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MINIMIZING WEAR THROUGH COMBINED THERMO CHEMICAL AND PLASMA ACTIVATED DIFFUSION AND COATING PROCESSES

MINIMIZIRANJE OBRABE S KOMBINIRANO TERMOKEMIČNO IN PLAZEMSKO AKTIVIRANO DIFUZIJO IN PROCESI PREKRIVANJA POVRŠIN

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To improve surface properties as wear and/or corrosion resistance, thermochemical surface treatments in glow discharge plasmas are already well know. These new technologies are environmentally friendly and therefore RÜBIG PLASNIT® plasmanitriding, PLASOX® plasmanitriding with subsequent oxidation or PLASTIT® PACVD-coating processes are the future surface treatments.

The currently used industrial processes range from plasma-activation of component surfaces for following/additional treatments to diffusion and/or hard coating processes. By a combination of diffusion and coating processes the hard coatings attain an appropriate supporting effect, improved layer bonding and reduction of cracking underneath the surface.

Key words: plasmanitiriding, PACVD-coating, plant engineering, low friction coating

Za povečanje obrabne in korozijske obstojnosti se uporabljajo postopki obdelave površin v plazmi. Te nove tehnologije so prijazne za okolje, zato bodo nitriranje v plazmi RÜBIG PLASNIT® in PLASOX®, pri katerem sledi oksidacija, in PLASTIT® PACVD-nanosi bodoči procesi obdelave površine.

Sedaj uporabljani industrijski procesi obsegajo plazemsko aktivacijo površine komponent za naslednjo/dodatno difuzijo in/ali za procese nanosa trdih prevlek. S kombinacijo procesov difuzije in nanosa dobijo trdi sloji zadostno oporo, večjo trdnost vezave plasti in zmanjšanje nastanka razpok pod površino.

Ključne besede: nitriranje v plazmi, trde PACVD-plasti, inženirstvo naprav, nizkotorne prevleke

1 WEAR MECHANISMS

The improvement in wear/corrosion resistance with surface modifications by heat treatment processes as plasmanitriding, coating, hardening, carburising, ... is often used method to prolong the lifetime of tools or components. For the optimisation of a tribosystem it is necessary (for the heat treater) to know more about the tribosystem. Only with information about the application, used material, tribopartner and lubricants it is possible to find the right solution.

In **Figure 1** the different wear mechanisms are shown and in **Table 1** are listed the most common heat treatments used to increase the wear resistance of steel parts.

As shown in **Table 1** different heat treatment methods are used to increase the wear resistance and that plasma nidriding with or without postoxidation (PLASOX®; PLASNIT®) and PACVD-coating (PLASTIT®) provide the best wear properties.

2 PLASNIT® – PLASMA NITRIDING AND NITROCARBURIZING

Nitriding in general aims to improve wear, fatigue and corrosion characteristics of components. Plasma nitriding offers, in comparison to conventional procedures as gas or salt bath nitriding, several additional possibilities of parameter variation and therefore a better controllability of layer structure, morphology and service characteristics. This leads to a better reproducibility of the nitriding process.

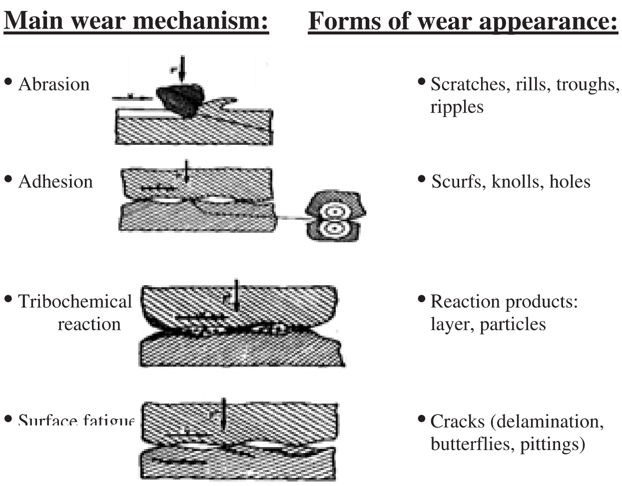

Figure 1: Wear mechanisms
Slika 1: Mehanizmi obrabe

Table 1: Wear reducing possibilities
Tabela 1: Možnosti za zmanjšanje trenja

		Wear resistance				
Heat treatment	Material	Adhesiv	Abrasiv	tribo-chemical	Disruption	Fatigue resistance
Hardening+ tempering	quenched and tempered steels	-	+	-	-	-
Induction hardening	quenched and tempered steels	-	++	-	-	-
Case hardening	Case hardend steels	-	+++	-	++	++
PLASNIT	quenched and tempered steels (nitriding steels)	++	++ (+)	++	++	++
PLASOX	**quenched and tempered steels (nitriding steels)**	**+++**	**++(+)**	**+++**	**++**	**++**
PLASTIT	**Tool steels (deep nitrided nitriding steels)**	**+++**	**+++**	**+**	**-**	**(++)**
Chrome-plating	independent	++	++	++	-	--

Beside the plasma parameters (discharge voltage, intensity of current and electrical performance) the gas type and composition, partial pressure, nitriding time and temperature can also be varied. Due to this flexibility plasma nitriding makes it possible to adjust nitriding characteristics as nitriding depth and white layer thickness over a wide range.

In addition the PLASNIT® process allows the nitrided layer to be taylored to the respective application by independent setting and control of all process parameters. As examples – nitriding without white layer, the treatment of high chromium steels and the partial nitriding of complicated geometries are possible.

3 PLASOX® POSTOXIDATION PROCESS

Plasma nitrocarburizing with an enclosed post-oxidizing (PLASOX® process) improves the corrosion resistance of the component surface. With the PLASOX® process components are plasma nitro/-carburized and then oxidized in the same plasma furnace with steam (in one process!). Expensive polishing prior to oxidation treatment can be dispensed as well as process interruption or cooling. This leads to substantial cost savings.

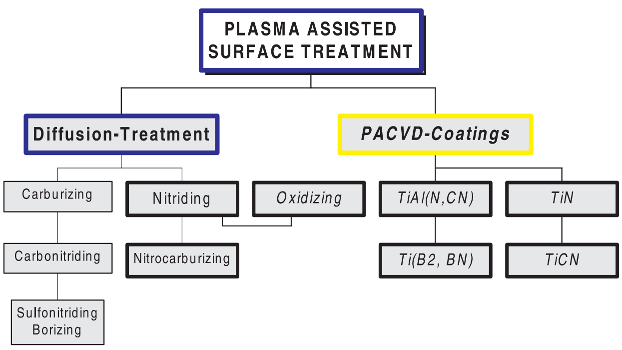

Figure 2: Overview of plasma assisted surface treatment processes
Slika 2: Pregled plazemskih procesov za obdelavo površin

PLASOX® layers show a very low friction coefficient and tremendous running-in characteristics even comparable with gas-nitrocarburized and oxidized surfaces. The combination of mainly ε-$Fe_{2-3}N$ nitride in the white layer and an oxide top layer is suitable for improving the running-in characteristics and also for reducing the wear.

Since 1994, components like camshafts and crankshafts for the automotive industry, hydraulic piston rods,… have been successfully treated using the PLASOX® process technology. The white layer with usually few pores underneath and the oxide layer causes an anthracite-like appearance. PLASOX® gives a surface for life to visible parts like air springs, mountings, pneumatic pistons and articles of daily use.

The PLASOX® layers can withstand higher pressure loads than galvanically deposited anti-corrosion layers. Compared with these, no electrochemically negative element is formed between the PLASOX® layer and the base material in the event of mechanical damage of the surface like scoring. Therefore there is no corrosion underneath the PLASOX® layer and no subsequent large-surface spalling.

4 PLASTIT® PLASMA NITRIDING WITH SUBSEQUENT PACVD COATING

Plasma assisted chemical vapour deposition (PACVD) combines the advantages of both todays popular coating techniques PVD and CVD.

By activation of the precursor gases by pulsed plasma, the process temperature of the chemical vapour deposition can be reduced below 500 °C. This enables the treatment of alloyed steels in a way that the previous microstructure (hardening/annealing) is preserved. Similar to conventional chemical vapour deposition, homogenous deposition is possible even for complex geometries.

In comparison to PVD processes the components to be coated do not need to be mechanically moved during coating. As PVD coating processes are sputter processes, the charging and manipulating effort can be significantly shortened.

A further advantage is that cleaning by sputtering and nitriding can be carried out in the same plant immediately before the coating process. The nitrogen enriched diffusion layer produces the necessary supporting effect for thin hard coatings. As mentioned, the process parameters of the nitriding can be optimized for every steel/coating combination.

5 PLANT TECHNOLOGY

Figure 3 shows a MICROPULS® plasma furnace manufactured by RÜBIG. An important feature is that the charge is heated by wall heating and by plasma. This permits an optimum adaptation of the plasma process parameters independently of the process temperature.

Especially in serial production (automotive industry) an excellent temperature uniformity is necessary to achieve small deviations in surface hardness, nitriding depth and white layer of the products. Therefore, the new generation of plasma nitriding furnaces from Rübig is equipped with 3 independent heating and cooling zones. The temperature difference between charging plates in different heights can therefore be reduced to less than 5 °C. Additionally, it is possible to install a controlled cooled inner anode. This leads to an excellent temperature uniformity to uniform nitriding results and to a high reproducibility. By using 4 to 6 thermocouples, spread all over the whole furnace, the temperature uniformity can be documented.

The plasma voltage is applied in form of rectangular pulses with a frequency of up to 50 kHz. Pulses of positive and negative polarity are possible, which permits the deposition of insulating layers. In the event of arcing, the voltage can be disconnected in less than one microsecond and the damage of workpieces prevented. The thermocouples can be attached directly to the workpieces by means of a special insulating amplifier.

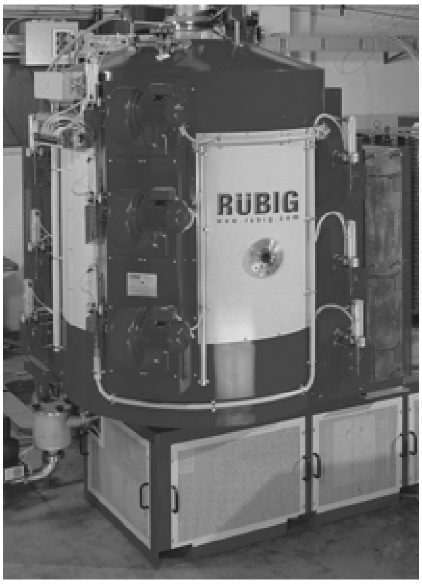

Figure 3: RÜBIG PLASNIT®/PLASTIT® plant layout
Slika 3: PLASNIT®/PLASTIT®–Rübigova naprava

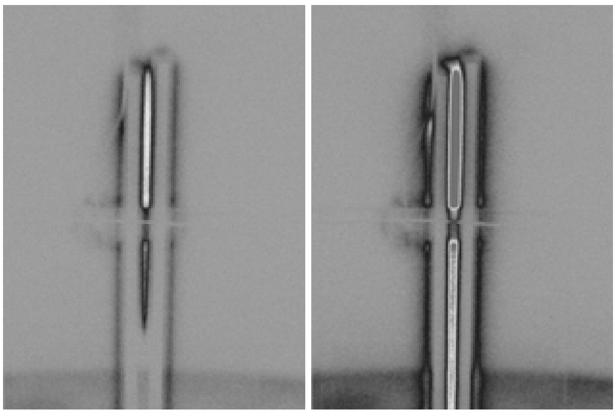

Figure 4: Example of the ignition without/with bipolar technology: left 80 µs unipolar mode right: 80 µs in bipolar mode
Slika 4: Vžig plazme brez bipolarne tehnologije in z njo. Levo: unipolaren način, 80 µs; desno: bipolaren način, 80 µs

Due to the capability of the RÜBIG MPP plasma generators it is possible to treat very complicated geometries by using the bipolar technology. This technology increases the velocity of the plasma ignition and permits the treatment/coating of small gaps and holes (**Figure 4**).

6 RÜBIG PLASTIT® PACVD HARD COATINGS FOR INDUSTRIAL APPLICATIONS

Increasing the lifetime of tools is one of the most important aim of tool manufacturers and users. The task for surface engineering is to understand the complex loading and tribological conditions of the working procedure and to develop countermeasures.

The plasma-assisted chemical vapor deposition (PACVD) technique is a well suited method to deposit hard coatings both on large dies and moulds as well as on small tools.

The aim of this study is to present and discuss results obtained with PACVD PLASTIT® hard coatings (i.e., TiN, Ti(C,N), Ti(B,N), (Ti,Al)N) in industrial applications.

Problems in industrial deposition techniques for moulds and dies

- High cost of dies and risk of damage
- Rotation of big and heavy moulds is difficult in PVD
- Negative influences of spark erosion manufacturing on adhesion of PVD coatings
- Low substrate hardness (*HRC* 29 – 48) gives insufficient load support to hard coatings
- Adhesion problems due to residual de-gassing during coating process

Solution with RÜBIG PLASTIT® PACVD hard coatings

- No risk: coating temperature between 480 °C and 510 °C
- Operating pressure in the range of mbar allows coating of big and heavy tools without rotation
- Substrate pre treatment like sputtering and/or plasma etching improves the adhesion
- Pre nitriding in the same process is possible
- Higher operating pressure allows lower pumping times for degassing

Conclusions:

The benefits of RÜBIG PLASTIT® processes are essentially based on the possibility of combining pre-treatment methods like sputtering and chemical etching with plasma-nitriding, on the ability to coat large three-dimensional tools homogeneously without substrate rotation and on the development of new low-friction TiN-based hard coatings with low chlorine contents.

7 PRACTICAL EXAMPLES FOR COATING DEVELOPMENT

Aluminum pressure die casting

In aluminum die casting (**Figure 5**), the hard coating primarily has to reduce erosion, corrosion and soldering due to the liquid aluminum. Thus, to achieve an optimum performance, adhesion, hardness, soldering propensity, oxidation resistance and stress state have to be carefully optimized, before big and heavy dies are coated.

The end of the lifetime is determined by heavy soldering of aluminum or insufficient surface quality of the casting.

- Tenifer® treated mould:
  - after 8500 shots heat checks
  - after 50000 shots roughness > 10 ìm
- PLASTIT® Ti(C,N) coated mould:
  - slightly higher soldering at start
  - after cleaning soldering much lower
  - then 45000 shots without interruption
  - after 65000 shots recoating
  - total number of shots: **160000**

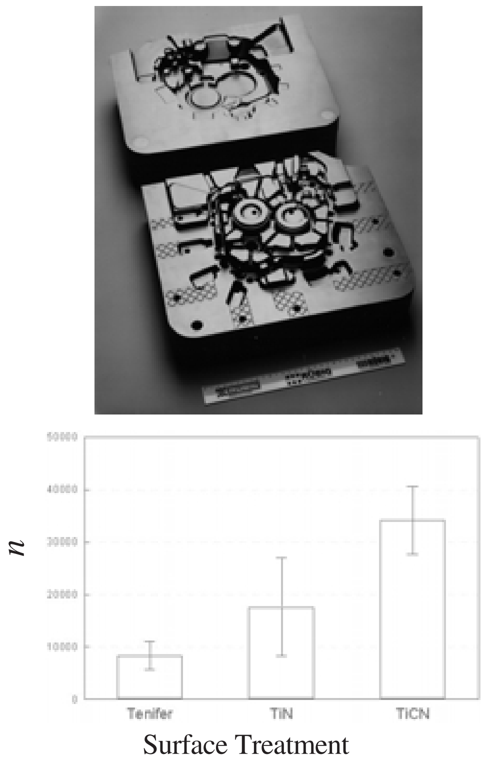

Figure 5: Number of shots *n* achieved in aluminum pressure die casting for core pins with different mould surface treatment
Slika 5: Število tlačnih ulitkov *n* aluminija za središčne trne z različno obdelano površino kokile

Figure 6: Reflector injection mould
Slika 6: Injekcijska kokila za avtomobilski reflektor

Plastic injection molding

In plastic injection molding, wear of the moulds occurs due to corrosion caused by exhaust gases or decomposition products, abrasion from the flow of material in contact with tool surface and adhesion between tool surface and molten material. An industrial application where surface quality is extremely important is the production of reflectors for automotive headlamps, made of polyetherimide (PEI, ULTEM® 1010). Injection mold (**Figure 6**) made of AISI H11 hot work steel.

Without coating:
the mould had to be polished manually after a few hours of operation

PLASTIT® Ti(C,N) coating:
the adhesion tendency was significantly reduced; the service life without polishing was increased to more than one week and a signficant cost reduction due to reduce polishing, scrap production and maintenance was achieved.

8 SHEET METAL FORMING

In sheet metal forming, the main wear mechanisms have been identified as adhesive wear due to the high loads applied, abrasive wear e.g. by highly strain-hardened wear debris, and mechanical fatigue due to cyclic loading.

The uncoated tool: is lubricated after every 20th stroke and disassembled for repolishing after 2000 parts. Tools treated with

- PLASTIT® Ti(C,N)
- low friction are
- lubricated after every 50 strokes. The
- production of 26000 parts without cleaning (until test was stopped) was achieved.

Tribometer measurements show very low friction values for TiN and Ti(C,N) coatings. Dependence of the friction coefficient of an unalloyed steel ball sliding against a PACVD TiN coated disc on the sliding

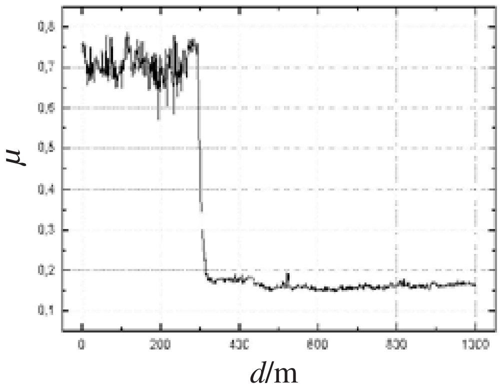

Figure 7: Fricition coefficient μ PACVD TiN unalloyed steel
Slika 7: Koeficient trenja μ PACVD TiN za nelegirano jeklo

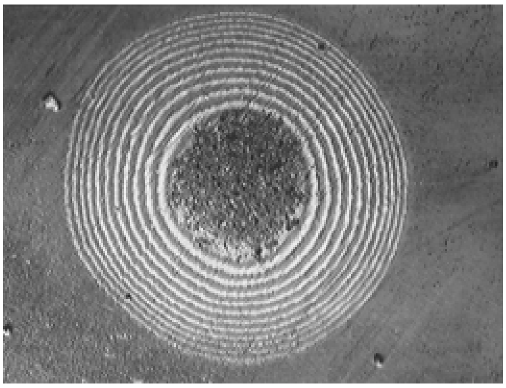

Figure 8: Multilayer
Slika 8: Multilayer

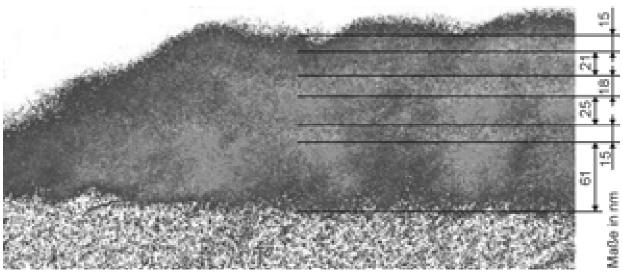

Figure 9: TiN/TiBN mulitilayer. The thickness is given in nm.
Slika 9: Prerez mnogoplastnega prekritja TiN/TiBN

distance (normal load, 2 N; sliding speed 10 cm/s; relative humidity, 35 %) is shown in **Figure 7**.

New developments

The boronic layers are especially noticeable, as they do not only feature a high degree of hardness but also an unusually fine layer microstructure. These layers are often applied as multilayer coating. Two or more layer systems are alternately applied which significantly improves layer stressing conditions and strengthens the bonding.

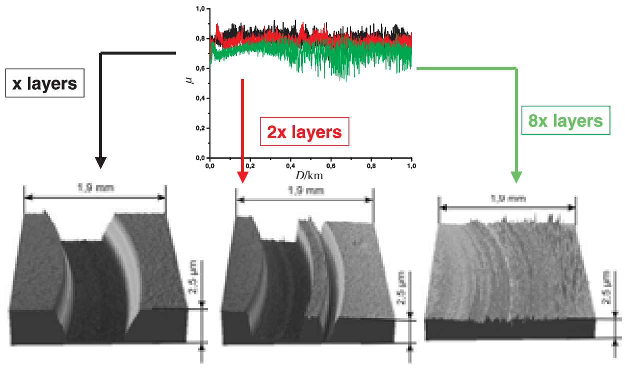

Figure 10: Pin on disc 3d test
Slika 10: 3d test segmenta na disku

Figure 8 shows a calowear section of a component that was coated using the multilayer technique. In this example, one TiN and one TiB_2 were applied alternately, whereby the individual layers are less than 0,2 µm thick.

Depending on the layer thicknesses and the B-concentration the abrasive wear characteristics can change significantly (**Figure 10**).

9 SUMMARY

The possibilities of plasma assisted heat treatment are wide-ranging. They have been known for some time and should be considered a technical standard. The PLASTIT® process, which combines a PACVD process with preceding plasma nitriding is a very young process that Rübig has sold successfully and world-wide for 7 years. More than 15 PACVD plants were supplied to America, Asia, Canada and Europe, with a know-how exchange through ongoing user meetings. Especially the field of application of large tools for forming, diecasting and injection moulding industry this process is ideal. However, corrosion resistance and sliding characteristics of components can be significantly improved not only by coating, but also by simple oxidation after a plasma nitrocarburizing (PLASOX®) process.

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