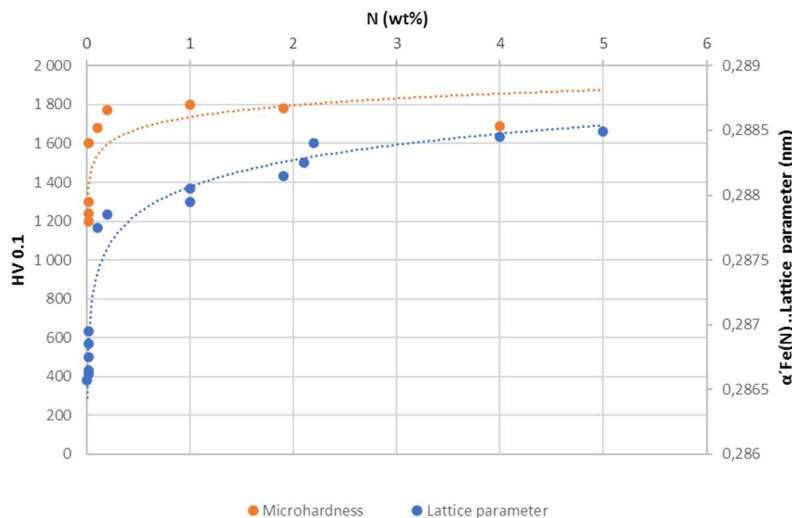


## Nitriding for duplex coating

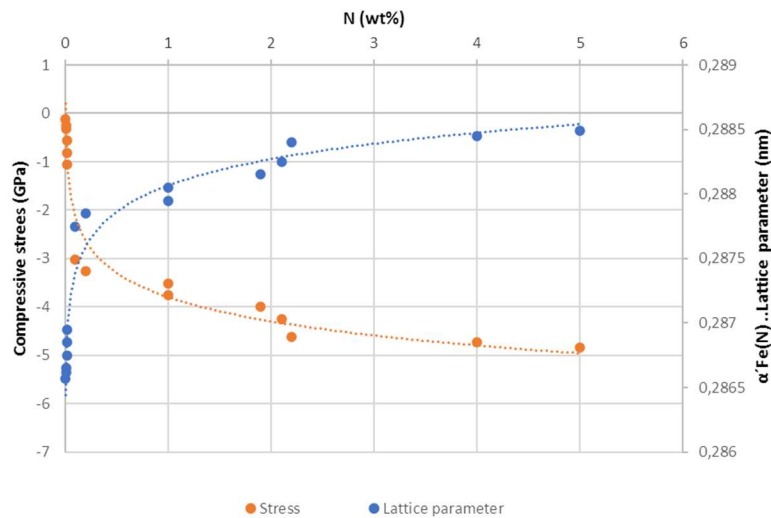
Duplex coating technology is based on a combination of nitriding and thin film deposited by **PVD** or **PACVD** technology (**TiN**, **TiCN**, **TiAlN**, **TiB<sub>2</sub>**, etc.). Because the adhesion of the layer on the metal substrate is given only by inter-atomic forces, one of the conditions for its maximization is a metallurgically clean surface, without oxides, which allows strong bonding between atoms at the layer and nitrided substrate interface, ie between **TiN**, **TiCN** and tempered martensite of coated tool.

Thus, the substrate itself is usually in the form of tempered martensite, a supersaturated solid solution of carbon in iron  $\alpha$ . However, during nitriding, interstitial nitrogen is also deposited in the lattice, thus creating a doubly supersaturated  $\alpha'$ -Fe (N, C) structure, with a nitrogen content of **0.0 - 5.9 wt%** and a carbon content according to the chemical composition of the steel and the degree of martensite tempering. For high-alloy **HSS** steels also with a certain content of cementite and **MC**, **M<sub>2</sub>C** or **M<sub>6</sub>C** carbides [1]. By incorporating nitrogen into the  $\alpha$ -lattice, the compressive stresses in the nitriding layer increase significantly, on the order of several GPa.



**Fig. 1** – Dependence of the change of the lattice parameter  $\alpha'$ -Fe (N) and microhardness on the nitrogen content (wt%) in the nitriding layer [2]

The adhesion of the layer on the surface thus prepared is influenced by many factors, but it is always an inter-atomic interaction between the substrate and the layer. For duplex layers based on nitriding of hardened and tempered steel with subsequent coating by PVD / PACVD technology, no other type of bond can be assumed. Due to the mismatch of the  $\alpha$  (Fe) and **TiN** lattices, epitaxial layer growth cannot be expected, although it is reported in the literature that such epitaxial growth may occur on some types of carbides.

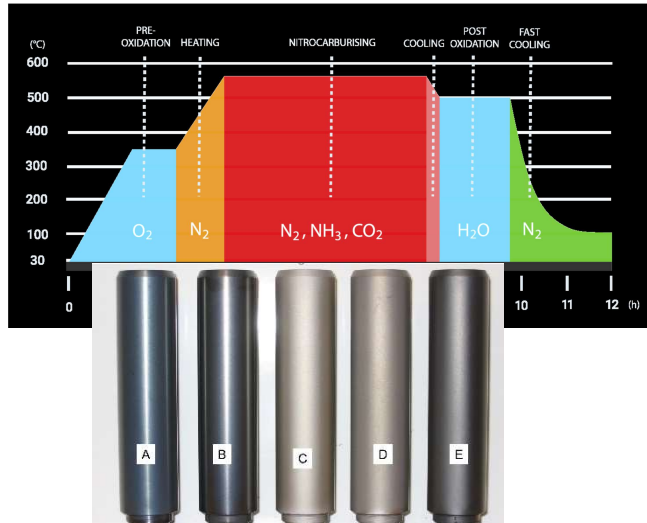


**Fig. 2** – Compressive stresses and lattice parameter in  $\alpha'$ -Fe (N) depending on the nitrogen content in the layer [2]

Because there is a step change in stress at the substrate / layer interface due to the difference in thermal expansion between the layer and the substrate, it is very important to remove all impurities with weak energy bonding to the substrate and minimize stresses at least within several atomic planes, in which the crystal lattices of the substrate and the layer will be adapted. The coating itself, in addition to the stresses due to the difference in thermal expansion (13.2%), is also burdened by stresses from built-in argon during deposition (11.3%) and, of course, stresses affected by bias on the substrate during deposition (75.5%). [3]

There is very little information on how to nitride for duplex layers, however, it can be concluded from the logic of the matter that it is in the interest that the nitriding process does not form a white nitride layer, neither  $\gamma'$ -Fe<sub>4</sub>N nor  $\epsilon$ -Fe<sub>2-3</sub>N, and at the same time the surface of the substrate after nitriding to be free of any oxides.

So which nitriding processes are suitable for a duplex system? It is generally known that so-called pre-oxidation is used to activate the surface during nitriding in a gas. It is applied at temperatures below 500 °C. Only after this pre-oxidation phase does the nitriding phase begin. This is done in ammonia, either alone or with the addition of hydrogen from the cracked ammonia, but in some cases other gases such as nitrogen or oxygen-containing gases such as CO<sub>2</sub>, CO or N<sub>2</sub>O are also permitted.



**Fig. 3** – Typical surface of nitriding process in gas: A - pre-oxidation phase, B - heating to nitriding temperature, C - phase of one or two-stage nitriding, D - cooling to post-oxidation temperature, E - cooling after process (<https://wiki.aalto.fi/display/SSC/Nitriding+and+Nitrocarburizing>)

So what is the consequence? This can be seen from the colour of the parts in Fig. 3 during the individual nitriding phases. Either real oxides are formed on the surface, or a nitriding or carbonitriding layer is formed containing all the above-mentioned elements **N**, **C** and **O**. Because oxygen accelerates the growth of the surface layer of nitrocarbides, it is this element in the form of **CO** or **CO<sub>2</sub>** gases, for LPN then **N<sub>2</sub>O**, which is commonly used in nitrocarburizing processes for this purpose.

But we want to nitride under **PVD** or **PACVD** coating. So how to deal with the above facts?

- Any layer of nitrides or carbonitrides on the surface is undesirable. Therefore, we must nitride with **Kn < 1** and at temperatures that correspond to this according to the Lehrer diagram
- All nitriding processes using pre-oxidation should be avoided as they are based primarily on the formation of iron oxide layers.
- All oxygen-containing gases should be excluded from the process for the same reasons mentioned above

So what do we have left? There are only two options. Either nitride directly in the coating machine, which has all the prerequisites to ensure an optimal nitriding process, except for working pressure, or in another, separate device for plasma nitriding, where there is no significant technical limitation in terms of nitriding, and where we can use pure **N<sub>2</sub>** and **H<sub>2</sub>** gases.

For other nitriding technologies for duplex layers, their suitability may be questioned, but they are not excluded if their reproducibility is guaranteed and their applicability is verified by practical results. However, since the optimal values of the nitriding layer for duplex coatings can be achieved if there is **1-2 wt%** nitrogen in the **α'-Fe (N)** lattice, it will be very difficult to set these process parameters in conventional gas nitriding furnaces.

[2] Vlastnosti otěruvzdorných vrstev TiN nanášených pomocí planárních magnetronů na difuzně nasycení povrch oceli zpracované metodou iontové nitridace (Properties of abrasion-resistant TiN layers deposited by planar magnetrons on diffusion saturated steel surface treated by ion nitriding method), Kandidátská disertační práce, ; J. Stanislav, 10/1991

[3] Properties of magnetron deposited polycrystalline TiN layers, J.Stanislav, J.Sikač, M. Čermák, Thin Solid Films, 191 (1990), p. 255-273

June 6, 2022

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