AN INTRODUCTION TO THE HEF/TS

SURSULF & ARCOR

SALTS BATHS NITROCARBURISING PROCESSES

1. Introduction

The ARCOR salts baths nitro-carburising treatments can be applied to all types of ferrous materials, from carbon and lightly alloyed construction steels to highly alloyed tool steels, sintered steels and all types of cast irons.

2. The processes

The salts baths nitro-carburising processes are particularly well suited to improve the mechanical properties of the surface of treated parts with little or no deformation, particularly with thin section components, if they have been stress relieved at either the same or slightly higher temperature than that utilised in the processes.

The processes produce a duplex layer at the surface of the treated components, an outer compound (compact) layer of high hardness, with an underlying nitrogen diffusion zone. The relative depths of these layers will vary with the alloy grade of the material treated, and can also be adjusted by altering the processing parameters.

The compound layer comprises only ε iron nitride in a compact hexagonal structure which confers outstanding friction properties together with high hardness, providing excellent wear and abrasion resistance. The diffused nature of this layer means that it is relatively ductile (not fragile), and the layer exhibits excellent resistance to cracking with a high level thermal stability up to approx. 600-650 °C.

The nitrogen concentration in the compound layer is between 8.4% and 9.6%, and depending on the specification of the treated material, can also contain between 0.5% and 2.1% carbon. A small amount of oxygen is also present in the form of iron oxides which are regularly dispersed in the first few microns at the surface.

A second stage, controlled oxidation processes is available to greatly improve the corrosion resistance properties of the nitro-oxynitro-carburised layer.

The diffusion of nitrogen into the substrate not only improves its mechanical properties, but also introduces residual compressive stresses which greatly improves the treated component’s fatigue resistance.
3. Processes

3.1 Chemistry and temperature

The chemistry of the baths are principally a mixture of cyanates and alkaline carbonates, with the cyanates providing a sufficient nitrogen potential for the processes to take place. It is important to emphasise that the processes are cyanide free.

The standard operating temperature of the baths are between 570 °C and 580 °C, but for certain application the processes can either be operated in the ferritic range from 480-490 °C, or in the austenitic range at up to 630 °C.

3.2 Treatment times

For a standard carbon or lightly alloyed steel, a typical treatment times will be between 60 and 90 minutes during which a compound layer of 15μm +/-5 will be formed, together with an underlying diffusion zone of 0.4-0.5 mm.

The treatment times can either be reduced to between 10 and 40 minutes for example in the case of high speed or stainless steels in order to increase the surface hardness, or increased to 2 – 2.5 hours to introduce residual compressive stress into the surface of the component and therefore increase its fatigue resistance.

3.3 Post-treatment cooling and washing

After the nitro-carburising treatments, the treated components can be air or vacuum cooled, water or oil quenched or intermediate quenched in salts (oxidising) baths, depending on the specification of the treated components with respect to distortion, roughness and visual appearance.

Whichever cooling method is used, all treated components are thoroughly washed, finally in hot (80-85 °C) water to ensure that all traces of salt and other superficial contamination is removed.

Note:

a. Oxidising salts baths quenching can be operated in two ways, either ;

- as an intermediate cooling stage to eliminate the risk of distortion. The bath operates at 440-450 °C and reduces the temperature of the treated components to below its critical level. A short, 5-10 minute oxidising bath quench will also provide a uniform dark grey / deep black visual appearance to the treated components, with the additional benefit of the oxidation of any remaining nitro-carburising salts on their surface.
as an oxidising treatment of between 15 and 40 minutes during which the outer compound layer is converted to a dense unbroken thick layer of black iron oxides (particularly \text{Fe}_3\text{O}_4), which provides a significant increase in the corrosion resistance of the treated components. (cf appendix)

b. A surface finishing (polishing) operation can be combined with the oxidation process which enables mechanical characteristics, (wear and abrasion resistance etc.) to be maintained whilst retaining or improving on the quality of the surface finish / roughness and the corrosion resistance of the treated components.

4. Types of duplex combination layers

The rate of formation, and thickness ratio between both the compound layer and nitrogen diffusion zone varies with both the type and condition of the material treated.

In general, with low carbon steels a relatively thick compound layer of medium hardness is formed with an underlying deep nitrogen penetration zone of low hardness. Conversely, in highly alloyed steels the compound layer formed is less thick, but of increased hardness, while the nitrogen diffusion zone is also less deep but because it contains a greater concentration of precipitated complex iron nitrides demonstrates improved mechanical properties, particularly with regard to the high level of residual compressive stresses.

Cf appendix illustrates the different layer characteristics of various treatment times on C40, 49MVS 3, 42 Cr Mo 4, 38 Cr Mo V 5, and 32 CrMoV 13 steels.

5. The effects of treatments on different types of materials.

5.1 Carbon and low alloy steels.

The processes are particularly well suited to the treatment of low carbon or lightly alloyed steels, with the formation of a durable homogeneous and thick compound layer (10 to 25 $\mu$m) providing increased resistance to wear and abrasion with a relatively deep nitrogen diffusion zone (0.3 to 0.7mm) which increases the rigidity, particularly in carbon steels.

5.2 Highly alloyed and stainless steels.

The compositions of the treatment baths include specific de-passivants, which rapidly eliminate the passive layer formed in particular on stainless steels. In traditional treatments this passive layer can lead to poor growth of the compound
layer and the presence of soft spots on the treated components. The processes enable the treatment of highly alloyed or stainless steels and allows, for example, the formation of a thick and hard compound layer (>1200HV) on alloy steels of a Cr-Si base, or alternatively, a deep nitrogen diffusion zone on alloys steels of a Cr-Ni or Cr-Mn base.

5.3 High speed and sintered steels.

The processes can be applied to high speed steels at a low temperature (490-520 °C) in order to obtain a high surface hardness (1200 to 2000HV), without the formation of a compound layer. On the contrary, sintered steels of density >6.8 can be treated to provide a deep compound layer with high hardness and improved friction properties.

Note: Preliminary testing on specific components is recommended.

5.4 Cast irons

Whichever type, lamellar or spheroidal cast iron is considered, the processes allow the development of compound layers with retained graphite enabling excellent friction properties even under poor lubrication. Routine maintenance of the treatment baths means there is little or no graphitic pollution which enables the formation of compact or slightly porous layers.

Industrial applications

The processes can provide performance benefits to many areas of manufacturing industry, particularly automotive, and with suitably adjusted treatment parameters, the following components are amongst those currently being treated:

- crankshafts, camshafts, valves, gears, tappets, timing gears, pinion shafts, push rods, injectors, brake pistons/sleeves, bearings, nozzles, rings, wiper shafts, pin balls, steering gears, lockers etc.....

Dimensional and roughness variations

Dimensional changes after treatments are very low, but the processes offer excellent reproducibility. Consequently, the dimensional changes only need to be taken into account on components manufactured to very close tolerances. On carbon and alloyed steels a typical growth on diameter of 10µm +/-2 can be expected.

Surface roughness can develop quite quickly at an operating temperature of 570 – 580 °C, and can increase by a factor of between x 1.5 to x 4. In cases where surface finish is critical, for example in PTFE joints, post treatment polishing can be carried
At lower operating temperatures, either 540 – 550 °C or 490 – 500 °C, there is very little increase in surface roughness.

8. Standard treatments sequences

A typical treatment sequence would be as follows:

- Degrease (vapour or alkaline solution)

- Pre-heat to 350/380 °C to reduce the risk of thermal distortion in the nitrocarburising bath, and to improve productivity.

- Nitrocarburising

- Quenching / cooling, either air cooling, water, oil or salt bath quenching. The cooling cycle is determined by the ultimate treatment objectives in terms of deformation and/or the improvement of corrosion resistance.

- Washing in hot water to remove all traces of treatment salts.

- Drying

- Packaging

Note: To achieve increased corrosion resistance whilst maintaining or improving on surface roughness, specially adapted treatment regimes can be used:

- Nitrocarburising plus standard post oxidation plus impregnation
  ARCOR C2 which guarantees a minimum corrosion resistance of 300-400hrs to standard salt spray tests (ASTM B117).

- Nitrocarburising plus post oxidation plus surface finishing plus impregnation.
  ARCOR PC2 which guarantees a corrosion resistance of 300-400hrs with a controlled maximum surface roughness.

- Nitrocarburising plus short cycle post oxidation plus impregnation.
  ARCOR PC3 which provides a corrosion resistance of between 100 and 150hrs.

- Nitrocarburising plus very short cycle post oxidation plus impregnation
  ARCOR PC4 which provides a corrosion resistance < 100 hrs
Surface finishing can be carried out by a variety of methods according to the shape and specifications of the treated components. These methods include centreless polishing, 'vapour' blasting with glass or ceramic beads or vibratory polishing with controlled polishing medium (trowalisation). All processes are completed by a surface impregnation.

9. Post-treatment and combination treatments.

9.1 Post treatment

In the previous section adaptations of treatments sequences were described incorporating either mechanical finishing or post nitrocarburising salts baths oxidation of the surface to improve the corrosion resistance.

The post-oxidation salts baths treatments operate at between 400 and 440 °C (ferritic nitrocarburising), or between 125 and 160 °C (austenitic nitrocarburising) and when compared with direct water quenching, can provide, as well as greatly improved corrosion resistance, a certain measure of stress relieving in the diffusion zone, improving the ductility of the treated parts.

9.2 Combination treatments
It is possible to obtain very specific properties by combining the ferritic nitrocarburising process (nitrocarburising ARCOR V) with other processes in the following way:

Nitrocarburising V plus induction hardening  
Gas carbonitriding plus Nitrocarburising V  
Gas cementation (carburising) plus Nitrocarburising

*Note: This sort of combination treatment is particularly suited to components where high performance is sought, for example, steel camshafts and gears. It can also be used on plastic injection mould and metal forming tools.*

10. Post treatment machining / masking or protection of surfaces from treatments.

In general, the nitrocarburising treatments are the final stage of manufacture and afterwards the components are considered finished. We have seen (section 7) that it is possible to carry out surface finishing operations and in certain cases it is possible to carry out post treatment machining using, because of the extremely high surface hardness, either hard grinding stones or carbide tipped tools.
As a rule it is not possible to protect areas of components from the treatment medium, particularly if the parts have a complex shape. For simple parts however, areas that do not require treatment can either be masked using specially made jigs and sleeves, or if the parts are very large, by controlled partial immersion in the treatment baths.

Note: It is possible to treat very large components by double immersion, i.e. one end at a time. In these case it is important to take particular care of the component at the point at which it enters the bath, using mechanical protection to prevent excessive oxidation.

11. Summary of the properties conferred by the Nitrocarburising treatments.

- Improved friction properties
  The compound layer is comprised of compact hexagonal phase structure (ε) and can contain both iron oxides and microporosities in the first outside microns which improve the surfaces friction properties as well as its wear and fatigue resistance by surface adaptation.

  Note: Although it is very hard, the compound layer can adapt and deform and is capable of being used in many applications where it is subject both impacts and high pressures.

- Absorption of oil film / dry lubrication
  Due to the microporosities at the surface the nitrocarburising processes provide a certain amount of dry lubrication without seizing, for a short period of time. In a lubricated environment, the microporosities absorb part of the oil film greatly increasing the load required to break that film down.

- Abrasion and fatigue resistance
  It is possible to adjust both the chemistry and the operating parameters of the treatments to obtain wear and abrasion resistant compound layers on most types of steel.

  It is possible to control the nitrogen diffusion between 490 and 630°C to adjust the total penetration and hence the quantity of residual compressive stresses which increase the fatigue resistance of the treated components.

- Corrosion resistance
  By using post oxidation processes, if necessary combined with a surface finishing process, it is possible to increase the corrosion resistance of components
to between 400 and 600 hrs in a salt spray test to ASTM B117.

*Note: ARCOR C is a cost effective alternative to traditional Hard Chrome plating, electro-NiCr or electroless Ni plating processes.*

12. **Characteristics of the impregnation**

The impregnation is done with well selected products like polymers according to the problems to be solved: corrosion resistance improvement, friction properties (sticking effect), etc.

One of the impregnating products for ARCOR C is the COROLAC-S. The efficiency and reproducibility of this COROLAC-S are controlled as follows:

- **one the production line**: Impregnation is done from room temperature up to 40 °C max. by deeping during 15 min minimum.
- **lab. control**: Once a week active products concentrations
- **quality control**: Corrosion resistance tests done in SPC.