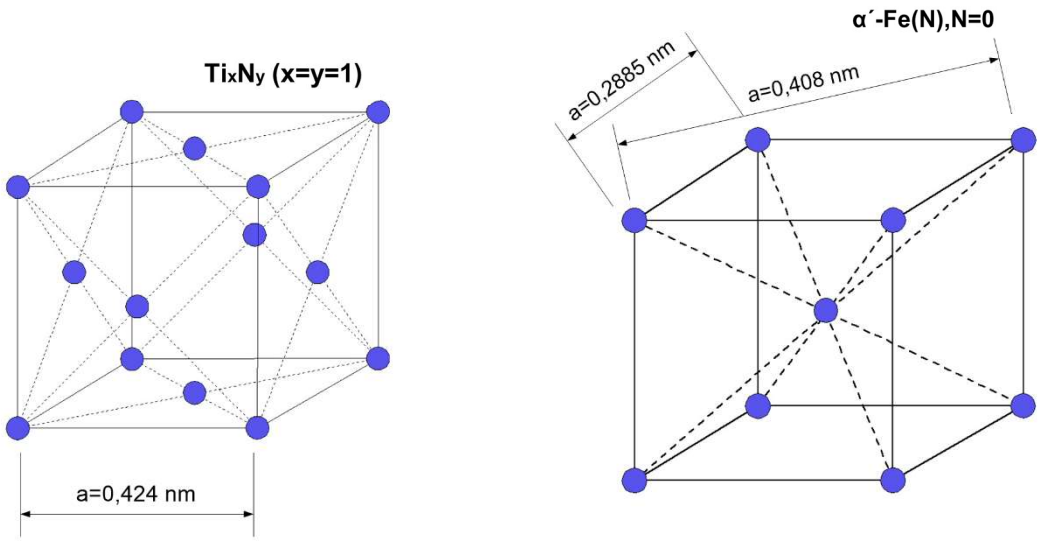

Fig. 2 *– Crystal lattice Ti_xN_y (x=y=1) (fcc) and α´-Fe(N),N=0 (bcc)*

3. Experiment

The following experiment was performed to assess the adhesion behavior of the **TiN** layer on the nitrided surface. The sample made of HSS 19830 (1.3343) with a length of 100 mm was plasma nitrided in a atmosphere of dissociated **NH_3**. The nitriding process created a nitriding layer with **NHD = 0.125 mm** and with a nitride surface layer with a thickness of **2-3 µm**. (Fig. 3)

Subsequently, a wedge in the ratio of 1: 1000 was ground on the sample, and a layer of TiN with a thickness of. 3.23 + 0.2 µm in a Leybold Z700 installation with two pairs of planar magnetron.

A complete phase X-ray analysis was performed on the sample after nitriding, and the microhardness was measured at individual points of the wedge. After deposition of the TiN layer, the adhesion of the layer was measured on a scratch test with acoustic emission.

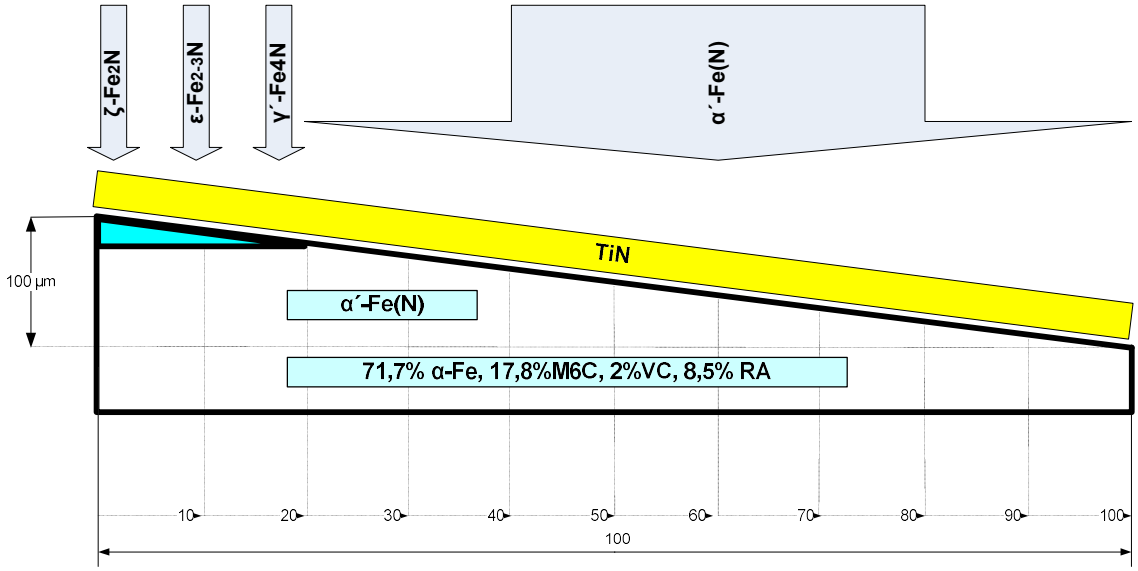

Fig. 3 *– Schematic drawing of the experiment*

4. Result of measurement

Using phase X-ray analysis, lattice parameters were calculated (Fig. 4), and macroscopic stresses from the shift of diffraction lines (Fig. 5). For consistency of values, a correction was made for alloying elements in steel 1.3343.

The results of the **TiN** layer adhesion measurement are shown in Fig. 6, surface hardness measured by **HV0,1** at Fig. 7 and nitrogen content in **wt%** on Fig. 8.

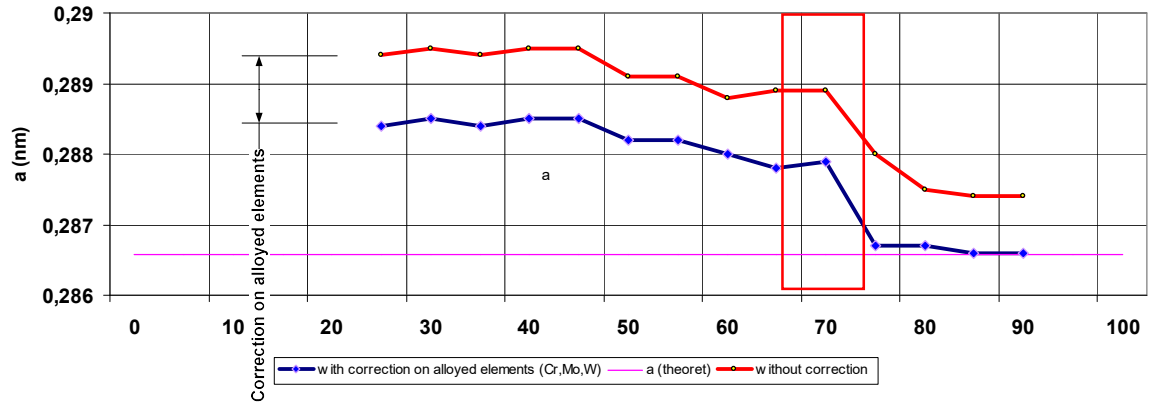

Fig. 4 *– The size of the lattice parameter of a solid solution α′-Fe(N), N=0-5,7 wt%*

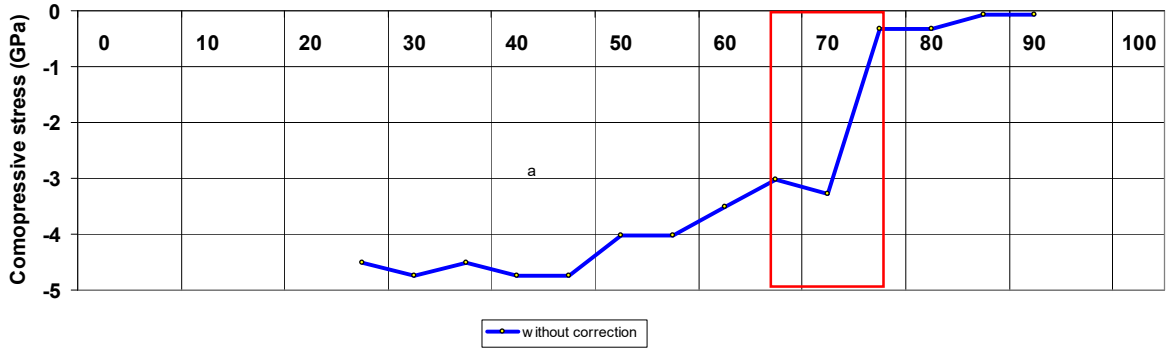

Fig. 5 *– Recalculated compressive stresses in the nitriding layer α′-Fe(N), N=0-5,7 wt%*

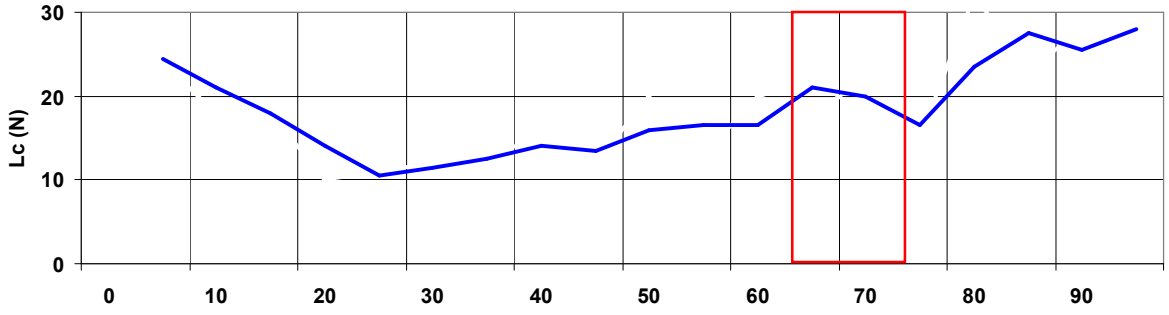

Fig. 6 *- The values of the critical force Lc when measuring the adhesion of the TiN layer*

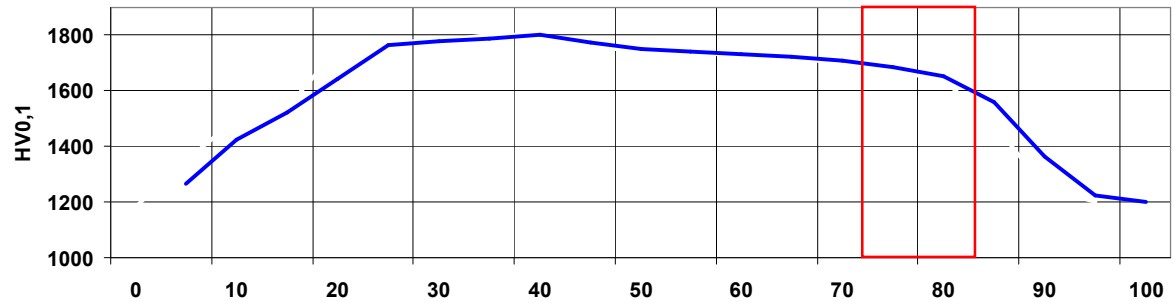

Fig. 7 *– HV0,1 hardness of the nitride surface*

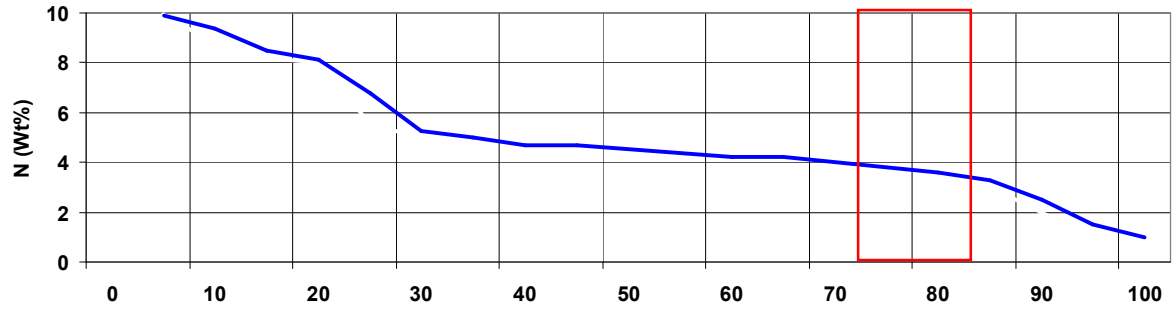

Fig. 8 *– Nitrogen content in wt%*

5. Discussion

Fig. 9 shows the dependence of the compressive stress values on the lattice parameter **a** (nm). This dependence is linear and expresses the expansion of the **α´-Fe (N)** lattice due to interstitial nitrogen. If we also assign the nitrogen content at individual measurement points, we get the dependence of the size of the lattice parameter on the nitrogen content (Fig. 10) and microhardness (Fig. 11).

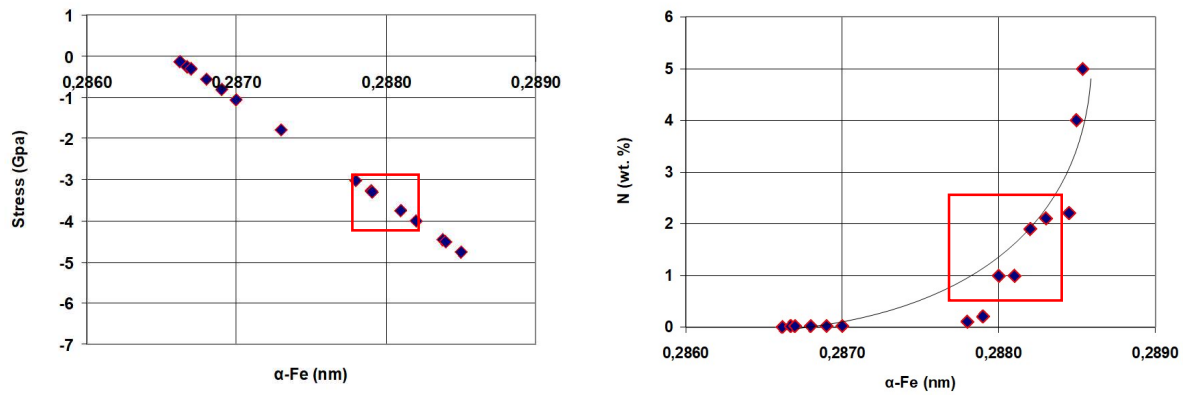

Fig. 9 and 10 *– The dependence between the lattice parameter and the values of the compressive stress, and the dependence of the change in the lattice parameter based on the nitrogen content in the solid iron solution* ***α****.*

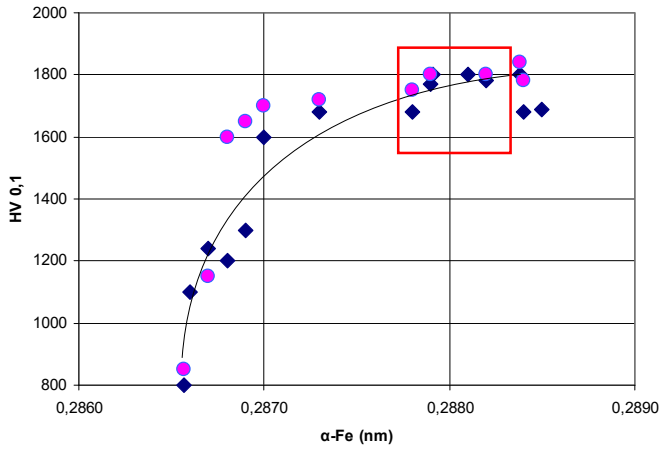

Fig. 11 *– Correlation between lattice parameter α´-Fe(N) and microhardness*

It is clear from the adhesion measurement that the minimum critical force is at the interface between the solid solution **α´-Fe (N)** and the area where the nitride layer begins to form. With lower nitrogen content, adhesion increases. The optimal combination of properties is in the area where the lattice parameter is about **0.288 nm**, where the nitrogen content is **3 - 4% wt%**, and microhardness up to **1600/1800 HV0.1**. Maximum layer adhesion is also achieved in this area.

6. Conclusion

In practical applications, areas where any nitride layer (**γ´-Fe_4N**, **ε-$Fe_{2-3}N$**, **ζ-Fe_2N)** is already formed can be completely eliminated. Although the adhesion of the layer achieves relatively good results, the nitrided layer itself will tend to have brittle behavior and crack formation.

The relationship between the **TiN** layer and the nitrided surface of HSS steel is significantly affected by compressive stress. Maximum adhesion is achieved when the surface of HSS steel is saturated with nitrogen at the level of **3 - 4 wt.%** Of nitrogen and where the compressive stresses do not exceed the order of **3-4 GPa**. This area can therefore be considered as the area of optimal nitriding of this type of steel for subsequent coating with PVD layers.

The implementation of the nitriding process in this saturation area is very difficult. If we consider that the nitriding number **aN ~ pN2**, then it is necessary to nitride with **pN2 = 3 - 4 Pa**. This is completely impossible with conventional gas nitriding equipment, so only plasma nitriding processes are possible. The equipment that allows this must be perfectly tight, as only the presence of the residual air atmosphere can mean that this value is exceeded. Atmospheric control using mass flow meters is also a prerequisite.