Comparison of different nitriding processes on PM materials and their effect on properties

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Abstract

To meet the need of improved properties, e.g. resistance against fatigue and wear, a variety of hardening treatments can be chosen on steel components. These improved properties are in fact the result of high hardness, the introduction of residual stresses and, with some diffusion treatment methods, a modified chemistry close to the component surface. To avoid larger changes of form and dimension, the hardening process temperature could be kept low, e.g. in the ferritic area. With this temperature restriction in mind, the nitriding diffusion hardening method is often a suitable alternative to achieve the improved properties in question on conventionally wrought steel. The presence of porosity in a PM component could however affect the result. This paper will discuss how properties are influenced by different nitriding processes, PM material grade and component density.

Key words: Nitriding, Powder Metallurgy

1. Introduction

In general terms, there are two main methods to perform a diffusion hardening heat treatment. What separates them both is the process heating temperature and the subsequent cooling rate. At process temperatures above A_1 (723ºC), i.e. when transformation to austenite starts, heat treatments like atmospheric carburizing, carbo nitriding and low pressure carburizing could be found [1]
To avoid larger changes of form and dimension on diffusion treated steel components the process temperature could be settled beyond the A_1 temperature, i.e. the transformation from ferrite structure to austenite will never take place. Furthermore, the subsequent cooling sequence becomes less dramatic with these processes. Two methods, very look alike, exists and are carried out at temperatures 480ºC to 600ºC. The main difference between them is the use of carbon element or not.

- Nitriding
- Nitrocarburizing, also called Ferritic Nitrocarburizing (FNC)

Basically, there are two ways to carry out nitriding and the similar nitrocarburizing [1]; with gas or with liquid salt baths to diffuse nitrogen and, possibly, carbon into the surface. When using gas as element carrier the process can be used together with plasma (“glow discharge” or “ion discharge”) but this require special furnaces and equipment. By using gas nitriding assisted with plasma the affected regions, close to the surface (“compound layer” and “diffusion zone”), and the total affected depth could be controlled and adjusted in more various ways. In Figure 1, a schematic overview of the regions close to the surface for a nitrided iron-based ferritic specimen [2] are shown, with explanation of their properties and advantages.

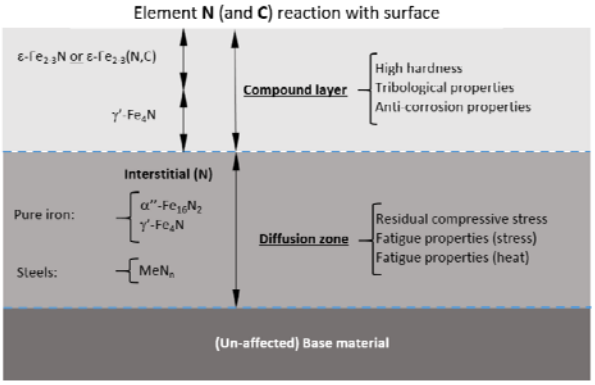


***Figure 1**. Schematic cross section of nitrided iron-base ferritic steel.*

To enhance the diffusion hardening effect some alloy elements should (can or could) be selected that are especially strong to form nitrides, both as thick compound layer and also as single precipitations close in

the diffusion zone. These alloying elements are Al, Cr, Mo, V and W, i.e. some of the same group of elements to form carbides as well [1].
One of the features of sintered PM components is a certain level of porosity due to the applied compaction pressure and the corresponding obtained density. At low densities the porosity could be of coherent nature, i.e. open porosity, making the total exposed surface larger compared with the geometrical envelope surface of the actual component. With this open porosity a diffusion heat treatment, e.g. a traditional gas nitriding, could have a large and un-wanted penetration deep down in the microstructure. This open porosity could however be minimized or removed by previous operations. By densifying the surface with plastic deformation, e.g. by shot peening, the gas permeability will decrease [3]. Another way to close the pores could be achieved by replacing the pores with other material, e.g. with iron oxide through a steam treatment [4].

In this paper a comparison was made where the performed heat treatment was either gas or plasma nitriding, on sintered PM components at different densities and where a shot peening surface densification was carried out on some of the components.

2. Experimental Procedure

A pre-alloyed and water atomized powder material, Astaloy™ 85 Mo (0.85% Mo, Fe bal.), was used in all tests. An Intralube® E mix was prepared with Astaloy 85 Mo and addition of 1% Ni, 0.4% graphite and 0.6% Lube E. With this powder mix samples of two different geometries were prepared. Ring samples with geometry Ø40/Ø20 x 16 mm were compacted in a Result EHP120 press to densities 7.0 and 7.3 g/cm³. These samples were sintered in a belt furnace at 1120ºC for 30 minutes in an atmosphere of 90%N_2 and 10%H_2 without addition of hydrocarbon. To establish test samples at almost full density, powder forged samples with geometry Ø25 x 25 mm were manufactured. Before the powder forging the compacted blanks were heated at 1120ºC for 30 minutes in 100% H_2.

Some of the sintered Ø40/Ø20 rings (both densities) were shot peened with small cuts of cylindrical wires, i.e. “Cut Wire Shot” (CWS), in order to densify the surface. The average weight loss after this process was only 0.06%, independent of density. The powder forged samples were turned on the outside to remove an oxide layer and drilled through, with 8 mm drill, to a final geometry of Ø24/Ø8 x 24 mm. This geometrical change was made in order to compare samples with same shape i.e. cylindrical. A final blasting was performed after the turning and drilling operation on the powder forged samples to smooth up the whole mantle surface.

After shot peening (CWS) or machining, these treated samples were stress relived by a normal re-sintering i.e. at 1120ºC for 30 minutes in an atmosphere of 90%N_2 and 10%H_2 without addition of hydrocarbon.

As the gas nitriding process, a ferritic nitrocarburization was performed at 580ºC in an atmosphere with NH_3, CO_2 and N_2 (as dilution), for 2 hours. The plasma nitriding process was carried out at 480ºC in an atmosphere with N_2 and H_2 gas at low pressure (close to vacuum) for 10 hours. Both processes were performed in industrial equipment. The ferritic nitro-carburization is hereafter designated as **FNC** and plasma nitriding as **PN** in this report. The total experimental setup matrix is shown in Table 1.

Table 1*. PM-samples, density, secondary operation and their treatments.*

Geometry [mm]	Density [g/cm³]	Sec. operation	Diffusion heat treatment
Ø40/Ø20 x 16	7.0	None	FNC
Ø40/Ø20 x 16	7.3	None	FNC
Ø40/Ø20 x 16	7.0	CWS	FNC
Ø40/Ø20 x 16	7.3	CWS	FNC
Ø24/Ø8 x 24	7.8	Turned, drilled	FNC
Ø40/Ø20 x 16	7.0	None	PN
Ø40/Ø20 x 16	7.3	None	PN

Ø40/Ø20 x 16	7.0	CWS	PN
Ø40/Ø20 x 16	7.3	CWS	PN
Ø24/Ø8 x 24	7.8	Turned, drilled	PN

3. Results and discussion

Mass change during nitriding process.
The gas pickup during the diffusion process, e.g. as nitrogen interstitials, nitride needles and/or as a nitride rich compound layer, could be calculated as total mass change, i.e. a comparison between mass before and after the conducted nitriding process, shown in Figures 2 and 3. It is possible to consider the powder forged sample associated to the variable density, i.e. the group from 7.0 to 7.8 g/cm³, but also associated to CWS-treated samples as infinite surface densification.

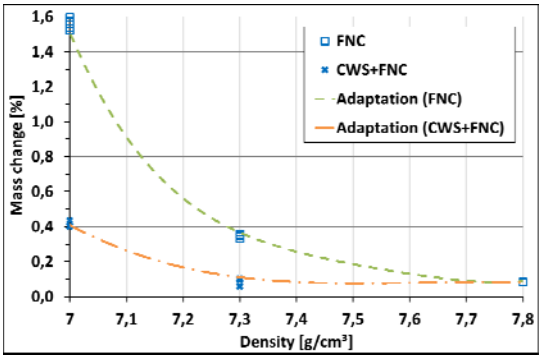


***Figure 2**. Mass change after FNC.*

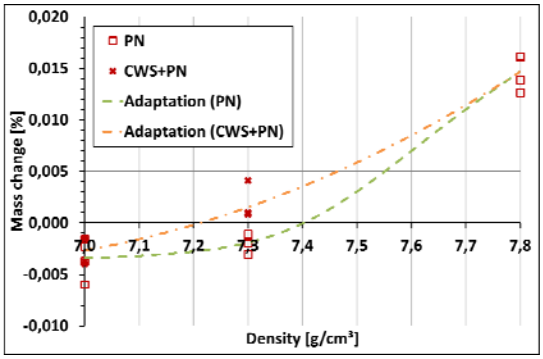
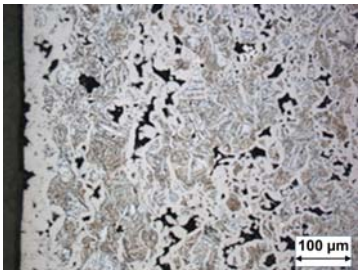


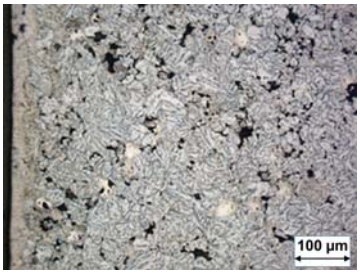
***Figure 3**. Mass change after PN.*

The density and surface densification influence on FNC-treated samples are clearly shown in Figure 2, e.g. where a significant change was found at 7.0 g/cm³ with CWS-treated samples. At 7.3 g/cm³ the mass change with FNC and CWS-treated samples are at same level as the powder forged ones treated with FNC. The mass changes of PN-treated samples are, even if the values are much lower compared to the FNC-treated ones, opposite as shown in Figure 3. At the lowest density 7.0 g/cm³, regardless of whether the samples are surface densified or not, and at 7.3 g/cm³ the PN-treated material appears to reduce in mass, probably due to reduction of oxides during the nitriding process.

Metallographic examination of nitrided samples.
All metallographic images shows cross sections close to the surface of the outer ring diameter. The FNC-treated samples are shown in Figures 4 to 8 and the PN-treated ones in Figures 9 to 13. In as-sintered condition of the material, the microstructure consists of high temperature bainite, some areas of tempered martensite and nickel rich austenitic spots. Powder forged samples were found not to be 100% dense and some pores were found before the nitriding processes took place.

The influence of density or densification (CWS), with respect to (un-controlled) nitride penetration towards the sample core, were apparent with the FNC-treated samples and most widespread in sample with density 7.0 g/cm³ (Figure 4). In the FNC-treated samples, shown in Figures 6 to 8, i.e. the CWS-treated and the powder forged samples, a thick and distinct compound layer was established together with thin nitride needles further down from the surface. In the PN-treated sample (Figures 9 to 13) an extremely thin, and sometimes discontinuous, compound layer was generated and beneath this, fully developed nitride needles could be observed. In the samples treated with both CWS and PN, shown in Figures 12 and 13, a dense and much finer microstructure of, apparently, nitride needles were observed compared with the fully dense and PN-treated sample in Figure 11.





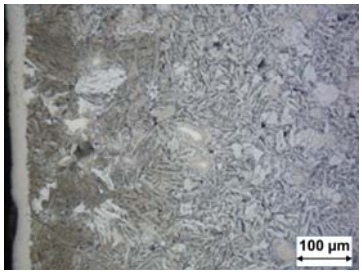


***Figure 4**. FNC, 7.0 g/cm³.*

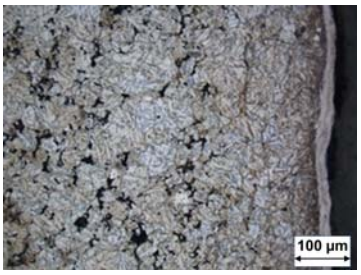


***Figure 5**. FNC, 7.3 g/cm³.*



***Figure 6**. FNC, 7.8 g/cm³.*

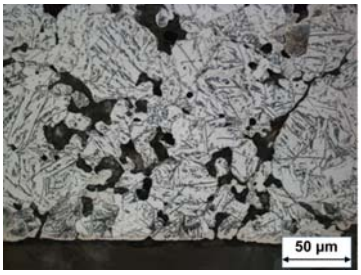


***Figure 7**. CWS+FNC 7.0 g/cm³.*

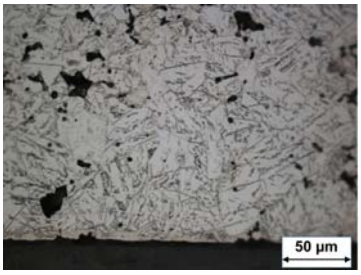


***Figure 8**. CWS+FNC, 7.3 g/cm³.*

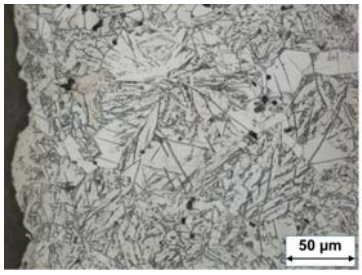


***Figure 9**. PN, 7.0 g/cm³.*

***Figure 10**. PN, 7.3 g/cm³.*

***Figure 11**. PN, 7.8 g/cm³.*

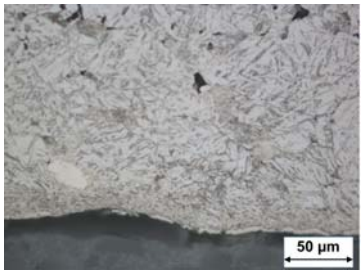


***Figure 12**. CWS+PN 7.0 g/cm³.*

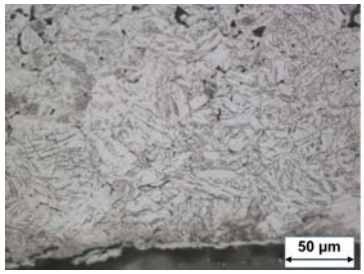
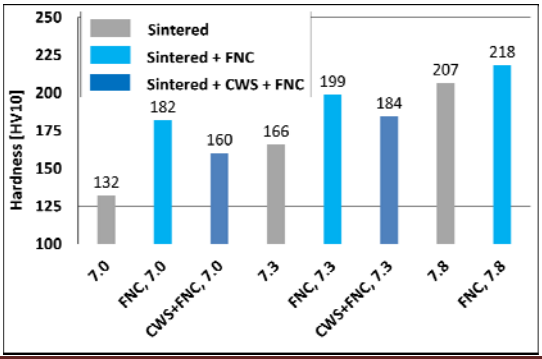


***Figure 13**. CWS+PN, 7.3 g/cm³.*

Core macro hardness, HV10, of samples.

By comparing the macro hardness of the sintered samples, shown in Figures 14 and 15, the influence of density was easily stated, i.e. with increased density the hardness was also increased. The influence of nitride penetration became very clear by comparing density, both at macro level and with CWS-treated surfaces, with FNC-treated samples shown in Figure 14. Even with the almost full dense sample Ø24/Ø8 x 24 mm the core hardness was increased by the FNC-treatment. The core macro hardness of the PN-treated samples, shown in Figure 15, were however very stable within each density level, independent the CWS-treatment or in fact the nitriding process itself.



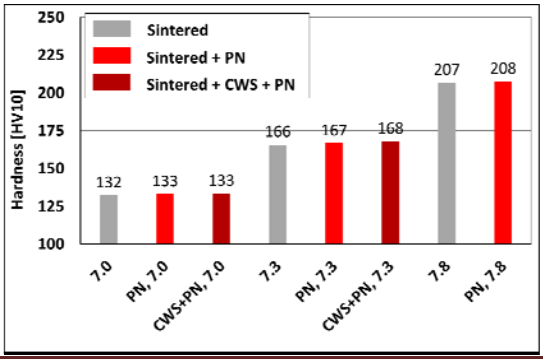


***Figure 14**. Core hardness of FNC-treated PM.*

***Figure 15**. Core hardness of PN-treated PM.*

Micro hardness profiles, HV0.1, of nitrided samples.

The micro hardness profiles of the FNC- and PN-treated samples are shown in Figures 16 and 17. When taking the microstructure and macro hardness into account the appearance of the micro hardness profile of FNC-treated sample with density 7.0 g/cm³ make sense. The effect of CWS had a dramatical impact on FNC-treated samples, best shown with samples at 7.0 g/cm³, but also to density of 7.3 g/cm³. In general terms, the hardness profile of CWS+FNC treated samples of 7.0 and 7.3 g/cm³, together with the FNC-treated powder forged sample with density 7.8 g/cm³, are quite similar to the characters.

The corresponding micro hardness profiles of PN-treated samples, shown in Figure 17, differs significantly from the FNC-treated ones. With the microstructures in Figures 9 to 13 as reference it can be concluded that hardness increase ought to be found in a diffusion zone, i.e. apparently as interstitials of nitrogen and fine nitride needles, in the absence of a well-developed compound layer. While the highest values were found with the CWS-treated samples, regardless of density, the lowest values were found with the samples without CWS, i.e. the ones with highest surface porosity.

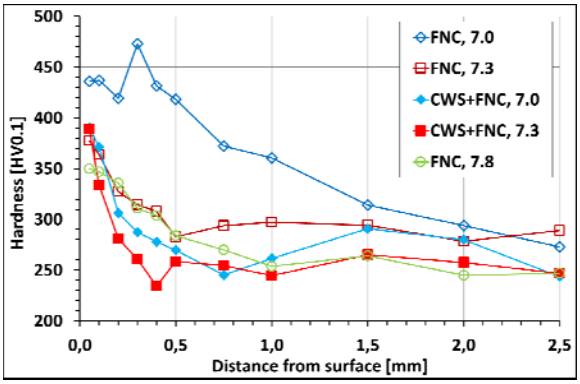


***Figure 16**. Hardness profile of FNC-treated PM.*

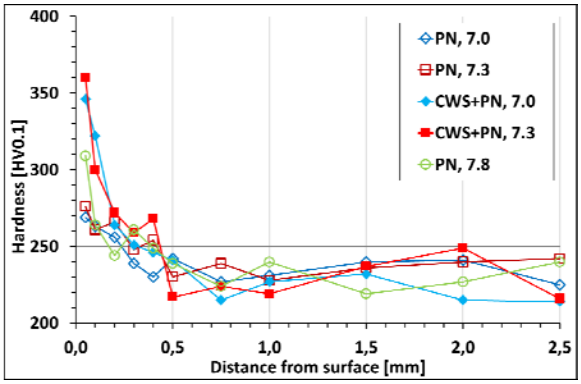


***Figure 17**. Hardness profile of PN-treated PM.*

Chemical analysis of carbon, oxygen and nitrogen

To analyze the nitrogen (and possible oxygen) pickup, achieved from both diffusion processes and also additional carbon pickup during FNC-process, the ring samples top surfaces were turned and the very small and tiny chips were collected. Depending on different diffusion depths (shown in Figures 4 – 13) three millimeters from top surface were turned away in order to establish average values from the collected chips. A very low cutting speed was used (~2 m/min) to eliminate heat generation, i.e. to avoid oxidation or other unwanted reactions, during the chip removal. The reference samples, i.e. the sintered ones without subsequent diffusion treatment, were analyzed in the same way.

In Table 2 all the values of carbon, oxygen and nitrogen are shown. By comparing the analyzed nitrogen pickup, within the region of three millimeters from top surface, the reactions from FNC-treatment corresponded very well with mass change (Figure 2). The FNC-sample with lowest density, i.e. highest porosity, showed the highest nitrogen level (3.03%), but at the same time the highest oxygen level, apparently from the use of an initial pre-heating in air as a surface cleaning process [1] or due to the use of CO_2 as carbon carrier during the FNC-process. By increasing density, both as macro density but also by CWS in the surface, the nitrogen diffusion of the FNC-treated samples decreased and, positively, so did the oxygen pickup. The carbon pickup, most likely in form of $Fe_{2\text{-}3}(N,C)$ [2], was found to be at highest level with CWS+FNC at 7.0 g/cm³ in density, where the oxygen level was on reasonable level.

In contrast to the reaction of FNC-treated samples, the nitrogen pick-up of the PN-samples was considerably lower and independent of the porosity, but still higher compared to as-sintered samples. Both carbon and oxygen levels with the PN-treated samples were in principle at the same level as the as-sintered ones. As shown earlier, with the metallography examinations (Figures 9 to 13) and the hardness profile, nitrogen was without a doubt found in the diffusion zone, apparently as nitrogen interstitials and fine nitride needles.

***Table 2**. Averages values of C, O and N at sample surface.*

After process	Density [g/cm³]	C [%]	O [%]	N [%]
Only sintered	7.0	0.332	0.040	0.023
Only sintered	7.3	0.331	0.036	0.024
Only sintered	7.8	0.327	0.033	0.001
FNC	7.0	0.312	0.260	3.030
FNC	7.3	0.433	0.213	0.374
CWS+FNC	7.0	0.452	0.054	0.311
CWS+FNC	7.3	0.352	0.031	0.069
FNC	7.8	0.331	0.012	0.047
PN	7.0	0.339	0.037	0.055
PN	7.3	0.346	0.029	0.048
CWS+PN	7.0	0.343	0.038	0.043
CWS+PN	7.3	0.356	0.042	0.048
PN	7.8	0.338	0.017	0.032

4. Conclusions

Ferritic nitrocarburization (FNC) of the as-sintered PM material Astaloy 85 Mo + 1%Ni + 0.4%C:

- The material is fully nitrided with an established and pronounced compound layer.
- The core hardness is affected to some extent, depending on (surface-) porosity.
- The (surface-) density strongly affects the results.
- At lowest density (7.0 g/cm³) the nitrogen diffusion can be regarded as destructive.
- The CWS-treatment, before the diffusion hardening process, controls in a useful way the distribution of white layer depth i.e. compound layer.

Plasma nitriding (PN) of the as-sintered PM material Astaloy 85 Mo + 1%Ni + 0.4%C:

- The material is nitrided with a minimal and discontinuous compound layer and apparently a well-established diffusion layer according to micro hardness profile measurement.
- The core hardness is not affected by the plasma nitriding process.
- The (surface-) density affects the hardness profile.
- The highest profile hardness are found with the CWS-treated samples.

References

1. Swerea IVF. *Steels and its Heat Treatment – a Handbook.*
   Publication No. 12801, 2012
   ISBN_987-91-86401-11-5
2. E.J. Mittemeijer. *Fundamentals of Nitriding and Nitrocarburizing*.
   ASM Handbook, Volume 4A, Steel Heat Treating Fundamentals and Processes
   2013 ASM International
3. B. Rivolta et al. *Wear performances of surface hardened PM steel from pre-alloyed powder.*
   https://www.sciencedirect.com/science/article/pii/S004316481200097X [Retrived 2018-04-18]
4. C. Larsson and U.Engström*. Aspects of nitrocarburising of PM materials for improved wear resistance*.

Presented at EuroPM in Gothenburg, Sweden, 2013.