Aspects of nitrocarburising of PM materials for improved wear resistance

Caroline Larsson, Ulf Engström, Höganäs Sweden AB, S-263 83 Höganäs SWEDEN
caroline.larsson@hoganas.com, ulf.engstrom@hoganas.com

Abstract
PM components are commonly used in applications where they are exposed to different degrees of wear. Often various heat treatments are used in order to increase the hardness and thereby the wear resistance. In this paper we will take a closer look at aspects of the thermochemical nitrocarburising process when used for PM materials. The porosity is having a very large influence on the formation of the compound layer. This can to some extent be controlled by applying a steam treatment before the nitrocarburising step. Chemical composition of the PM part is another factor having great importance for the surface hardness. Here the presence of chromium shows great benefits.

Background
Belt pulleys for water pumps and fuel injection are typical PM applications that have been on the market for many years. Today the global market for cars is growing both volume wise and geographically. The latter means that more cars are used on dust roads under more severe conditions, why the requirements on the pulleys increase. More dust containing hard particles will get into the system and result in more severe abrasive wear. Particles may also be trapped between the belt and the pulley causing wear on the pulley which may lead to slipping of the belt and possible severe damage on the motor. Such particles may also get into the surface pores where they may be stuck, causing excessive wear on the belt.

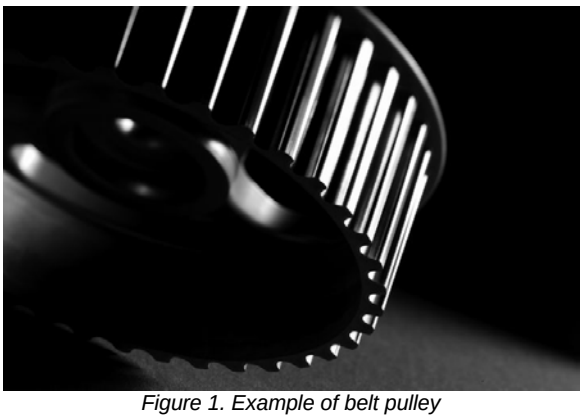


Figure 1. Example of belt pulley

In this study we are looking on the possibility to utilize steam treatment and nitrocarburising in combination with a material with good heat treatment response in order to decrease the wear on the pulley as well as on the belt.

Nitrocarburising can be done in gas, plasma and salt bath. The latter is not common today due to environmental reasons and it is not suitable for PM as salt tend to penetrate the surface pores. Nitrocarburising is a relatively low-cost method to increase hardness and thereby wear resistance and fatigue properties. Corrosion resistance is also improved. It is a dimensional stable process as it takes place at low temperature (560-580˚C) with no general phase transformations (austenitisation). This minimizes distortion and volume change. A compound layer (or white layer) is formed on the surface of the steel consisting of ε ($Fe_{2-3}N$, HCP), γ' (Fe_4N, FCC) or ε+γ'. It may also contain cementite and various alloy carbides and nitrides. Corrosion resistance and tribological properties are mainly determined by the compound layer. Under the compound layer there is a diffusion zone. The hardness and depth of this diffusion zone determines the load carrying capacity and fatigue strength [1,2].

In the beginning of a typical nitrocarburising process of a carbon steel, ε followed by γ' is formed in the evolving diffusion zone (α + cementite → α + ε and α + ε → α + γ'), see figure 2 [3]. This is followed by the continued growth of ε and γ' on the expense of α, in the fully developed and growing compound layer (α + γ' → γ' and γ' → ε) [3]. With higher nitrogen and carbon activities the higher the amount of ε-phase will be.

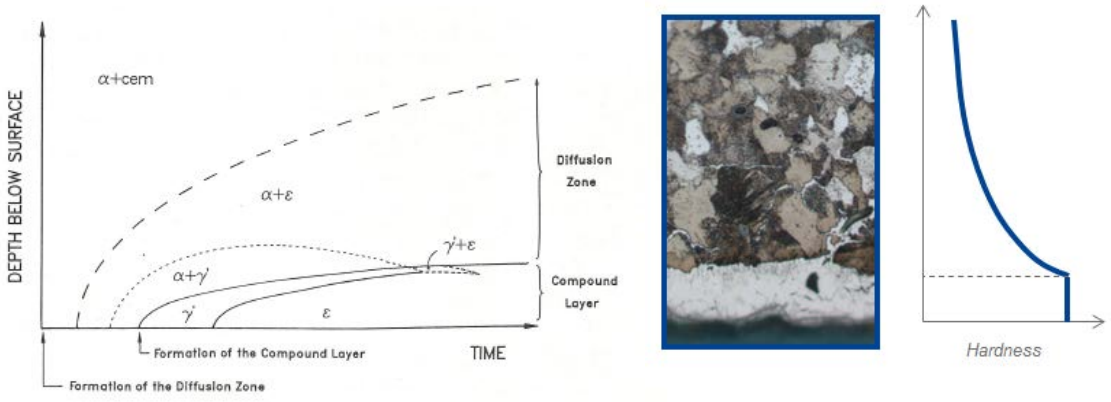


Figure 2. Schematic illustration of evolution of diffusion zone and compound layer during nitrocarburising of carbon steels [2] together with corresponding microstructure and hardness profile.

Some alloying elements like chromium and molybdenum form both carbides as well as nitrides. In low alloyed steel there are mainly carbides before heat treatment. As nitrogen is added some of these are transferred to nitrides as both chromium and molybdenum have a stronger affinity to nitrogen compared to carbon. This will free carbon that can form cementite in grain boundaries of the diffusion zone. Some of the cementite will also transform to Ɛ, making it look like the compound layer has grown into the diffusion layer, see figure 7. Grain boundary precipitates cause brittleness and crack propagation [4].The presence of alloying elements will in general decrease the growth rates of both the diffusion as well as the compound layer.

Experiments

Two different base powders have been used in this investigation. These have been mixed according to table 1. The first material is an iron-copper-carbon mix and has a typical composition used for pulleys today. Material number 2 and 3 are based on a chromium prealloyed grade, Astaloy CrA with 1,8 % chromium, where mix 3 also contains MnS as many pulleys are machined. All mixes have been prepared as Intralube E mixes with an addition of 0.70 % Lube E for good lubrication and with the syntactic graphite F10.

Table 1. Material compositions

No.	Material
1.	ASC100.29 + 2,0 %Cu (-200) + 0,50 %C (F10) + 0,70 %Lube E
2.	Astaloy CrA + 0,35 %C (F10) + 0,70 %Lube E
3.	Astaloy CrA + 0,35 %C (F10) + 0,30 %MnS 0,70 %Lube E

Different sample geometries have been prepared according to table 2. All samples have been sintered at 1120˚C for 30 minutes in 90/10 N_2/H_2 atmosphere in a laboratory belt furnace. Steam treatment and nitrocarburising have been done in production batch furnaces. Microhardness profiles have been measured on one sample with 3 indentions per depth.

Table 2. Samples geometries used in different trials

Sample	Description
Blanks I	Ø=80 mm, h=40 mm, GD=6,9 g/cm^3
Machined pulleys	Machined out of the sintered blanks I above
Compacted pulleys	Compacted in production equipment to different densities
Blanks II	Ø=80 mm, h=10 mm, P=550 MPa
Wear samples	Machined out of sintered blanks II above. 25x58x10 mm

Effect of density

One difference when gas nitrocarburising PM materials compared to wrought materials is that the process gases penetrates the pores and the nitriding reactions takes place both at the part surface as well as along pore surfaces, see figure 3. By increasing the density the penetration depth can be reduced. Another way to limit the penetration is to make a steam treatment that closes the surface pores before nitrocarburising. This limits the nitrogen penetration and improves dimensional control.

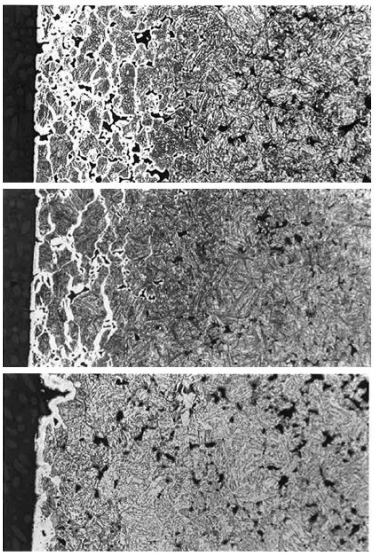
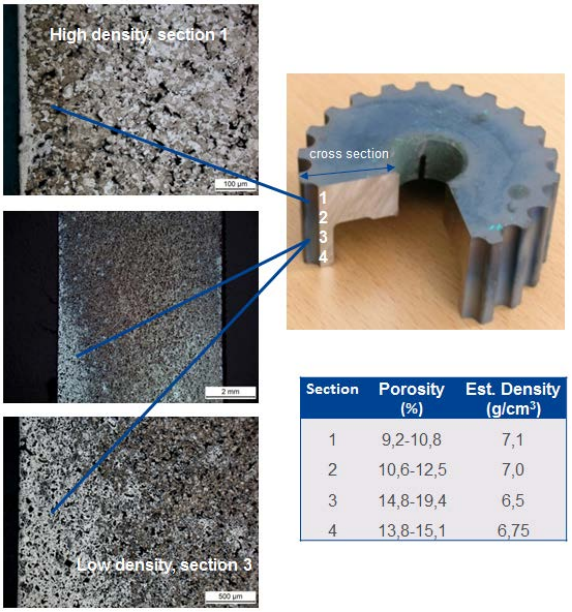


Figure 3. Nitrocarburising of Astaloy Mo + 0,5 %C at different densities, with and without steam treatment.



Section	Porosity (%)	Est. Density (g/cm³)
1	9,2-10,8	7,1
2	10,6-12,5	7,0
3	14,8-19,4	6,5
4	13,8-15,1	6,75

Figure 4. Steam treated and nitrocarburised part made of Astaloy CrA and the effect of large internal density variation.

In this investigation a pulley was compacted of material 2, Astaloy CrA + 0,35 % C, in order to intentionally give internal density variations. The porosity was measured, on 4 pulleys in 4 different sections, by metallography. The porosity of the sections was then converted to a sintered density, see figure 4. The steam treatment applied was running for 90 minutes at 510˚C followed by a nitrocarburising for 60 minutes at 580˚C. This resulted in a well-defined compound layer at the surface for the higher densities whereas the area with the lowest density also got a compound layer along the pore surfaces to a depth of 700 µm. To optimize the heat treated layer you must either secure a higher density of the low density areas or the steam treated layer must be made thicker.

Optimization of heat treatment parameters

The optimization of suitable parameters for steam treatment and nitrocarburising was done on blanks I made of material 2. One initial trial was done together with wrought steel with its standard settings. The steam treatment was done at 430˚C for 120 minutes and the nitrocarburising at 570˚C for 180 minutes. As expected, this resulted in a too thin oxide layer that was reduced during the nitrocarburising step and there after the nitrogen could penetrate the pore system, causing a too thick compound layer at the surface. The compound layer also got built up around the pores to a depth of 600 µm, see figure 5. In another trial the oxide layer was fine but the nitrogen activity became too low. This was caused by a too small amount of ammonia added in combination with a too small load in the furnace, the latter resulting in limited free Fe-surfaces for the ammonia to crack on. Due to this a diffusion zone was built up, which could be seen on the micro hardness (mhv) profile that was analysed, but the amount of nitrogen was not enough to build up a solid compound layer under the set time, see figure 6. Figure 7 shows a sample of material 3 that has been steam treated at 510˚C for 90 minutes, resulting in a good oxide layer of 3-4 µm, which is reduced at the surface during nitrocarburizing. The nitrocarburising was then done at 580˚C for 8 hours, resulting in a significantly too thick compound layer of about 100 µm.

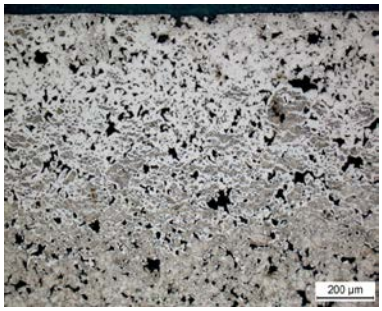


Figure 5.Etched material 2 with too low steam treatment temperature.

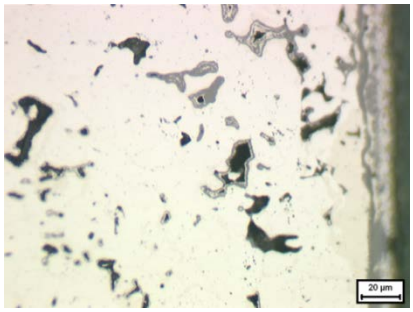


Figure 6. Unetched material 2 nitro-carburised with too low nitrogen activity.

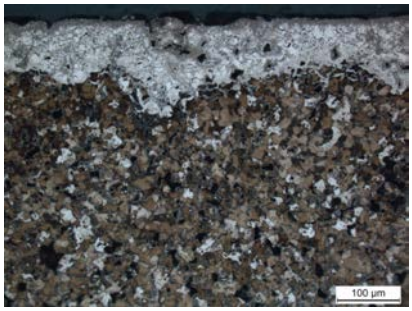


Figure 7.Etched material 2 nitrocarburised for too long time.

After further trials it was concluded that the optimal parameters for a machined pulley of material 2, in this set up is a steam treatment at 510˚C for 90 minutes followed by a nitrocarburising at 580˚C for 90-110 minutes. With these settings we got closed pores by the steam treatment with an oxide layer of 3-4 µm. This is then partly reduced during the nitrocarburising down to a couple of microns. Below this a compound layer is formed with a thickness of 15-20 µm, see figure 8. Micohardness profiles were measured at the thin and the thick section of the machined pulley. These can be seen in figure 9 with Vickers microhardness (mhv or HV0,1) values of 615-650 just below the compound layer and with a hardening depth, where the mhv is 450, of 0,4-0,5 mm. The microhardness of the compound layer is above 700 mhv measured perpendicular to the component surface, whereas the core hardness is 200 mhv. The latter is determined by the carbon content and can be tailored by adjusting the graphite amount.

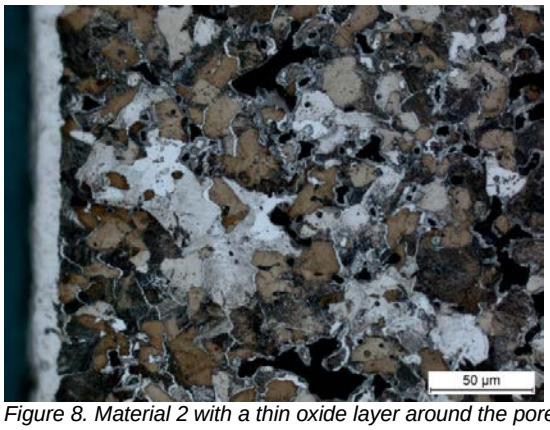


Figure 8. Material 2 with a thin oxide layer around the pores and at the surface. Below this a well-defined compound layer.

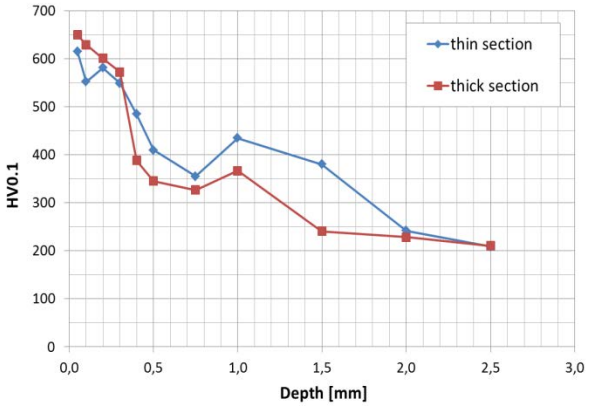
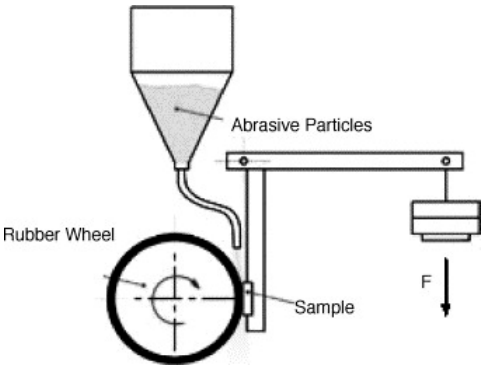


Figure 9. Microhardness profiles taken at different heights of the blanks.

Wear resistance

Wear testing was done using the ASTM G65-04 standard [5], dry sand-rubber wheel method for abrasive wear, according to procedure C. Figure 10 shows schematically how the equipment is set up and the used testing conditions. Procedure C was selected which is a short term testing of thin coatings. It is used for ranking of different materials and results are reported as volume loss in cubic millimetres. The wear resistance was measured on the Fe+Cu+C material and Astaloy CrA in sintered, steam treated as well as steam treated and nitrocarburised condition. The Astaloy CrA + MnS were only tested in the steam treated and nitrocarburised condition.



[5]

Testing conditions, procedure C	
Test specimens	*25x58x10 (mm)*
Wheel	*CIIR lined steel wheel*
Abrasive sand	*Ottawa silica sand, AFS 50/70*
Feed rate	*250-275 (g/min)*
Rotation speed	*200 (rpm)*
Contact force	*130 (N)*
Wheel revolutions	*100*
Linear abrasion	*71,8 (m)*

Figure 10. Schematic picture of the dry sand-rubber wheel testing equipment used in the standard test method ASTM G65 for abrasive wear and used testing conditions.

The wear resistance, expressed as adjusted volume loss, AVL, is presented in figure 11. In the sintered condition we can see that the Fe+Cu+C material show a considerable larger volume loss, 18,2 mm^3,compared to Astaloy CrA with 11,3 mm^3. Explanations can be found in the metallography, see figure 11. First it can be seen that the Fe+Cu+C material contains a mixture of ferrite and perlite whereas the Astaloy CrA material has a very fine perlitic structure with some smaller ferritic areas. This finer structure of Astaloy CrA improves the wear resistance since in abrasive wear the mean

distance between the hard constituents, in this case perlite for both of the materials, have a main effect.

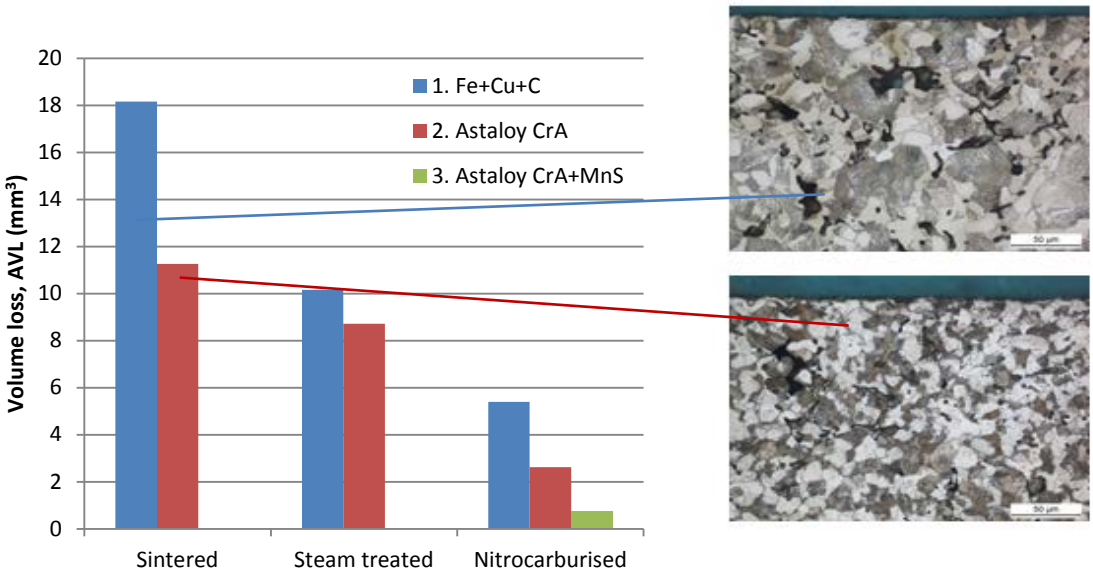


Figure 11. *Wear resistance expressed as Adjusted Volume Loss, AVL, according to the ASTM G65 standard, together with microstructures of the sintered samples.*

As steam treated the volume losses are reduced to 10,2 and 8,7 mm^3 respectively. During steam treatment an oxide layer of 2-5 µm is formed. According to Bocchini [6], the thickness of the oxide layer should not exceed 7 µm in order to avoid flaking. The oxide layer is slightly thicker and more even on the Astaloy CrA material compared to Fe+Cu+C. In this condition there is not so much difference in wear resistance between the materials. The hardness is similar (due to different carbon contents) and both have similar oxide layers that decrease the friction.

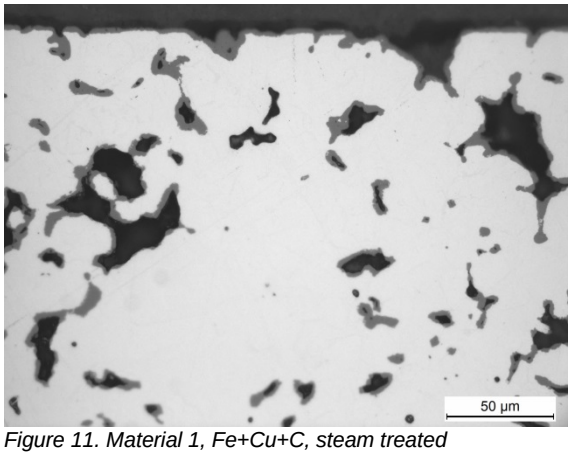


Figure 11. Material 1, Fe+Cu+C, steam treated

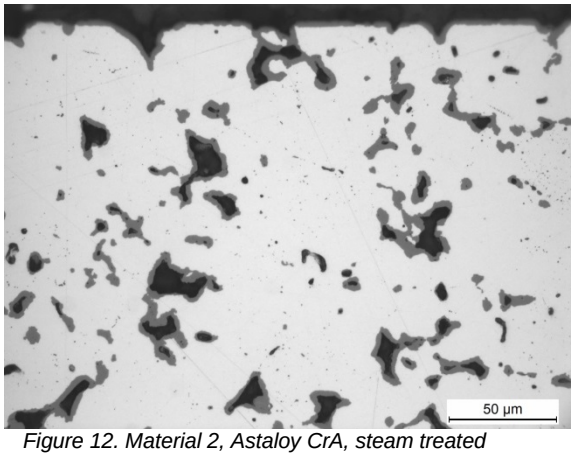


Figure 12. Material 2, Astaloy CrA, steam treated

Applying nitrocarburising reduces the volume loss to 5,4 mm^3 ,half that of steam treated, for the Fe+Cu+C. The Astaloy CrA is reduced even further to 2,6 mm^3. The Astaloy CrA sample with addition of MnS showed an even smaller wear of 0,7 mm^3. This is however not expected to be due to the MnS as such as there are hardly any MnS particles in such a small volumes that has been worn. The reason is more probable to be a higher carbon content of this series that has caused a finer perlite with a higher hardness and thereby a better wear resistance.

What is most important for the wear properties is the compound layer. A high hardness and a low friction coefficient are beneficial. During nitrocarburising some of the oxide layer has been reduced and a compound layer of about 10 µm is formed on the Fe+Cu+C material and of about 15 µm on the

two Astaloy CrA materials. In the Fe+Cu+C material some ɣ' needles are precipitated in the ferrite, see figure 13, but they do not have any major effect on the microhardness. The microhardness of the diffusion zone is slightly below 300 mhv and decreases gradually to a hardness of about 200 in the core, see figure 16. The hardness in the diffusion layer of the Astaloy CrA materials are starting much higher with 650 and 720 just below the compound layer. In the Astaloy CrA fine ɣ' and Ɛ nitrides are precipitated in the diffusion zone, which increases the hardness significantly. The hardness of the compound layer was measured perpendicular to the cross sections seen in figure 13-15. This is necessary as the compound layers are too thin to make hardness indents in.

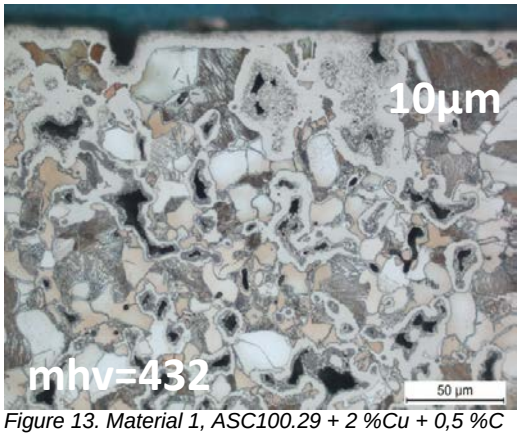


Figure 13. Material 1, ASC100.29 + 2 %Cu + 0,5 %C

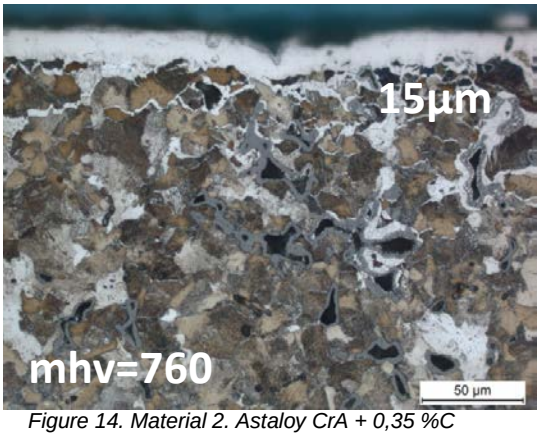


Figure 14. Material 2. Astaloy CrA + 0,35 %C

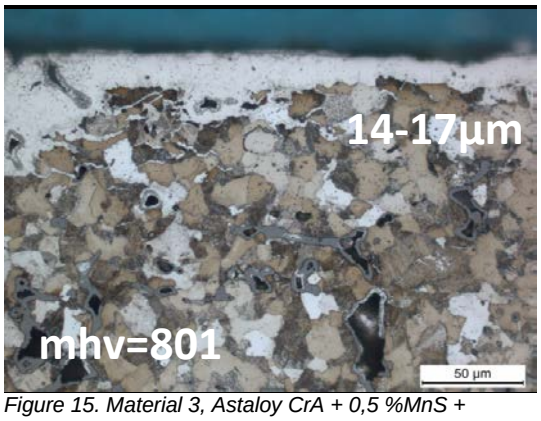


Figure 15. Material 3, Astaloy CrA + 0,5 %MnS + 0,35 %C.

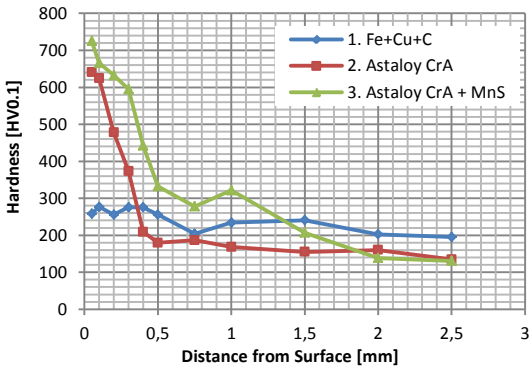


Figure 16. Microhardness profiles for material 1-3 as steam treated and nitrocarburised..

The wear surfaces were also investigated in the scanning electron microscope after wear testing. Here we could see scratched, deformed and smeared surfaces on the as sintered samples, see figure 17-18. Impressed sand grains could also be seen on these surfaces. Mapping of Si was used in order to identify the sand grains and estimate their amounts.

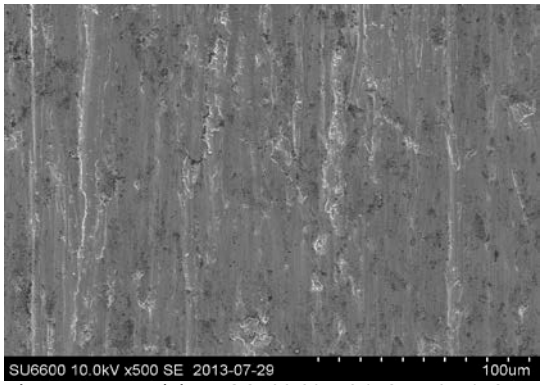


Figure 17. Material 1, ASC100.29 + 2 %Cu + 0,5 %C, as sintered.

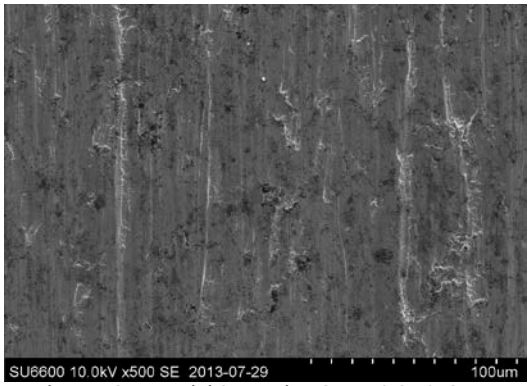


Figure 18. Material 2. Astaloy CrA + 0,35 %C, as sintered.

The nitrocarburised surfaces look quite different. Scratches are seen but to a much smaller extent and with fewer scratches for the Astaloy CrA compared to the Fe+Cu+C material. The surface pores are still open and have not been smeared for either of the materials, see figure 17-18.

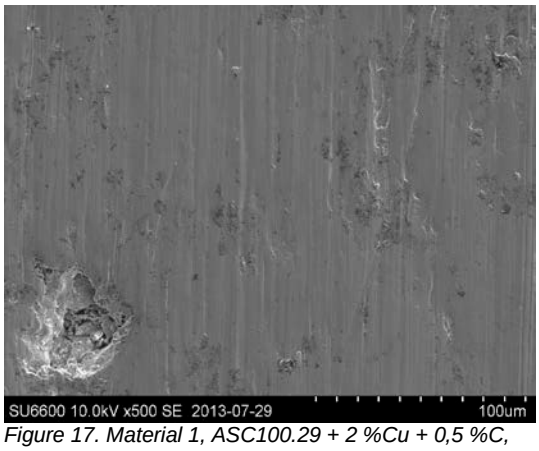


Figure 17. Material 1, ASC100.29 + 2 %Cu + 0,5 %C, as nitrocarburized.

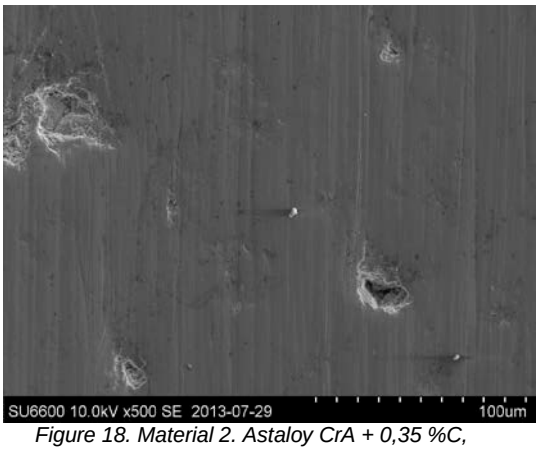


Figure 18. Material 2. Astaloy CrA + 0,35 %C, as nitrocarburized.

The wear depth was determined on the nitrocarburised samples by using the light optical microscope. The wear specimens were cut along the width of 25 mm. In the un-etched microstructures in figure 19, you can see some surface area to the left that has not been in contact with the rubber wheel and therefore there is no wear. The right of the microstructure is from the centre of the wear specimen and is where you can see the largest wear as most of the sand goes into the centre. The height difference, which represent the wear depth, was determined between the surface and the centre. The largest wear depth of 20 µm was measured on the Fe+Cu+C specimens. This should be compared to 11 and 8 µm for the two Astaloy CrA samples.

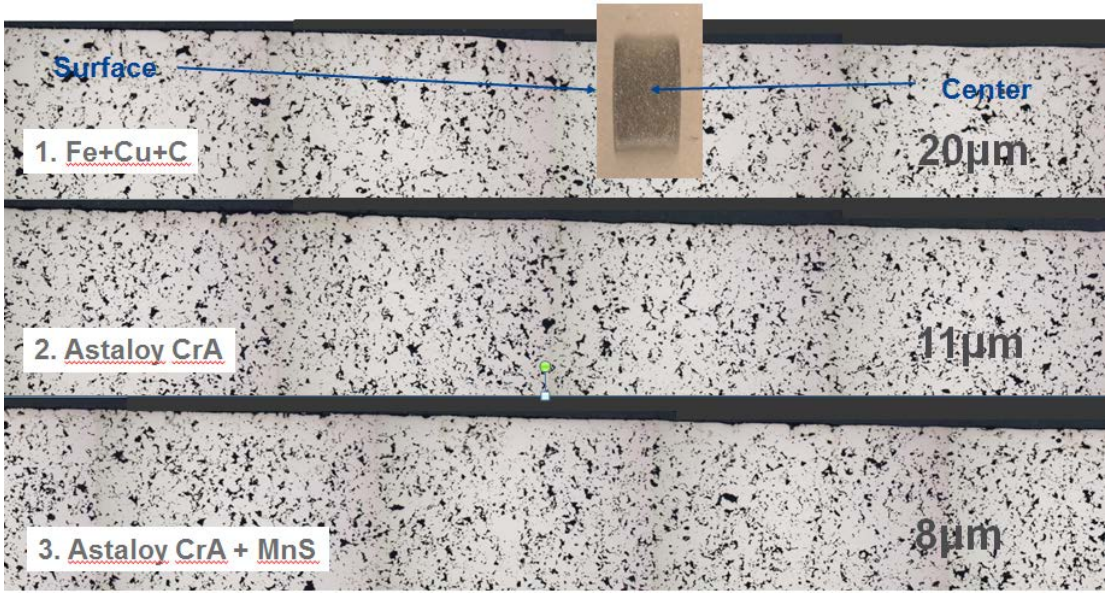


Figure 19. Un-etched microstructures of wear samples showing the untested surface to the left and the centre of the wear path to the right.

The wear tested samples were also looked at in the etched condition. There it could be confirmed that with these wear depths, the entire compound layer is worn off for the Fe+Cu+C material. For the Astaloy CrA samples there is still some 5-10 µm remaining after this rather tough wear testing.

Conclusions

- Thickness of compound and diffusion layer depends a lot on the density of nitrocarburised PM parts
- A pre-steam treatment before nitrocarburising of PM materials is very effective in controlling the thickness of both compound as well as diffusion layer
- Under the tested conditions Astaloy CrA compared to Fe+Cu+C show:
    - Very good response for nitrocarburising
    - Optimal mhv-profile
    - Half or less wear volume according to ASTM G65
    - Half wear depht

References

1. T. Holm, L. Sproge “Furnace atmospheres 3, Nitriding and Nitrocarburizing” AGA Report GIM 89267
2. K-E Thelning, Bofors Handbook, Steel and its Heat Treatment, second edition 1984, pp 492-543
3. J. Slycke, L. Sproge “Kinetics of gaseous nitrocarburising process” Surface Engineering 1989 Vol. 5 No. 2 p. 125-140
4. A Molinari et al. “Wear Behaviour of the Diffusion Layer and the Compound Layer of Nitrided Steels” Surface Engineering, 1998, vol.14, no 6, pp 489-495
5. ASTM G65-04 “Standard test Method for Measuring Abrasion Using the Dry Sand/Rubber Wheel Apparatus”
6. G. F. Bocchini, “Steam Treatment of Ferrous P/M Parts. A State of the Art”, 1992 Powder Metallurgy World Congress, MPIF – APMI, San Francisco, June 21-26, 1992, Proceedings Vol. 4, (77-106).