

Metallographic preparation of nitrided and nitrocarburised components

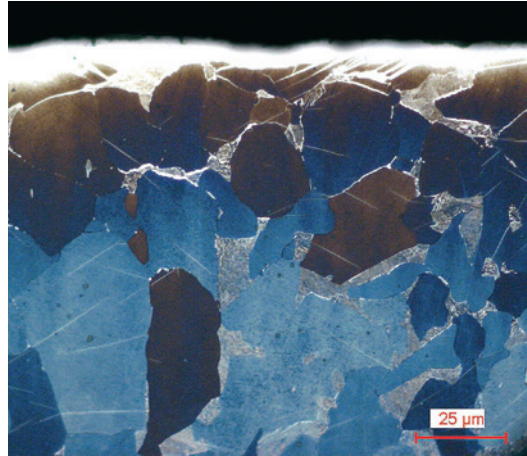
Application Notes

Nitriding is a thermochemical process by which the surface of a ferrous metal is enriched with nitrogen to improve the wear resistance of components. In **nitrocarburising** not only nitrogen but also small amounts of carbon are involved in the process. The result is a nitrided layer consisting of the compound layer ("white layer") and the diffusion zone immediately below the compound layer.

The nitriding and nitrocarburising process using gas or salt bath was developed in the early 20th century in Germany and the United States. The development of ion or plasma nitriding started in the 1930s but was not commercially used until the 1970s. All three nitriding methods have advantages and the selection of a particular method depends on the specific application of the nitrided component.

Nitriding produces a hard, wear resistant layer on carbon and low alloy steels and cast iron. In addition, it considerably improves fatigue strength and by oxidizing the nitrided surface, it enhances corrosion resistance.

The main advantage of nitriding and nitrocarburising over other means of surface hardening is the low process temperature (500-600°C), preferably 580°C. Components can often be nitrided in the fully hardened and tempered condition without the core properties being adversely affected. An additional advantage of the low temperature process is the low risk of distortion. Consequently the parts can be machined to final

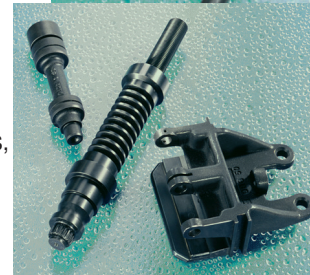


Nitrided steel, colour etched with Beraha's reagent

dimensions and do not need costly finishing work such as grinding or straightening after nitriding.

Nitriding and nitrocarburising are mainly used for ferrous components such as valves, camshafts and piston rods in the mechanical engineering and automotive industries. Other applications are cutting tools or large forming dies. Cast iron parts, such as pump and gear houses, can also be nitrided.

Metallography of nitrided and nitrocarburised components is mainly used for controlling the nitriding process through examination of the layer. The white layer, diffusion zone and porous zone are measured and evaluated. In addition, failure analyses of used parts are carried out to see if faulty material, surface deterioration or the nitriding process were contributing factors.



Difficulties in the preparation of nitrided parts:

- Chipping and cracking in the layer

- Edge-rounding

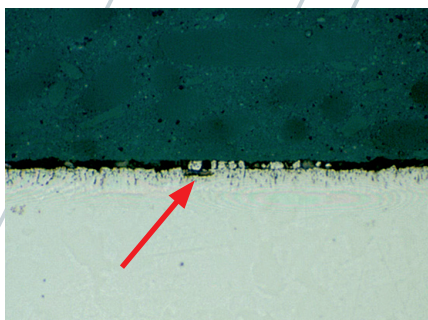


Fig. 1: Shrinkage gap between specimen and mounting resin can cause flaking of the nitrided layer and trap abrasives

500x

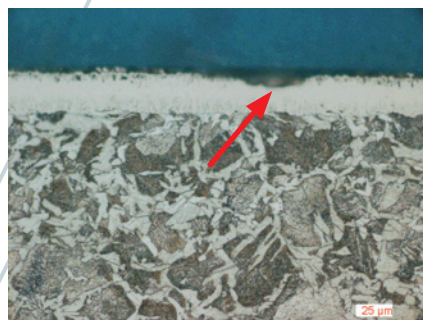


Fig. 2: Without edge retention, the layer is not in focus at high magnification

Solution:

- Proper mounting
- Plane grinding with SiC paper
- Fine grinding with diamond
- Diamond polishing on hard cloths

Formation and composition of the nitrided layer

At nitriding temperature the nitrogen diffuses into the steel surface and reacts with iron, forming γ' iron nitride (Fe_4N), containing up to 6 wt % N. With increasing nitrogen the ϵ -phase (Fe_3N) is formed, which can absorb up to 11 wt % N.

These two iron nitride phases, $\epsilon+\gamma'$, form the compound layer, also called “white layer”, because it stays white when the steel is etched with Nital. This compound layer does not contain any metal but consists of a non-metallic phase formed by iron and nitrogen that can be called a “nitride ceramic”. In the outer areas of the compound layer a porous zone can be found (see Fig. 3).

The percentage of γ' and ϵ -nitride depends on the carbon content of the steel: higher carbon content promotes the formation of ϵ , lower carbon content forms more γ' iron nitride.

With an optical microscope the differentiation of ϵ and γ' iron nitrides in the compound layer is only possible by using very special and difficult etching methods. A correct analysis of the composition can only be made by quantitative structural x-ray analysis using deeply penetrating radiation.

The compound layer is relatively hard and the hardness increases with increasing content of nitride forming alloying elements, at the same time the case depth decreases. Nitrided carbon steels have a surface hardness of 300-400 HV and alloyed steels from 700 HV to more than 1000 HV.

Below the compound zone is the diffusion zone containing nitrogen in solid solution. In addition, it has stable metal nitrides formed by the various alloying elements of

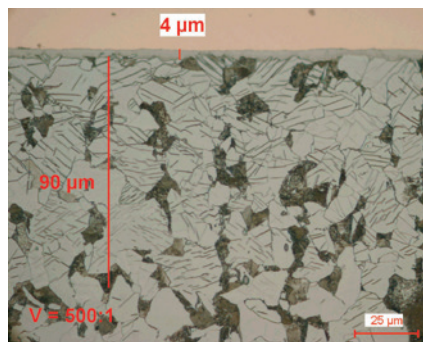


Fig. 4: Nitrocarburised carbon steel after heating for 45 min/300°C, etched with 1% Nital showing nitride needles in the diffusion zone.

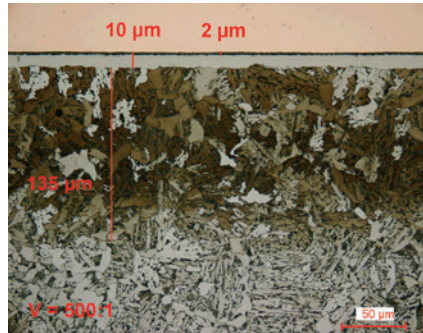


Fig. 5: Alloyed steel, nitrocarburised, etched with 1% Nital, shows dark diffusion zone, and white compound layer with dark oxide coat.

the steel, such as aluminium, molybdenum, chromium and tungsten.

Because of their sub-microscopically fine distribution the nitrides in the diffusion zone of low carbon steels generally can not be seen after etching of the metallographic sample. However, after heating the sample to tempering temperature (200-400° C for 15-30 min), the nitrogen in solid solution precipitates in the form of γ' nitride needles. These nitride needles can be etched so that the diffusion zone becomes visible and its thickness can be measured (Fig. 4).

On alloy steels the diffusion zone will be etched dark with Nital, but the nitrides can not be resolved with an optical microscope (Fig. 5).

The thickness of the white layer and the diffusion zone depends on various parameters of which the most important ones are time, temperature and steel composition. The white layer can be between 0-20 μm and the diffusion zone up to 0.8 mm, depending on the requirements of the application.

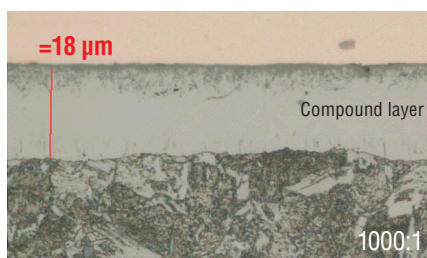
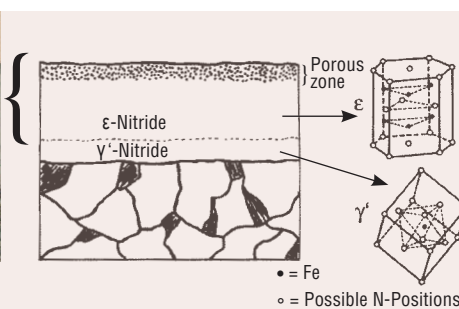


Fig. 3: Details of composition of nitrided layer



Nitriding processes and application of nitrided parts

Before nitriding, the components have to be thoroughly cleaned and degreased. Any surface contamination from grinding particles, oil or metal chips will result in an uneven formation of the nitrided layer. This can cause cracks in the coating which leads to flaking and corrosion (see Figs. 6 and 7) After cleaning, the parts are dried and preheated and then transferred to the actual nitriding environment.

The various nitriding processes can be differentiated mainly by their nitrogen source and the energy supply. Salt bath-, gas- and plasma nitriding have different advantages regarding investment cost, process time, environment, safety and quality. The properties of the resulting nitrided or nitrocarburised surface are in many cases independent of the production process. The required case depth is determined by the application of the nitrided component and can be regulated through the nitriding temperature and time.

In the following paragraphs the different nitriding processes are briefly described and the application of the nitrided parts mentioned.

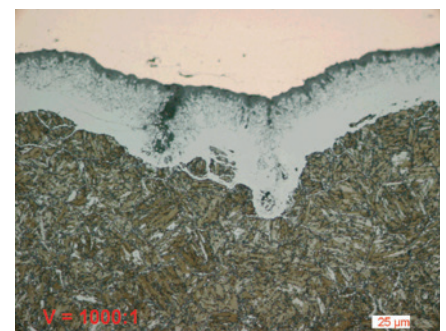


Fig. 6 and 7: Impurities in the steel and on the surface can lead to faulty areas in the nitride layer and cause cracking or corrosion.

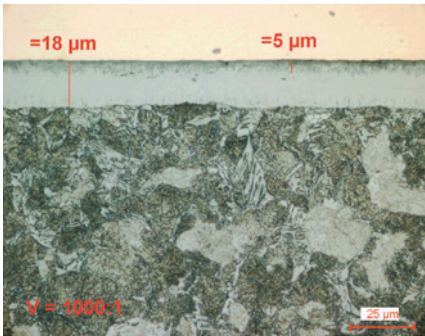


Fig. 8: Salt bath nitrocarburised alloyed steel (16MnCr5), etched with 1% Nital, diffusion zone is etched dark, compound layer with porous zone shows white.

Salt bath nitrocarburising

Salt bath nitrocarburizing is carried out in gas or electrically heated crucible furnaces. The preferred material for the crucible is titanium. After preheating to 350°C, the components are submerged into the salt-bath, either hanging or lying in charging racks, or as bulk material in stainless steel or Inconel baskets. The salt bath consists of alkaline cyanate and alkaline carbonate. Through oxidation and thermal reaction with the immersed component surface, at nitriding temperature the alkaline cyanate releases nitrogen and carbon which diffuse into the surface of the component. Pure nitriding is not possible with the salt bath as small amounts of carbon will always diffuse into the surface. The usual process parameters are 90 min at 580°C.

The active nitrogen releasing agent of the salt bath is the alkaline cyanate. Through the reaction of the cyanate ions the amount of alkaline carbonate in the bath increases. By adding an organic polymer the optimal cyanate content of the bath is replenished again.

After nitrocarburising, quenching in an oxidizing salt bath (380-420°C) produces a black iron oxide (Fe_3O_4) on the surface. It fills the pores of the compound layer and acts as additional corrosion resistant protection. After cooling to room temperature the components can be polished and then re-oxidised depending on the application.

Nitrocarburised cases are particularly resistant against abrasive wear, scuffing, sliding friction and corrosion. The porous surface can retain lubricants which adds to the running properties of, for instance, camshafts. (Fig. 8)

Salt bath nitrocarburising is a fast, flexible and economical process. Typical applications are parts for the automotive industry such as piston rods, crank and camshafts, valves and gears. In addition, nitrocarburised components are used in the aircraft and off-shore industry and in mechanical engineering.

Gas nitriding and nitrocarburising generally takes place in a sealed, bell-type nitriding furnace which provides good gas circulation. The process is mainly controlled by the degree of dissociation of ammonia. The ammonia gas reacts at 500-520°C with the steel surface and decomposes, thereby releasing nascent nitrogen which diffuses into the steel surface. As gas nitriding uses a lower temperature, process times are 40-80 hrs. By adding gases containing carbon, gas nitrocarburising is also possible (Figs. 9 and 10). As a consequence process times are reduced.

The formation and properties of the compound layer and diffusion zone are similar to those produced by salt bath nitriding. However, the thickness of the compound zone can be more accurately controlled or even completely suppressed with gas nitriding. This makes the steel surface very hard but not brittle. Deep diffusion zones can be produced that have a beneficial effect on mechanical strain caused by vi-

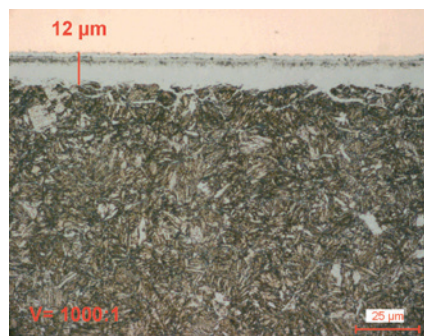


Fig. 9: Alloyed steel (42CrMo4), gas nitrided 510°C/36 hrs, etched with 1% Nital, showing dark diffusion zone, white compound layer with porous zone.

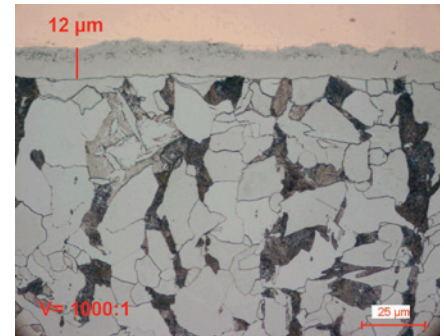


Fig. 10: Gas nitrocarburised carbon steel, 580°C/1.5 hr.

bration and torsion. Components with bore holes, undercuts and cavities, for instance sintered steels, are suited for gas nitriding because the gas can easily enter everywhere as it circulates in the retort. Copper plating or special resistant materials can be used for masking areas that should not be nitrided.

Gas nitrided parts are typically machine spindles, ductile iron pump housings, door lock mechanisms, water pump components and pistons for gas compressors.

Plasma nitriding and nitrocarburising is carried out in a nitrogen - hydrogen atmosphere at 400-600°C and a pressure of approx. 50-500 Pa. For nitrocarburising, gases containing carbon, such as methane, are added. The plasma is produced in a vacuum chamber with a high voltage whereby the work-piece acts as cathode and the vacuum vessel as anode. Because nitrogen and hydrogen are brought into the vacuum chamber as individual gases, the ratio of nitrogen to hydrogen can be controlled allowing variations of thickness and composition of the compound layer. Consequently, not only low carbon steels, but also austenitic steels, powder metallurgy ferrous metals and refractory metals can be plasma nitrided. Plasma nitriding gives a very fine surface

Difficulties during metallographic preparation of nitrided steels

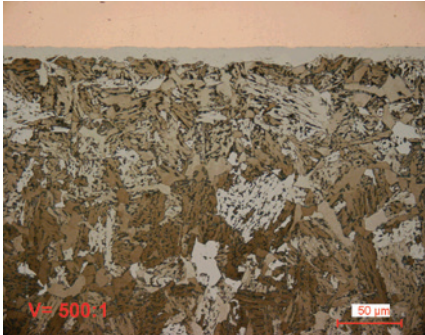


Fig.11: Alloyed steel (16MnCr5N), plasma nitrocarburised, 570°C/ 6 hrs

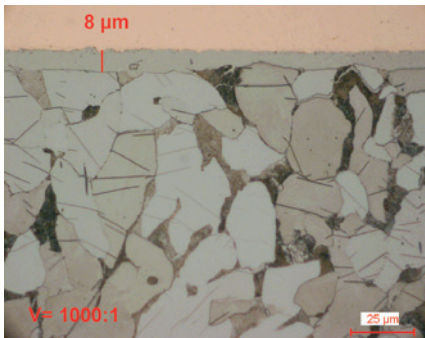


Fig.12: Carbon steel, plasma nitrocarburised, 570°C/ 6 hrs. Both nitride layers are without porous zone and have a very fine surface finish.

finish, almost free of pores, that lends itself for a high polish (fig.11 and 12). Due to this low porosity plasma nitrided and nitrocarburised cam- and crank shafts are for instance used for high performance motors. As plasma nitriding allows a large variety of nitride layers, its fields of application are also varied. Examples are the surface treatment of forming dies such as large plastic extrusion dies and auto body blanking dies, tools for stainless steel deep drawing, casting -, hot forging- and extrusion dies. Other specific applications are corrosion resistant engine valves, high speed steel cutting tools and many applications in mechanical engineering.

The main problem during the preparation of nitrided components is the chipping of the porous zone and cracking of the compound zone (see Figs.1, 2 and 13). This damage is mostly introduced during the first grinding step. Incorrect mounting and long polishing with soft cloths results in rounded edges. As the evaluation of the coating is carried out with 1000x magnification, rounded edges lead to incorrect thickness measurements.

Recommendations for the preparation of nitrided steels

To avoid damage to the nitride layer, it is recommended that **sectioning** is carried out carefully on a cut-off machine with water cooling, suitable for metallographic purposes. For cutting an aluminium oxide wheel is selected according to the hardness of the nitrided component. This is usually a medium hard to soft cut-off wheel.

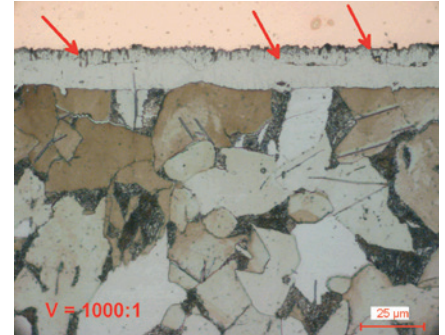


Fig.13: Cracks in the coating caused during preparation.

Mounting: To avoid shrinkage gaps hot compression mounting with a fibre reinforced resin is recommended (DuroFast). In addition, wrapping the sectioned specimen before mounting with a thin, pure copper foil (0.05 mm) promotes good edge retention.*

*The foil is stretched like a ribbon with the blade of a pair of scissors, attached to the sample with instant glue, wrapped around and attached again. Then the excess foil is bent over the surface and pressed down tightly with fingertip or nail. The copper foil on the sample surface is removed by the subsequent plane grinding.

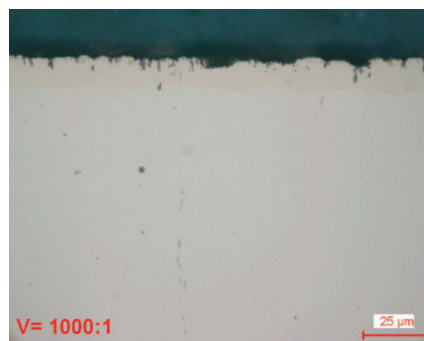


Fig.14: Alloy steel (16MnCr5N) salt bath nitrocarburised, mounted without copper foil. There is flaking of the nitride layer and the thin oxide layer can not be distinguished from mounting resin.

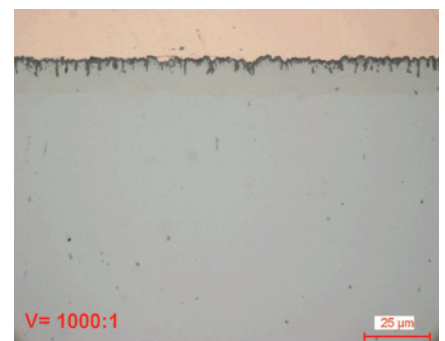


Fig.15: Same as Fig.14, mounted with copper foil, dark oxide layer is clearly visible against the copper colour of foil. The layer is well preserved.

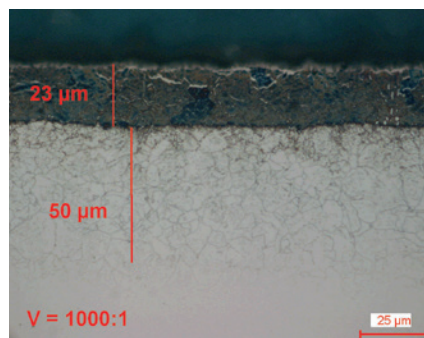


Fig.16: High alloy steel (X45CrSi9V), salt bath nitrocarburised, oxidised, etched with 1% Nital, diffusion zone is etched dark, compound layer can not be distinguished from mounting resin.

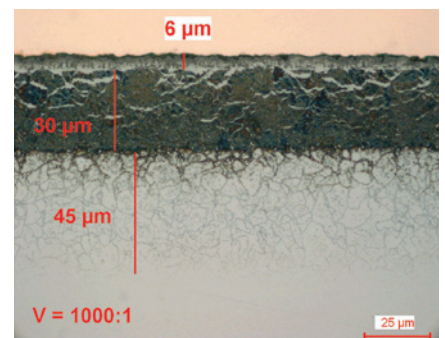








Fig.17: Same as Fig.16, mounted with copper foil, the compound layer can clearly be seen against the copper foil and can be measured.

Grinding

| Step | | PG | FG |
|---|--------------------------|------------|---------------------------|
|  | Surface | Foil/Paper | MD-Largo |
|  | Abrasive | Type | SiC |
| | | Size | #220 |
|  | Suspension/ Lubricant | Water | DiaPro Allegro/Largo 9 |
|  | rpm | 300 | 150 |
|  | Force [N]/ specimen | 25 | 25 |
|  | Time (min) | As needed | 5 |

Also, the copper colour enhances the contrast of the coating against the mounting resin, which is particularly helpful when working with oxidised components (compare Figs. 14 and 15, 16 and 17).

Grinding and polishing: Plane grinding is carried out with silicon carbide Foil/Paper 180# and/or 220#. To ensure edge retention, it is important to fine grind with diamond on a fine grinding rigid disc (MD-Largo). This is followed by a diamond polish on a satin woven acetate cloth (MD-Dac), and a brief final polish with 1 µm diamond or colloidal silica. The following method has given good, reproducible results for nitrided steels. Depending on sample size and type of coating, the polishing times can be slightly modified.

Etching: The nitrided coating is first examined unetched to evaluate the porous zone and the shape and size of the pores. Etching with 1-3% Nital shows the white compound layer and in alloyed steels the dark diffusion zone. For a good nitride case a very good base material is essential. Cracks, inclusions, banding or deformation of the initial surface decisively influence the quality of the nitrided layer. Therefore it is also important to evaluate the structure of the base material. In low carbon steels the diffusion zone can be identified by heating the sample at 300°C / 45 min, and then etching with 1% Nital (see Fig. 4)

Summary

Nitriding is a thermo chemical process by which the surface of a ferrous metal is enriched with nitrogen to improve the wear and corrosion resistance of components. Three nitriding methods can be used: salt bath nitrocarburising, nitriding and nitrocarburising in gas or plasma. Nitriding and nitrocarburising result in the formation of a very hard surface consisting of the compound layer and the diffusion zone. Metallography of nitrided layers is mainly used for quality control, controlling the nitriding process and for failure analysis.

Polishing







| Step | | DP 1 | DP 2 | OP* |
|---|--------------------------|--------------|---------------|------------------------|
|  | Surface | MD-Dac | MD-Nap | MD-Chem |
|  | Abrasive | Type | Diamond | Alumina/Silica |
| | | Size | 3 µm | 0.02 / 0.04 µm |
|  | Suspension/ Lubricant | DiaPro Dac 3 | DiaPro Nap B1 | OP-A or OP-U NonDry |
|  | rpm | 150 | 150 | 150 |
|  | Force [N]/ specimen | 30 | 25 | 15 |
|  | Time (min) | 6 | 1 | 1 |

Table 1: Preparation method for samples of nitrided steels, mounted, 30 mm diameter, using the semi-automatic Tegramin, 300 mm diameter.

As an alternative to DiaPro polycrystalline diamond suspension P, 9 µm, 3 µm and 1 µm can be used together with green/blue lubricant.

*Optional step

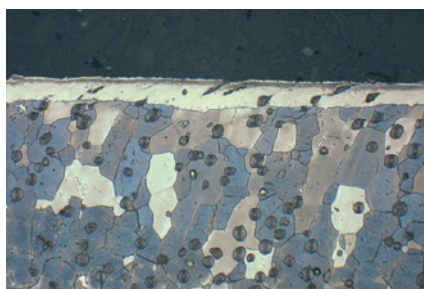


Fig. 18: Ferritic nodular cast iron, gas nitrided, 500x etched with 3% nital.

The main problems when preparing nitrided layers are rounded edges and cracking or chipping of the layer during grinding and polishing. By carefully wrapping the sample in a thin copper foil before hot compression mounting, this problem can be overcome. For fine grinding silicon carbide Foil/Paper or diamond on a fine grinding disc can be used, whereby the latter results in a better edge retention. The subsequent diamond polishing needs to be carried out as long as needed to remove any damage in the layer introduced by the preparation.

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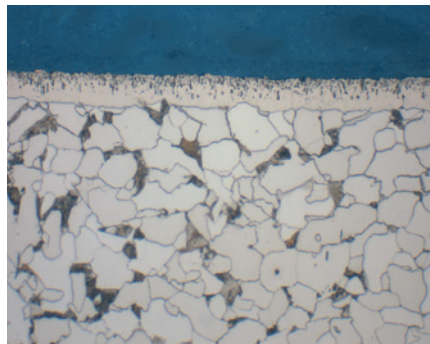
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White layer with porous zone on
 low carbon steel

500x