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Coatings against Friction and Wear

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1. Surface Technologies

1.1. Introduction

Surface coatings have acquired great technological and economic significance. Surface finishes create aesthetic as well as functional components and commercial goods. Low-priced materials can be used as central components. The finishing of the surface ensures the functions. Scarce and expensive raw materials can be saved.

Surface engineering provides extensive applications in the electrical and optical industries. In medicine, coatings are applied onto implants to improve compatibility.

Another field of surface finish application is corrosion and wear protection.

The damage caused by corrosion and wear is high. In America, 70 billion dollars were specified by the Department of Commerce for the year 1975 alone, which is roughly 4 % of the gross national product /1/.

For the Federal Republic of Germany, estimates for economic losses due to corrosion and wear are put at DM 45-50 billion a year, approx. DM 10 billion being caused by wear /1.2/ /1.3/ /1.4/ /1.5/.

The loss could be reduced by approx. 50 % by consistent applications of surface technologies.

The demands made on the finish are often multifarious. Thus, for example, thermal barrier coatings must simultaneously exhibit wear- and corrosion-resistant properties. Figures 1.1 and 1.2 illustrate the interplay of the most important fields of application.

Conventional application of surface finishing

friction and wear	corrosion	thermal insulation	electrical insulation	electrical engineering electronics	optics	medicine	decoration
				maintenance and repair			

Fig 1.1: Conventional applications

Application of surface finishing techniques for PNP components

friction and wear	corrosion	thermal insulation	permeation
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Fig 1.2: Applications for PNP components

The possibilities of surface finish stressing require the application of a large number of treatment processes in order to meet all requirements. The constant further development of known and long-used techniques and the exploration of additional application possibilities lead to improved or even new products.

In the following, above all, the metal-processing applications with their bordering areas will be covered.

Electrical engineering, optics, medicine and applications of surface finishes for decorative purposes will only be casually mentioned.

1.1.1 Protection against Friction and Wear

A far-reaching task of surface finishing is to reduce the friction and wear of components that are in contact with each other.

According to DIN 50320, wear is the progressive loss of substance from the surface of a solid body caused by mechanical action, i.e. contact and relative motion of a solid, liquid or gaseous counterbody.

This tribological stressing, which manifests itself in the form of detached particles, changes in the substance and shape of surfaces, differentiates between 4 main wear mechanisms /1.7/.

- | | |
|---------------------------|---|
| - Adhesion | cold welding "seizure" |
| - Abrasion | abrasive wear process |
| - Rolling-contact fatigue | fatigue of surfaces
(fractures and cracks) |
| - Tribochemical reactions | chem. reaction body/medium |

Adhesion

Adhesion is linked to the direct contact of two bodies. The technically induced "rough" surfaces due to surface pressure and/or relative motion cause anti-adhesive oxide scales to break followed by cold welding in the microscopic range.

If the shear strength of the material is exceeded due to the adhesive forces that occur, relative motion causes material shearing in the surface regions. Shearing preferentially occurs in regions of minimum shearing force and not in the original contact plane strengthened by plastic rough peak deformation.

Metallic adhesion bonding is connected to the electron density in the contact region. Metals of high electron density tend more to adhesion.

The tendency to adhesion bonding becomes greater if one partner can serve as electron donor and the other as electron acceptor /1.8/.

Materials with poor cold welding performance (fcc) and lubricants offer themselves for friction and wear reduction.

On account of their large microcontact surfaces, fcc material combinations should be avoided. A hexagonal lattice structure exhibits more favourable properties for friction- and wear-reducing component pairings.

Carbides do not tend to metallic adhesion bonding either /1.8/.

Abrasion

Abrasion causes the formation of grooves. This effect preferentially occurs in the case of differences in hardness of the wearing partners. The roughness peaks of the harder partner penetrate into the softer one and abrasive wear occurs due to relative motions.

The application of hard materials can reduce abrasive wear. If hard materials are used, the brittleness of the material must be adequately taken into account.

Wear fatigue mainly occurs due to rolling, shock and overflow (e.g. solid/gas with particles) loads. Consequential phenomena are cracks and pitting in the material. The appearance form is independent of the sliding processes.

Wear life due to rolling-contact fatigue can be determined by empirically obtained values.

Tribochemical reactions

This is understood to be the chemical reaction of the outer surface layer of a substrate with the counterbody or adjacent medium. Tribochemical reactions form reaction products (often at elevated temperature), which can lead to changes in surface strength. Scales that are formed (e.g. protective metal oxides) and/or particles can be detached.

Combined action of wear mechanisms

In practical wearing processes, wear mechanisms are superimposed.

For example, the contacting body is damaged by adhesion and the surface by tribochemical reactions, whereas material removal occurs due to abrasion (abrasive wear) and rolling-contact fatigue.

The diversified interaction of influential parameters illustrates that it is difficult to transfer individual test specimen results to operationally loaded components. A consideration of the whole tribological system is required.

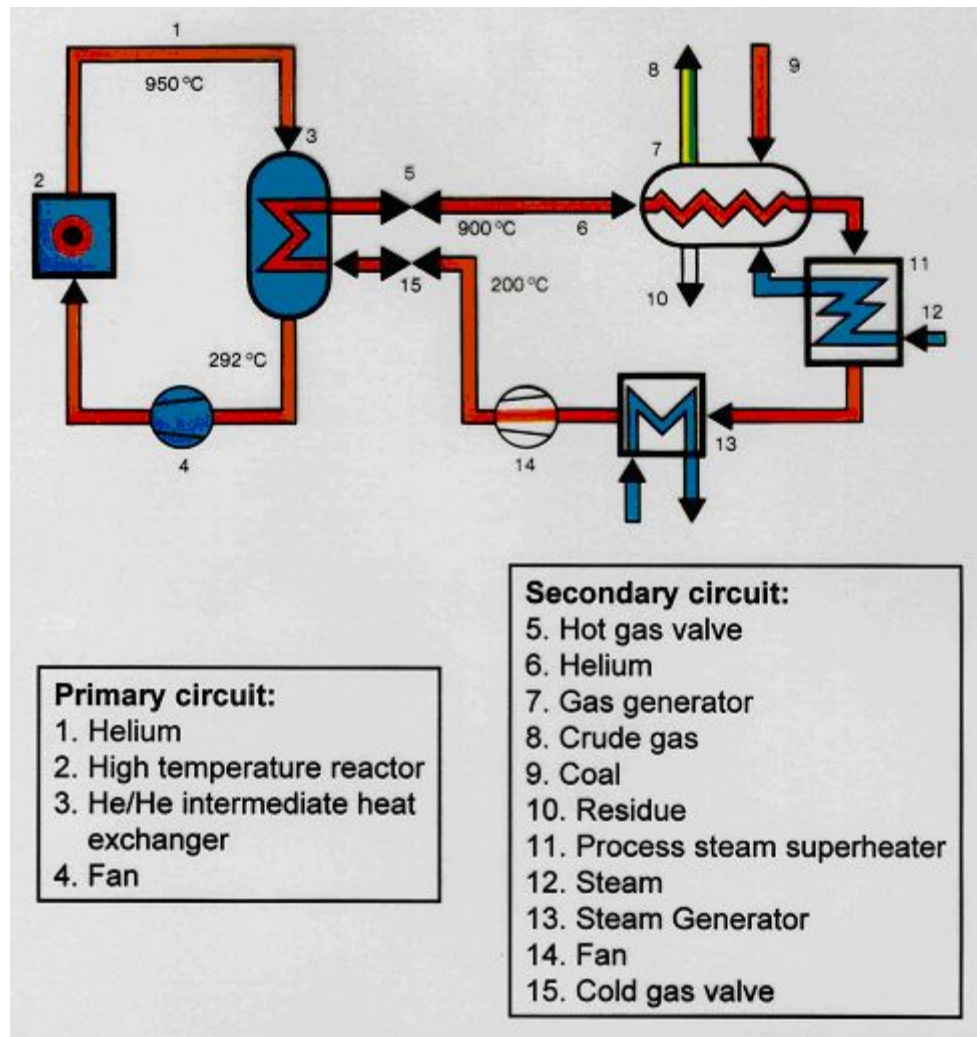
1.1.1.1 Conventional Applications

The application of liquid lubricants to reduce friction in conventional fields of application is common practice. However, this possibility reaches its limits as soon as the physical and chemical requirements become more extreme.

In the Japanese sheet fabricating industry, which is confronted with working high-strength, stainless and clad steels, surface-treated tools are used instead of lubricants for such materials difficult to work. In addition, the costs for surface treatment are lower than in the case of a lubrication of the shaped parts which must be constantly renewed /1.9/.

For parts subject to friction and wear at low and high temperatures, in high vacuum, inert gas atmosphere and oxidizing or corrosive environment, solid lubricants can be a possible alternative /1.10/. Thus, for example, a ball bearing coated with solid lubricant has a service life when running in dry atmosphere which may be up to 50 % longer than the normal life of a grease-lubricated bearing /1.11/.

1.1.1.2 Application for PNP Plants



Abrasive wearing up to self-welding of the metal parts can also occur in metallic structural parts of gas-cooled high-temperature reactors working at operating temperatures of up to 1000 °C in partially reducing, partially oxidizing atmosphere /1.12 - 1.14/.

The thermal expansions of differently hot components lead to relative elongations of structural material. Vibrations induced by the helium flow also make a "protection" against wearing and increased friction coefficient necessary. If this "protection" is lacking, a non-positive component connection may result /1.15/. Depending on the

geometrical conditions, this may lead to restrictions in component performance, reduced life and on critical components to failure of the component /1.16/.

In general, the friction and wear processes on the surface of HTR components can be divided into two types /1.12/.

1. Sliding motions, which occur due to the thermal expansion of components or due to mechanically given processes.
2. Fretting motion sequences, which occur due to gas-induced vibrations or due to mechanically induced vibrations (shop machines).

Further factors of influence are the geometry of contacting parts, surface pressure, temperature, atmosphere and motion sequence.

The system of heat exchanger tube and support with the small tube wall thicknesses used for thermal reasons is such a strongly stressed arrangement in which fretting phenomena must be expected.

By means of a protective sleeve arrangement, the wearing zone can be shifted from the tube surface to the sleeve surface /1.13/ /1.17/. However, protection against self-welding of the metal pairing is also required here. If no protection can be produced by the metal pairing, it is possible to achieve protection by suitable surface techniques.

Anti-friction bearings operated at elevated temperatures in helium atmosphere show fewer traces of wear with surface coatings compared to normal bearings, but functional reliability and maintenance intervals can also be extended here by treating the friction surfaces /1.14/.

Control mechanisms of the reactor in wearing locations, internals that are subject to sliding wear or exhibit points of contact between metal and graphite reactor can be protected by influencing the surfaces /1.13/.

2. Processes, Goals, Materials and Market Areas of Surface Treatment and Coating

Two types of surface finishing processes are to be distinguished:

1. surface treatment
2. surface coating

Surface treatment involves a modification of the surface layer of a component by external influences in such a way that the workpiece surface can take over extended functions. This may be done by:

- mechanical treatment (e.g. blasting, polishing)
- thermal/chemical processes (e.g. flame hardening, carbonitriding)
- action of high-energy ion or laser beams (e.g. ion implanting, laser hardening).

By the application of coats (surface coating) layers are applied onto the substrate material.

Possible process variants are:

- spraying (e.g. thermal spraying, plastic coatings)
- electrolytical and chemical deposition (e.g. metal layers, dispersion layers)
- physical and chemical vapour deposition (e.g. ion plating, vapour deposition)
- cladding, welding and dipping
- others (e.g. sintering, enamelling).

In the treatment and coating of surfaces, the core of the workpiece should satisfy e.g. the strength and toughness requirements and the treated surfaces should exhibit the corresponding anti-corrosion and anti-wear properties.

Possible processes for the treatment and coating of surfaces are compiled in Fig. 2.1.

Treatment	Coating	
<p>mechanical strengthening</p> <ul style="list-style-type: none"> - blasting (shot peening) - rolling - pressure polishing <p>electrochemical techniques</p> <ul style="list-style-type: none"> - electropolishing <p>surface layer hardening</p> <ul style="list-style-type: none"> - flame hardening - induction hardening - dip hardening - laser beam hardening - electron beam hardening - surface layer remelting - surface layer realloying <p>ion beam techniques</p> <ul style="list-style-type: none"> - ion implantation - ion beam mixing <ul style="list-style-type: none"> • static • dynamic 	<p>lacquer coating</p> <p>plastic coatings and linings</p> <ul style="list-style-type: none"> - whirl sintering - dipping - spraying - vulcanizing <p>electrolytically and chemically produced layers</p> <ul style="list-style-type: none"> - electrolytical deposition - chemical deposition - dispersion layers <ul style="list-style-type: none"> • galvanically deposited • chemically deposited - anodically produced conversion layers <ul style="list-style-type: none"> • anodizing • production of HAE layers - chemically produced conversion layers <ul style="list-style-type: none"> • passivating • browning 	<p>thermal spraying</p> <ul style="list-style-type: none"> - flame spraying (wire, powder) <ul style="list-style-type: none"> • without thermal post-treatment • with subsequent fusing • with simultaneous fusing - electric arc spraying - plasma spraying, APS, VPS - hypersonic flame spraying - detonation spraying (D-gun) - laser spraying <p>chemical vapour deposition (CVD)</p> <ul style="list-style-type: none"> - conventional CVD - plasma-enhanced CVD - laser-induced CVD <p>deposit welding</p> <ul style="list-style-type: none"> - gas, plasma - TIG or MIG - electric arc - flux-cored wire

thermal processes - nitriding - nitrocarburizing - case hardening - siliconizing - boronizing - chromizing - alitizing - sherardizing - plasma treatment of metals	<ul style="list-style-type: none"> • phosphating • chromizing dip coatings - hot-dip coatings - salt-bath dipping physical vapour deposition (PVD) - vapour deposition <ul style="list-style-type: none"> • high-vacuum evaporation • gas scattering evaporation • reactive evaporation - sputtering <ul style="list-style-type: none"> • diode array • DC and HF sputtering • bias sputtering • reactive sputtering • high-performance sputtering • cathodic arc - ion plating <ul style="list-style-type: none"> • reactive ion plating 	- under powder cladding - roll cladding - explosive cladding enamelling sol-gel method soldered-on layers plasma polymerization
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Fig. 2.1: Treatment and coating processes

In the following, important processes will be briefly explained, the goals pursued will be described, the materials used listed and market areas of surface treatment and surface coating pointed out by means of production examples.

2.1 Mechanical Strengthening

2.1.1 Shot-Peening Process

Shot peening is a blasting technique. In this process, large amounts of globular blasting abrasive are propelled onto the component surface thus producing a compressive prestress in the substrate surface.

2.1.2 Goals

	Shot peening
Goals of the process	<p>Building up compressive stresses by compression blasting for:</p> <ul style="list-style-type: none">• reducing the danger of stress corrosion cracking• improving the fatigue strength performance of dynamically loaded parts• compensating other adverse surface treatment processes

The common goal is to increase operational reliability and the lifetime of highly stressed components made of high-grade materials /2.1/ /2.2/.

2.1.3 Materials

	Shot peening
Substrate Materials	<ul style="list-style-type: none">• low- and high-alloyed steels• Ni, Co, Mg, TiAl materials

2.1.4 Market Areas

	Shot peening
Market areas	<ul style="list-style-type: none">• steam generator tubing• turbine blading• aircraft construction for the machining of tiling parts, landing gear parts• gearing parts prior to further treatment

2.2 Electrochemical Process

- Electropolishing

2.2.1 Process

Electropolishing is allocated to the electroerosion fabrication processes according to DIN 8590 and, in principle, is the reversal of electroplating.

Material removal is completely effected by electrochemical dissolution of the anodically connected material surface in an electrolyte exposed to an external direct current. Electrolytes based on concentrated mixtures of phosphoric acid and

sulphuric acid are primarily used for the electropolishing of stainless steel /2.3/. Material removal takes place under levelling conditions on the entire material surface, increased current density leading to enhanced removal at corners, edges, burrs and flakes.

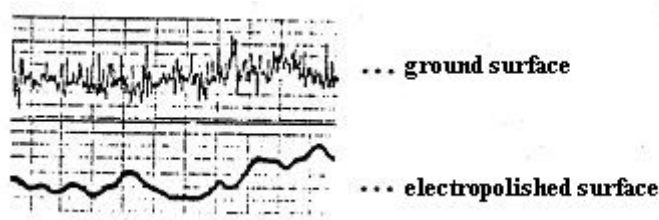


Fig. 2.2: Profile diagrams /2.4/

Small parts are dipped into electropolishing baths for machining, tubes and vessels can be partly or completely filled with electrolyte and polished with a suitable cathode.

Partial electropolishing is also possible.

2.2.2 Goals of Electropolishing

	Electropolishing
Goals pursued	<ul style="list-style-type: none"> • Achieving the best possible corrosion protection of the base material - faultless formation of the passive layer becomes possible <p>Passive layer is increasingly formed (stainless steel).</p> <ul style="list-style-type: none"> • removal of near-surface tensile and compressive stress layers • removal of impurities (extremely pure surfaces) • suppressing adhesion processes that may lead to scaling • improving the cleaning performance • fine and ultrafine deburring • friction and wear reduction • increasing the fatigue strength by eliminating crack nuclei • improving the decontamination performance in nuclear engineering • decoration, gloss and reflection

2.2.3 Materials

Materials capable of being electropolished should exhibit a homogeneous microstructure and a uniform distribution of the alloying elements. If possible, the fraction of nonmetallic impurities such as slags and carbides in the microstructure should be small. Process parameters and electrolyte can be tuned to the material /2.4/.

	Electropolishing
Materials	<ul style="list-style-type: none">• Primarily for austenitic chromium-nickel and chromium-nickel-molybdenum steels

2.2.4 Market Areas for Electropolishing

	Electropolishing
Market areas	<ul style="list-style-type: none">• pharmaceutical and biotechnical product installations• vessels, apparatus• pulp and paper industry (avoidance of scaling)<ul style="list-style-type: none">- vessels, apparatus (heat exchangers)- machines• nuclear engineering (decontamination)• vacuum technology (reducing desorption and outgassing rates) (e.g. inner surface of JET)

2.3 Surface Layer Hardening

2.3.1 Processes

The surface layer of a component is heated by heat supply, while the properties of the surface layer are modified by rapid cooling. The component itself should not be affected by heat treatment, if possible.

Surface layer heating can be effected by the application of

- flames (torches)
- induction or HF pulses
- beams (electron or laser)
- dipping (salt bath, metal bath, fluid bed).

Rapid cooling can be effected by:

- quenching with spray shower
- bath (water, oil, polymer system or molten salt)
- fluid bed
- gas stream
- the component itself.

Novel processes of interest are vitrifying and explosive hardening.

In the case of vitrifying, a cooling rate of more than 106 K/s becomes necessary to enable the formation of metastable phases up to amorphous metals. These coatings resemble commercial "metallic glasses" /2.5/.

In explosive hardening a thin surface is explosively evaporated on the workpiece by extremely short action at very high power density.

The shock wave of the plasma formed leads to hardness increase in the workpiece.

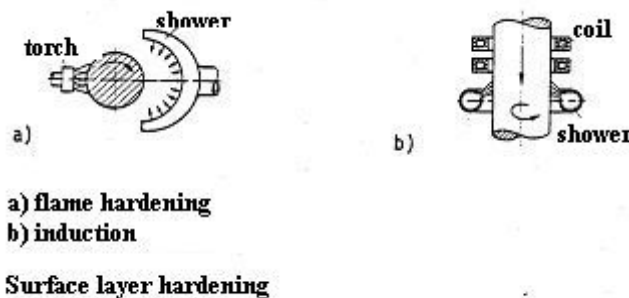


Fig. 2.3: Surface layer hardening

If, on the one hand, a C-containing, i.e. hardenable material, is required, then, on the other hand, the material surface can be "hardened" by

- surface layer remelting (production of a fine microstructure poor in segregations) and by
- surface layer realloying (production of a thin surface layer with improved properties by alloying elements) /2.6/.

In addition to induction and burning, significance is attached to the laser beam as a "recent" surface layer hardening process.

Defined surface conditions can be produced depending on the laser power, time and cooling rate.

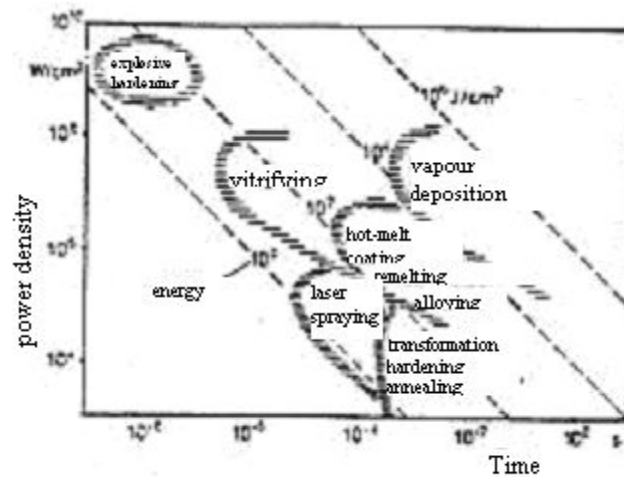


Fig. 2.4: Processes for thermal surface treatment with the aid of a laser beam after /2.3/.

2.3.2 Goals of Surface Layer Hardening

	Surface layer hardening
Goals	<ul style="list-style-type: none"> Increasing the wear resistance of the component surface, hardening - influencing the fatigue strength of the material

2.3.3 Materials Applied

Materials for surface layer hardening are covered by the DIN standard. The attainable hardness depends on the C-content (approx. 0.3 to 0.5 %) of the steel.

Hardening by surface layer melting or surface layer remelting can, in principle, be performed for all steels and cast materials.

	Surface layer hardening
Materials	<ul style="list-style-type: none"> C steels tool steels high-speed steels unalloyed and low-alloyed steels high-alloyed steels cast material <p style="text-align: right;">surface layer remelting and surface layer realloying</p>

2.3.4 Market Areas

The hardening of large-area components is reserved for the conventional techniques. Laser/electron beams are used for locally limited hardening or hardening at component locations difficult to access.

	Surface layer hardening	
Market areas	Conventional techniques: For partial hardening via laser/electron beam:	<ul style="list-style-type: none"> • punches • machine tool beds • mandrels • hardening of inner surfaces (cylinder sleeves) • camshafts • bearing seats • tappet guides • gear rings • piston rings

2.4 Ion Beam Techniques

2.4.1 Processes

- Ion implantation

In this process, high-energy ions of a desired element are introduced into the surface of the material in a vacuum chamber (10^{-5} - 10^{-6} mbar). In most cases, single-stage accelerators serve for ion production, furnishing ions in the energy range of 5 KeV-100 KeV and thus penetrating between approx. 1 nm to approx. 1 Nm into the material depending on the element/substrate [2.7].

An alloy or a chemical compound is produced in a thin layer underneath the surface.

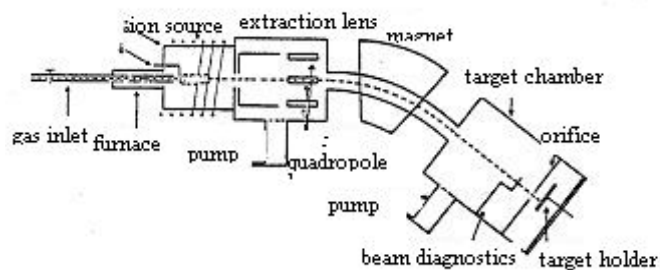


Fig. 2.5: Schematic representation of a low-energy ion accelerator [2.7]

Fig. 2.5: Schematic representation of a low-energy ion accelerator [2.7]

Static ion beam mixing is characterized by the fact that the tramp element is first applied onto the substrate in a thin layer by vapour deposition or sputtering and only then mixed or alloyed with the substrate by a beam of inert ions. Direct atomic collision superimposes with diffusion processes accelerated by irradiation. This leads to a very effective "smearing" of the phase boundaries /2.8/ /2.9/.

In dynamic ion beam mixing, the foreign atom layer and mixing are no longer separated in time and space.

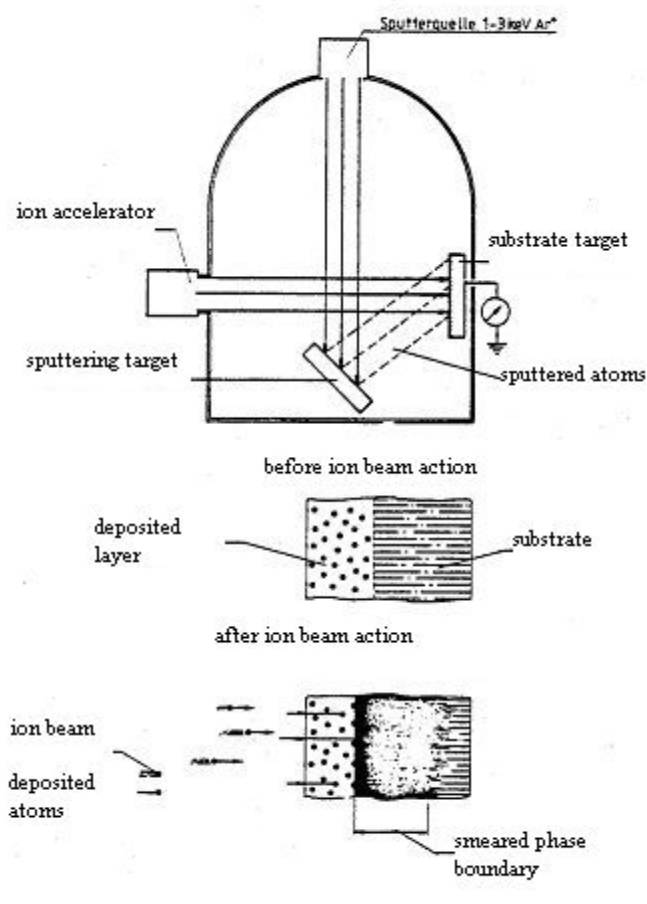


Fig. 2.6: Schematic representation of dynamic ion beam mixing /2.8/ /2.9/.

2.4.2 Goals of Ion Beam Techniques

Ion beam techniques	
Goals	<ul style="list-style-type: none"> • production of stable or metastable alloys with maximum adhesion of the coating layer • incorporation of nearly all elements into the workpiece surface at low temperatures • influencing the corrosion behaviour of metals • preparation of very thin hard wear protection coatings <p>property changes for optics, medicine and electrical engineering (e.g. metallization of plastics)</p>

2.4.3 Materials

Ion beam techniques provide the possibility of incorporating any element into almost any substrate material and to thus also produce multistable and amorphous surface structures /28/.

	Ion beam techniques
Materials	<ul style="list-style-type: none">• Nearly all elements possible<ul style="list-style-type: none">- wear reduction and decrease of the friction coefficient N, B, C Ta, Mo, Ti, Sn, Y Si₃N₄, BN or titanium carbonitride, diamond-like carbon coatings- corrosion protection Ti, Cr, Pd, Pt, Ta, Hg, Pb- oxidation protection Y, Cr- permeation inhibition of H₂ Pb, Pt

2.4.4 Market Areas

The methods of ion beam technology reach their application limits with the considerable technical expenditure and their small coating layer thickness.

The extreme diversity of material combinations and the infinitely adjustable transition between substrate and surface material, providing excellent adhesive strength of the coating, represent the special features of this surface treatment.

Suitable components for this technique are high-quality small components not subjected to excessive corrosion attack or wear erosion and whose surface destruction entails immense follow-up costs. Ion beam mixing is at the research and development stage, ion implanting is about to be industrially introduced (N-implantation).

	Ion beam techniques
Market areas	<ul style="list-style-type: none">• pressing and cutting tools• extruder nozzles• highly stressed bearings (turbines)• deep-drawing punches• medicine (hip joints)• semiconductor industry (doping)corrosion protection of turbine blades

2.5 Thermochemical Processes

2.5.1 Processes

In industry, a number of thermochemical diffusion processes are used, in which the elements to be diffused in are brought near the material surface by solid, liquid, gaseous or ionizing media.

Thermochemical processes can be classified according to the type and composition of the materials used.

Nitriding

Nitriding causes the enrichment of a workpiece surface layer with nitrogen. Depending on the type of nitrogen carrier, the following distinctions are made after /2.10/:

- gas nitriding (use of NH_3)
- bath nitriding (use of cyanides)
- powder nitriding (use of cyanamides)
- plasma nitriding.

In the conventional gas, bath and powder nitriding processes, nitriding takes place in special furnaces at temperatures between 490 and 600 °C /2.11/ /2.12/. Depending on the depth of penetration into the workpiece and on the process, the exposure time may be up to 100 h. Diffusion zones of up to 700 µm can be achieved. The actual connecting layer is 10-20 µm.

The exposure times can be shortened and the treatment temperature lowered using the plasma process.

Nitrocarburizing

In nitrocarburizing, also called carbonitriding, nitrogen or carbon formed by thermal reaction is accumulated in the surface layer of a steel. The process possibilities are similar to those of nitriding /2.13/. However, the treatment temperatures range between 600 °C and 900 °C in nitrocarburizing, depending on the process.

After application times of up to 5 h, the desired coating properties are achieved in salt bath facilities after quenching in oil or salt baths.

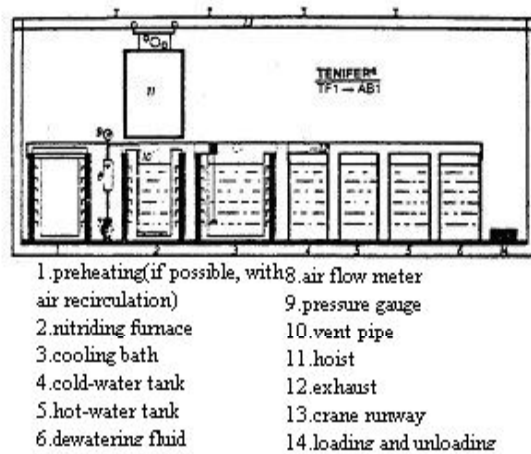


Fig. 2.7: Schematic setup of a salt-bath nitrocarburizing facility (Tenifer process) /2.11/.

- Case hardening

In case hardening, the surface layer of a workpiece (steels with low carbon content) is enriched with carbon by thermochemical treatment. The desired microstructure for the hardness of the surface is produced by subsequent heat treatment. Carburizing (cementing) can take place in the form of

- powder using charcoal and barium carbonate
- gas from carbon oxide, hydrogen and propane
- cyanide salt baths /2.15/.

The carburizing temperatures range between 900 and 950 °C. Usual application times are

for small parts	1 hour	(s = 0.1 - 0.2 mm)
for motor vehicle construction	5 - 15 hours	(s = 0.5 - 1.5 mm)
for large machine construction	15 hours	(s = 2 mm).

For hardening, the parts are heated in a protective gas atmosphere and quenched in oil or molten salt baths.

- Siliconizing

Silicon-containing component surface layers can be produced by gas or powder treatment up to a thickness of 250 µm.

In furnaces, gas (silicon halide and hydrogen) is passed over the workpieces; the silicon is set free and can diffuse into the surface /2.16/.

If workpieces in boxes are surrounded by silicon carbide powder, the liberation of silicon is enabled via chlorine gas supply at high temperatures. The necessary process temperatures are in the range of 1000 °C for both processes.

Brittle hard surface layers are produced.

- **Boronizing**

In boronizing, too, the material property is influenced by deposition and diffusion into the substrate surface.

Boron can be introduced into the workpiece surface by

- powder techniques, powder from e.g. B_4C and additives
- gas phase with boron compounds
- bath techniques via electrolysis in molten salts of borax or boron compounds mixed with alkali fluorides
- in molten bath boronizing in boron carbide B_4C , $NaCl$ and $NaBF_4$ (sodium tetrafluoroborate) (2.17/).

Boronizing requires furnace temperatures of up to 1050 °C.

If powders are used, work can be done without protective gas atmosphere. Layer thicknesses between 40 and 500 μm can be produced.

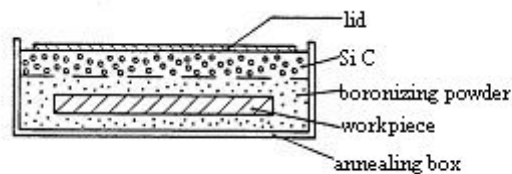


Fig. 2.8: Schematic arrangement in powder boronizing.

- **Chromizing**

Chromizing layers are produced by depositing chromium from a chromium carrier and diffusing into the material surface.

Coating via powders (chromium metal/alloy, activator (ammonium chloride) and diluent Al_2O_3) or via the gas phase (reduction of chromium chlorides by hydrogen) is possible.

The process temperatures range between 980 and 1060 °C. Depending on the substrate material used, layer thicknesses of up to approx. 80 μm can thus be produced.

- **Alitizing**

Alitizing (aluminizing) is similar to chromizing. The layer is produced by the deposition of aluminium and diffusion into the base material.

In powder coating, the workpieces are covered with powder (Al metal/alloy), an activator (ammonium halide) and a diluent (Al_2O_3) in a pack cementation process and treated in a furnace for several hours at temperatures of up to 1150 °C. Usual layer thicknesses range between 30 and 100 μm .

- Sherardizing

Sherardized zinc coatings are produced by diffusing zinc into the workpiece surface of cast materials or low-alloyed steel. Component, zinc dust and sand are treated in a furnace for several hours at approx. 400 °C /1.3/ /2.18/. The iron-zinc alloy coating formed protects from corrosion.

- Plasma treatment of metals

By means of plasma treatment, workpieces can be

- nitrided
- carbonitrided
- carburized or also
- boronized.

In the following, the treatment sequence will be described, referring to the most significant process, plasma nitriding.

In plasma nitriding, the workpiece to be treated is polarized as the cathode at a subatmospheric pressure of $1 \cdot 10^{-2}$ to $1 \cdot 10^{-4}$ bar. The anode is formed by the vessel wall. An N_2 - H_2 carbon-water mixture is used as the process gas. By applying a direct voltage, ions from "abnormal glow discharge", burning gas discharge in the current density range from 10^2 to 10^3 mA/cm² are propelled with high energy onto the workpiece /2.19/. The component is heated by this particle bombardment and the material surface sputtered. Iron nitride is formed, which deposits on the workpiece, is decomposed and then furnishes the diffused atomic nitrogen. The process operates in the temperature range of 350 - 600 °C.

In treatment times between 10 min. and 36 hours, depending on the steel variety, coating thicknesses of 30 - 300 µm are produced.

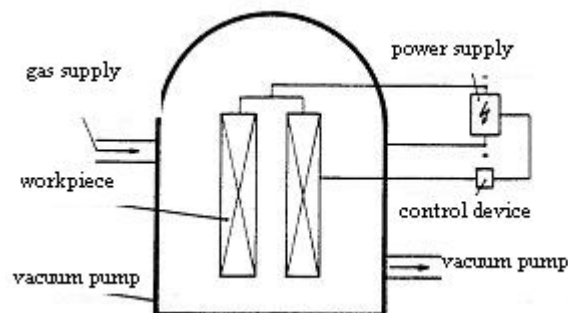


Fig. 2.9: Schematic arrangement of the plasma treatment facility

2.5.2 Goals of the Thermochemical Processes

	Thermochemical processes
Goals	<ul style="list-style-type: none"> - Nitriding, nitrocarburizing <ul style="list-style-type: none"> • reducing adhesive wear • increasing component life • reducing friction coefficients • improving the antiseizure properties • increasing the corrosion resistance (effect comparable to nickel coating) • increasing the fatigue limit - Case hardening <ul style="list-style-type: none"> • hardening a steel with low carbon content • wear protection for low application temperatures - Siliconizing <ul style="list-style-type: none"> • improving wear and corrosion protection of low-alloyed steels above all for elevated temperatures (700 °C) - Boronizing <ul style="list-style-type: none"> • utilizing the tribologically favourable properties (great hardness – high wear resistance to abrasive stressing) • corrosion protection - Chromizing <ul style="list-style-type: none"> • oxidation protection on highly heat resistant steels up to 800 °C • protection against abrasive wear • improving the bend fatigue strength - Alitizing <ul style="list-style-type: none"> • oxidation and corrosion protection up to 1000 °C without reducing the strength of the base material - Sherardizing <ul style="list-style-type: none"> • corrosion protection on cast material and low-alloyed steels up to 600 °C - Plasma treatment of metals <ul style="list-style-type: none"> • producing nitrided, carbonitrided, carburized and boronized layers <ul style="list-style-type: none"> - on all iron metals with controlled coating structure at relatively low process temperatures - in relatively short times, nonporous

2.5.3 Materials for thermochemical processes

	Thermochemical processes									
Suitable substrate materials	case hardening	nitriding	carbonitriding	siliconizing	boronizing	chromizing	alizing	sherardizing	plasma treatment	Materials
	+	+	+	+	+	+	+	+	+	low-alloyed materials
	+	+	+		+	+	+		+	Cr steels
					+	+	+		+	CrNi steels
					+	+	+		+	Ni alloys
					+					special metals
					+				+	cast iron
					+				+	sintered materials (iron)

2.5.4 Market Areas for Thermochemical Processes

Heat treatment techniques have long been introduced in industry, above all, to improve the mechanical properties of components made of ferrous, steel, cast and sintered materials.

The price, quality, economic efficiency and environmental aspects of the processes control their application. Thus, for example, a larger application range can be covered by plasma nitriding due to the different coating structures that can be produced in comparison to conventional nitriding processes /2.20/. On the other hand, carburizing workpieces in a plasma has not yet become established in practice despite many product- and process-engineering advantages /2.21/.

Further process developments and the combination of surface treatment and coating open up new application ranges. Reference should be made here, for example, to steel toothed wheels for gearings in space satellites. Nitriding the toothed wheels has led to low wear rates – a coating with lead ions serves as a dry lubricant film /2.22/.

Market areas	Thermochemical process
	Nitriding, nitrocarburizing, plasma nitriding <ul style="list-style-type: none"> wearing components from general mechanical engineering and toolmaking <ul style="list-style-type: none"> spindles, bolts, spars, worms (plastics machines) cold- and hot-working tools such as dies, presses, mandrels highly loaded gear and engine parts <ul style="list-style-type: none"> toothed wheels, racks, friction cone flanges, bearings

Market areas	<ul style="list-style-type: none"> • automotive engineering - valves, crankshafts, pump parts <ul style="list-style-type: none"> • chem. apparatus construction - valve spindles, nozzles <ul style="list-style-type: none"> • other areas - camera parts, mixer rotors, wearing parts of packing machines <p>Case hardening</p> <ul style="list-style-type: none"> • wearing components from general mechanical engineering and power plant construction - toothed wheels, anti-friction bearings <p>Siliconizing</p> <ul style="list-style-type: none"> • wear and corrosion protection of less vibration-stressed, hot-going components such as - valve pump parts - conveying equipment <p>Boronizing</p> <p>mineral wear protection of machine components</p> <ul style="list-style-type: none"> - moulds for fireclay brick production - grinding rings, tappets, cam disks <p>Chromizing</p> <ul style="list-style-type: none"> • wear protection of tools • oxidation protection coatings at elevated temperatures - furnace lining, outlet tubes <p>Alitizing</p> <ul style="list-style-type: none"> • prevention of scaling, oxidation and corrosion protection of hot gas ducting components - linings of conveyORIZED ovens, nitriding boxes, cementing boxes, cupola furnaces, turbine blades <p>Sherardizing</p> <ul style="list-style-type: none"> • corrosion protection of low-alloyed steels and castings such as small sheet metal and cast parts, pins, thread parts
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2.6 Plastic Coatings and Linings

2.6.1 Processes

Plastic coating is understood to be the application of a firmly adhering layer of amorphous, liquid or powder material onto a component /2.23/.

After a pretreatment of the material surface (blasting, pickling, adhesion primer etc.) the corresponding plastic is applied by spraying or dipping, electrostatic coating or whirl sintering. Depending on the plastic used, a heat treatment at temperatures between 200 and 400 °C can become necessary. This causes sintering and fusion of the thermoplastic coating particles, which leads to dense and thus corrosion-protecting surfaces.

Lining means establishing a firm bond between substrate material and corrosion protection material.

Linings are applied onto relatively simply shaped objects using contact adhesives and plastic plates. Sliding connections of the plates are welded /2.24/.

Layers of tenths of a millimetre up to several millimetres are possible by coating and lining.

2.6.2 Goals of Plastic Coatings and Linings

	Plastic coatings and linings
Goals	<ul style="list-style-type: none">• protection of the base material against chemical attack• increase of abrasion resistance• increase of sliding properties• corrosion protection, impermeable• anti-adhesion properties• electrical insulation• noise reduction• decoration• diffusion inhibition

	Plastic coatings and linings
Materials	<ul style="list-style-type: none">• soft and hard rubber• thermosetting plastics and thermoplastics- phenolic resins, PVC, PVDF, E-CTFE, FEP, PFA, PP, PA

2.6.3 Market Areas

The use of plastic coatings and linings is widely spread due to the versatile functional application possibilities, especially the extremely high resistance to chemicals.

	Plastic coatings and linings
Market areas	<ul style="list-style-type: none"> • Tank, pipe and apparatus construction <ul style="list-style-type: none"> - heat-exchanger chambers against corrosion due to service and salt water - heat exchangers against corrosion and incrustation - protection against chemical attack by nearly all bases, acids and solvents in components of the chemical industry - rolls, mixers, troughs, conveyor screws, stirrer tanks, reaction tanks, H₂SO₄ scrubbers, FGD systems (FGD = flue gas desulphurization) • Fitting construction <ul style="list-style-type: none"> - valves, stop cocks, bearings, shafts, rolls etc. against corrosion and as dry lubrication to improve the sliding properties • Vehicle construction <ul style="list-style-type: none"> - levers, cranks, wheels, bearing bolts • Mechanical engineering <ul style="list-style-type: none"> - cover plates, impellers, rolls, burner gates, holding forks, brackets, sleeves • Textile industry <ul style="list-style-type: none"> - washing coils, lever arms, ring rails, rolls • Construction sector <ul style="list-style-type: none"> - upper flights, roof water gutters, railings • Ventilation engineering <ul style="list-style-type: none"> - pipes, ducts, fans, clips • Food industry <ul style="list-style-type: none"> - shaped bodies (anti-adhesion) • Packaging industry <ul style="list-style-type: none"> - sealing of bags without gluing • Timber industry <ul style="list-style-type: none"> - saw blades

2.7 Electrolytically and Chemically Produced Layers

2.7.1 Coating Process

Electrolytically produced layers

Workpieces to be coated are placed into an electrolyte (acid or aqueous solution of metal salts concerned) after adequate pretreatment (degreasing, etching – activating the surface). By applying an external direct current to the workpiece polarized as the cathode and to the anodes introduced into the electrolyte solution, metal ions are discharged. They are deposited as metallic precipitate on the workpiece surface.

The layer thickness can be controlled via exposure time and current density. Since the current density is higher in recesses, the thickness achieved may be inhomogeneous.

The complexity of the objects to be coated is limited by the throwing power of the electrolyte bath used and the anode arrangement.

Chemically produced layers

In the case of the chemical production of layers, protective coatings can be deposited in baths without the use of direct current. The basic mechanism of chemical metal deposition is the chemical reaction of metal ions in an aqueous metal salt solution /2.25/.

If fresh solution is continuously fed, homogeneously thick layers can be built up even in boreholes and on edges/corners and fillets /2.26/. The coating property can be controlled by the bath, process parameters and subsequent heat treatment.

Dispersion layers

By admixing solid particles to the metal salt solutions it is possible to obtain dispersion layers electrolytically or by chemical deposition. The solid particles in the solution are suspended by whirling up, stirring or pumping over. During metal deposition the particles are incorporated into the metal matrix /2.27/. Depending on the type of coating matrix (metal, alloy) and the type and fraction of solid particles, the properties of dispersion layers can be varied within wide limits.

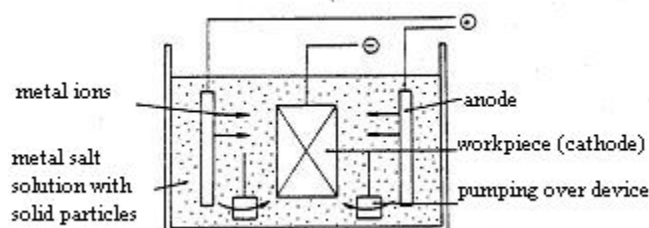


Fig. 2.10: Schematic of electrolytic dispersion coating

Anodically produced conversion layers

In order to anodically produce conversion layers, the component is dipped into an aqueous electrolyte solution. The component is switched as the anode by using an external direct-current source. With the participation of the metal and electrolyte, the metal is converted into the layer on the workpiece surface (conversion layer).

The metal ions anodically brought into solution react with partners of the electrolytes and form the layer (thickness between 1 and 100 μm).

Process types are governed by the component materials used.

Hard anodizing and anodic oxidation (anodic oxidation ions) for aluminium materials.

Anodic oxidation for titanium materials and production of HAE layers on magnesium materials.

Chemically produced conversion layers

The component is dipped into a chemical conversion solution. The coating is built up by reaction of the component with the partners of the chemical conversion solution.

The processes for these conversion layers include:

- application of passivation layers on high-alloyed steel and aluminium materials
- application of browning and phosphating layers on low-alloyed steels and the
- application of chromated layers on magnesium materials.

Depending on the process, layer thicknesses between 0.1 and 15 μm can be achieved.

2.7.2 Goals of Electrolytically and Chemically Produced Layers

	Electrolytically and chemically produced layers
Goals	<ul style="list-style-type: none">- corrosion protection- wear protection- improvement of sliding properties- repair coating- electrotechnical application- decoration in conjunction with corrosion protection- adhesion primer for further coatings

2.7.3 Materials

The deposition at relatively low temperatures comprises metals as well as their binary and ternary compounds. Several hundred depositable alloys are known on a laboratory scale. Approx. 50 of them have been investigated. Less than a dozen of alloys have found an application /2.26/.

Electrically conducting materials can be coated electrolytically. The chemical production of layers also permits electrically poorly conducting materials (plastics) to be coated.

	Electrolytically and chemically produced layers
Materials used	<ul style="list-style-type: none"> • usual: Ag, Au, Cd, Cr, Cu, Ni, Sn, Zn • special applications: Co, In, Pb, Pt, Rh • laboratory and in part minor application: Al, Mn, Mo, Ti, W • anodizable materials: Al, Mg, Ti • passivable materials: high-alloyed steels, Al • brownable and phosphatable materials: low-alloyed steels • chromatizable materials: Mg • dispersion layers - matrix: Ni, Co, Cr, Fe, Ag, Cd - dispersant: oxides, carbides, BN, CaF₂, PTFE, MOS₂ and others

2.7.4 Market Areas for Electroplating

Electroplated coatings have found widespread applications. In some branches of industry, their range of application is such that this branch would not be technically and economically viable without electroplating /2.29/.

In the following, some market areas will be mentioned from the variety of applications.

	Market areas for electroplating
Market areas	<p>Cadmium plating</p> <ul style="list-style-type: none"> corrosion protection of parts exposed to mechanical loads and temperatures of up to 220 °C: <ul style="list-style-type: none"> screws, braking systems in railway engineering anti-lock brakes in passenger cars electrical components <p>Chromium plating</p> <ul style="list-style-type: none"> corrosion protection along with decorative appearance <ul style="list-style-type: none"> automobile industry food industry, textile and paper industry (rolls, rollers ...) mechanical engineering hard chromium platings against corrosion and wear (hydraulic tappets) repair coating (bringing parts to scale), corrosion protection if Cd cannot be applied, solder matrix <ul style="list-style-type: none"> pump construction (shafts for turbines) graphic industry, printing industry (rollers) hydraulic systems (pistons, cylinders) drinking water plants furnace construction (scaling protection up to 500 °C) <p>Chemical nickels</p> <ul style="list-style-type: none"> wear and corrosion protection also for parts of complicated shape, repair coating, solder matrix <ul style="list-style-type: none"> valve bodies, extruder screws, bearing shells, compressor impellers, shafts electrical industry <p>Chemical nickels plus phosphorus</p> <ul style="list-style-type: none"> wear and corrosion protection, sliding behaviour, solderability <ul style="list-style-type: none"> petroleum industry (sour crude oil, pipelines, milling cutters) laser technology (smooth surfaces) <p>Nickel plus cadmium</p> <ul style="list-style-type: none"> corrosion protection at elevated temperatures <ul style="list-style-type: none"> structural steel components engine parts in the temperature range 300 - 500 °C <p>Aluminium with anodizing post-treatment</p> <ul style="list-style-type: none"> corrosion protection, electrical conductivity <ul style="list-style-type: none"> vehicle construction (substitute for cadmium) aerospace engineering (high-strength steels such as screws, rivets, bolts that may not be cadmium plated, light-metal

	<p>protection Al and Mg alloys or</p> <ul style="list-style-type: none"> - contact corrosion protection of titanium components - gas turbine blades (hot gas corrosion protection) - conductive coats (e.g. on carbon fibre) <p>Anodically and chemically produced conversion layers</p> <ul style="list-style-type: none"> • corrosion protection, adhesion primer, wear protection of components <p>Dispersion layers</p> <ul style="list-style-type: none"> • wear protection, reduction of the friction coefficient, dry lubrication <ul style="list-style-type: none"> - PTFE-Ni for throttle valves, tappets, moulds, rotors of pumps - Co + Cr₂O₃ in aircraft construction, compressor part blade coating

2.8 Dip Coatings

2.8.1 Processes

Hot-dip coatings

Hot-dip coatings are produced by dipping workpieces into a metal/alloy melt /2.30/.

Hot-dip aluminizing at T = 650 - 800 °C
and dipping times of up to 1 minute

Hot-dip galvanizing at T = 440 – 480 °C
and dipping times of up to 2 minutes

Hot-dip leading at T = 370 °C

Hot-dip tinning at T up to 325 °C

After dipping the workpiece into the melt, an intermetallic phase of hot-melt layer and base material is formed on the surface. When the workpiece is withdrawn, the remaining molten metal layer is solidified and forms a protective coating.

- Salt-bath immersion (TD process)

By means of the salt-bath immersion technique developed by Toyota Central Research and Development Lab., workpieces are dipped into a 850 - 1050 °C hot salt bath (borax) for 1 to 8 h to build up a carbide layer.

The carbide layer is formed by the reaction of the C atoms with the substrate material and the carbide-forming elements contained in the molten borax. The layer grows onto the front side of the carbides /2.31/.

Immersion is followed by hardening in oil, salt or air. The procedure for this carbide coating is then similar to usual salt-bath hardening. Simple furnaces are used. A protective gas atmosphere is not necessary for these salt-bath immersion methods.

Different layer thicknesses (usually 2 to 10 μm) can be produced by changing the bath temperature and immersion time /2.32/.

2.8.2 Goals of Hot-Dip and TD Coating

	Hot-dip and TD coating
Goals	<u>Hot-dip coating</u> Al: <ul style="list-style-type: none"> corrosion and oxidation protection electr. conductivity decoration Zn: <ul style="list-style-type: none"> corrosion protection Pb: <ul style="list-style-type: none"> reduction of the friction coefficient radiation protection Sn: <ul style="list-style-type: none"> corrosion protection <u>TD coating</u> <ul style="list-style-type: none"> wear protection reduction of friction, dry lubrication

2.8.3 Materials

	Hot-dip and TD coating
Materials used	<u>Hot-dip coating</u> <ul style="list-style-type: none"> Al on low-alloyed steels, Cr and CrNi steels, Cu and cast iron Zn low-alloyed steels, Cu and cast iron Pb low-alloyed steels, Al, Cu, Zn Sn low-alloyed steels, Al, Cu, cast material <u>TD coating</u> <ul style="list-style-type: none"> suitable for coating are nearly all steels with C fractions, preferentially, however, easily hardenable steels carbide coating such as VC; Nbc, $\text{Cr}_7\text{C}_3 + \text{C}_{23}\text{C}_6$

2.8.4 Market Areas for Immersion Layers

Hot-dip layers require relatively high bath temperatures for application onto components. A deformation of the product can therefore not be excluded. Components of complicated shape and fine components are not suitable for immersion coatings.

According to Japanese information /2.32/ salt-bath immersion has proved to be a friction-reducing and anti-wear coating technique for tools in sheet-metal processing in the Japanese automobile industry.

	Immersion layers
Market areas	<ul style="list-style-type: none"> • Aluminium immersion layers <ul style="list-style-type: none"> - steel structure protection against industrial atmosphere (hydrogen sulphide) - steel structure protection off-shore plants - component protection against condensable water vapour • Zinc immersion layers (hot-dip galvanizing) <ul style="list-style-type: none"> - corrosion protection of low-alloyed steel products (steel structures, off-shore, apparatus) • Tin immersion layers <ul style="list-style-type: none"> - corrosion protection in the food industry - conductor coating in the electrical industry • Lead immersion layers <ul style="list-style-type: none"> - corrosion protection in the chem. industry (petrochemistry, strongly oxidizable acids, oils, fuels, industrial gases) - shieldings, apparatus of radiation protection • TD coating <ul style="list-style-type: none"> - sheet-metal processing (pressing rollers, cutting and drawing tools) - cold-working tools (punching dies, calibration tools, straightening roll) - hot-working tools (upsetting die, forging die, guide rollers)

2.9 Physical Vapour Deposition (PVD)

2.9.1 Processes

The physical vapour deposition processes (PVD) are characterized by a multitude of characteristic process variants. The processes taking place in vacuum include:

- vapour deposition
- sputtering
- ion plating.

The PVD processes work in the range of glow discharge up to arc discharge to coat workpiece surfaces with a thin layer.

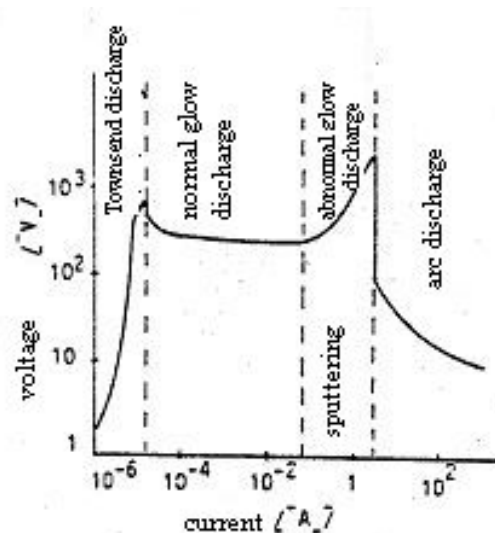


Fig. 2.11: Static current-voltage gas discharge characteristics - PVD processes /2.36/.

Vapour deposition

In vacuum vapour deposition, metals, compounds or oxides and fluorides contained in an evaporator source (crucible, boat) are evaporated by heating in vacuum with the aid of resistance heating, eddy-current heating, electron- or laser-beam bombardment or electric discharge and are deposited on the colder substrate /2.33/.

In the high-vacuum process the pressure is 10^{-5} to 10^{-6} mbars.

Temperatures above 1000° are often necessary to evaporate the coating material.

In order to achieve sufficient adhesive strengths of layer material, the surface must be cleaned; this can be done by ion bombardment of inert gases in a glow plasma or by heating the substrate.

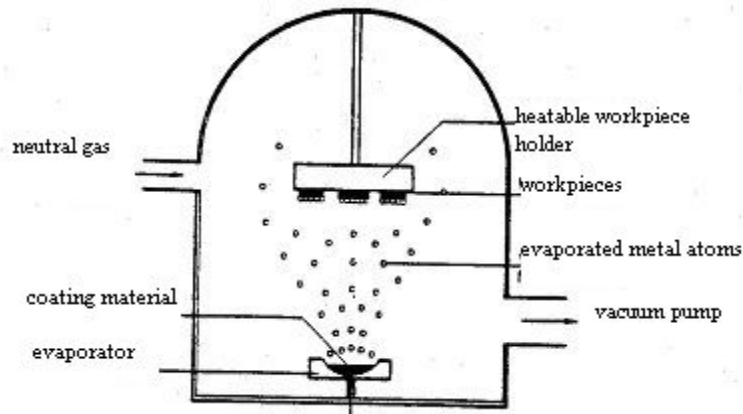


Fig. 2.12: Schematic diagram, vapour deposition in vacuum /2.35/.

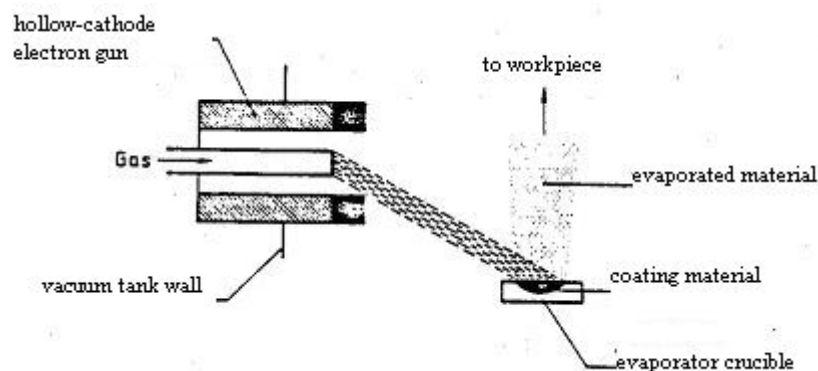


Fig. 2.13: Schematic diagram of heating by electron beam /2.35/.

Gas scattering evaporation (pressure plating) improves the layer homogeneity. In this process, a gas with a pressure of 6×10^{-2} to 6 mbars is introduced into the recipient. The evaporated material undergoes multiple scattering on its way to the workpiece. The process is suited for the all-around coating of workpieces.

In the **reactive evaporation** process, a metal or alloy vapour is produced in the presence of a reactive gas. The chemical compound can deposit on the workpieces by reaction with the gas atoms present.

Sputtering

At a subatmospheric pressure of 10^{-3} to 10^{-2} mbars, noble gas ions are produced from the noble gas (Ar) by applying a voltage between cathode (coating material) and anode and accelerated in the direction of the cathode /2.34/. The ions impinging on the coating material detach atoms. The sputtering coating material is passed through the vapour phase to the workpiece, where it is deposited. In conventional cathode sputtering, the workpiece is at anode potential. The coating material is heated by secondary particle bombardment and must be cooled. The workpiece is exposed up to temperatures of 300 - 500 °C depending on the sputtering rate, sputtering time, gas pressure and cooling.

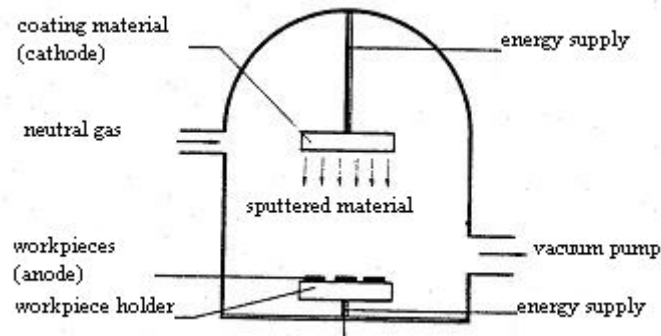


Fig. 2.14: Schematic diagram of sputtering, diode array /2.35/.

In **DC sputtering** the cathode is at a fixed d.c. voltage; the application is restricted to the sputtering of electrically conducting materials.

The **HF-sputtering** process, which works with a high-frequency a.c. voltage (MHz), is suited for sputtering poorly or non-conducting coating materials.

In order to improve the adhesion properties, in **bias sputtering**, a negative bias of a few hundred volts is applied to the workpiece. The workpiece is thus subjected to a constant sputtering process. The layers are improved in terms of purity and structure.

Another variant of sputtering is **reactive sputtering**. Reactive because additional gas atoms react with solid atoms and form a compound. The stoichiometry of the sputtered layer can be adjusted by means of the partial pressure of the reactive gas /2.35/.

High-performance sputtering devices are used to increase the condensation rate in the sputtering process /2.34/. A triode unit or a magnetic field is used to concentrate the ion beam bombardment onto the coating material and significantly increase the sputtering rate. The component temperatures can be kept between 100 and 250 °C.

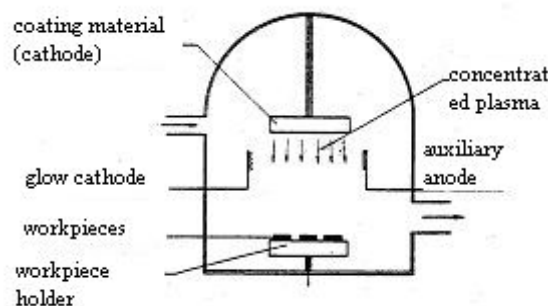


Fig. 2.15: Schematic diagram of high-performance sputtering device

The **cathodic arc** process works in the range of arc discharge and in the high-vacuum range for evaporation. This involves an increase of the degree of ionization. Complex alloys can also be directly deposited retaining the stoichiometry /2.36/.

Ion plating

A combination of sputtering and vapour deposition is ion plating [2.34]. The coating material is thermally evaporated at a pressure of 10^{-2} mbars. A plasma is generated between substrate (cathode) and anode (evaporation material). The noble gas ions are shot at the substrate; the surface of the component is constantly cleaned, etched and activated. The coating material particles introduced into the plasma from the evaporation source are accelerated towards the component by collisional ionization and in the electric field. Non-metals can also be coated by covering with a cathodically polarized wire mesh.

The high particle energy of several hundred electron volts leads to dense and highly adhesive layers.

The process described above is sufficient for depositing dense metal or alloys. **Reactive ion plating** is used for the application of hard material layers [2.37], where the ion current densities are sufficient to ensure a complete reaction process.

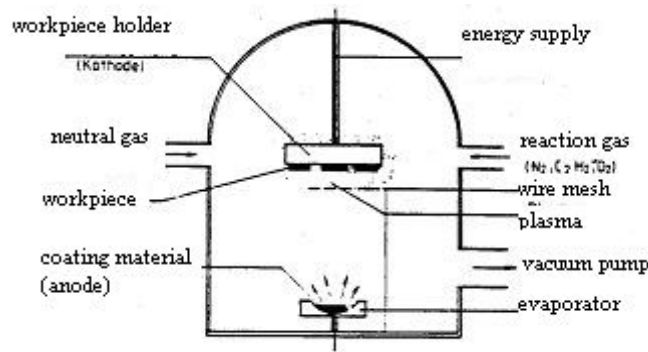


Fig. 2.16: Schematic diagram of reactive ion plating

2.9.2 Goals of PVD Coating

	Physical vapour deposition
Goals	<ul style="list-style-type: none">• generating surface protection at relatively low process temperatures• generating antifriction layers (solid lubricant layers)• corrosion protection (if galvanic layers cannot be used)• electrical engineering (insulating and conductive layers)• decoration• optical application

2.9.3 Materials

The advantage of being able to lower the process temperatures of the coating facilities down to 100 °C permits substrates of plastics through metals up to ceramic materials to be coated.

	Physical vapour deposition
Suitable substrate materials	Substrate materials suitable for PVD processes: <ul style="list-style-type: none"> • plastics • unalloyed steels • low-alloyed steels • high-alloyed steels • special metals • cast iron • sintered materials • ceramics

	Physical vapour deposition
Coating materials	<i>Vapour deposition:</i> metals, alloys, evaporable compounds <i>Sputtering:</i> metals, alloys, non-metals <i>Ion plating:</i> metals, alloys, non-metals <ul style="list-style-type: none"> • metals: Ta, Cd, Co, Ti, Al, Cu and others • alloys: NiCr, FeCr, brass and others • oxides: Fe oxides, SiO₂, Al₂O₃, PbO and others • nitrides: TiN, TaN, CrN, Si₃N₄, AlN, NbN and others • carbides: TaC, WC, CrC, TiC, B₄C, ZrC, (Hf-Zr), C • others: MoS₂, MoSe₂, WSe₂, CaF₂, graphite, PTFE, ZnS

2.9.4 Market Areas for PVD Layers

Vapour deposition and cathode sputtering have their market area primarily in decorative application. The cathode sputtering technique has been developed to such a level today that coatings are possible in continuous operation /2.38/. Although hard protective layers can also be produced with these methods, coating according to the ion plating process became established in the industry for metal-cutting tools, after it had been possible to lower the process temperatures below 500 °C. Ion

plating is still at the experimental stage for metal-working tools, bearing systems, guides etc.

	Physical vapour deposition
Market areas	<u>High-vacuum vapour deposition</u> <ul style="list-style-type: none"> • <i>decoration</i> <ul style="list-style-type: none"> - packaging industry products - automobile industry (trim strips, plastic strips, reflectors) - jewellery industry (watches, spectacle frames) • <i>corrosion protection</i> <ul style="list-style-type: none"> - continuous strip coating, wire coating - gas turbine blades (Al) • <i>optics</i> <ul style="list-style-type: none"> - reflection of mirrors, laser mirrors • <i>electrical industry</i> <ul style="list-style-type: none"> - semiconductor metallization - resistors
	<u>Cathode sputtering</u> <ul style="list-style-type: none"> • <i>decoration</i> <ul style="list-style-type: none"> - watches, jewellery, facades • <i>optics</i> <ul style="list-style-type: none"> - glass coating IR reflection
	<u>Ion plating</u> <ul style="list-style-type: none"> • <i>friction and wear protection (TiN and TiC)</i> <ul style="list-style-type: none"> - metal-cutting tools (drills, milling cutters) - forming tools - machine and plant parts (toothed wheels, piston rings)

2.10 Thermal Spraying

2.10.1 Processes

Wire or metallic or nonmetallic powder materials are melted in an energy source for thermal spraying, atomized with the aid of a carrier gas and propelled onto the component surface.

The highly heated, liquid spray particles solidify within a short time. The component surface is generally not melted. Pores can form in the sprayed material due to degassing droplets.

The layer formed, whose microstructure deviates from cast or wrought materials due to the inhomogeneous nature, shrinks during solidification, which may lead to high internal stresses in brittle oxidic components. In this coating process, different thermal expansion coefficients of base and spray material, the preheating temperature of the base material, reactions of the liquid spray droplets with gases/metals, layer thicknesses etc. must be taken into account [2.39/.

In order to obtain sufficient adhesive strength of the layers, a preparation of the surfaces to be coated is necessary. The surface of the component is cleaned, roughened and activated by blasting with corundum (Al_2O_3) or carborundum (SiC). Coating must take place immediately after activating. If oxides or metal/oxides are to be sprayed, a thermally sprayed adhesion primer of NiAl, NiCr or NiCrAlY must be applied.

An improvement of the corrosion resistance of the thermally sprayed layer is achieved by impregnation with organic or inorganic materials.

Thermally sprayed layers can be reworked by turning, grinding and brushing.

The most important thermal spraying processes are:

- flame spraying
- electric arc spraying
- plasma spraying
- detonation spraying
- hypersonic flame spraying (Jet Kote).

Laser spraying is being lab-scale-tested.

Flame spraying

Flame spraying utilizes the fuel gas/oxygen energy ($T = 2600 - 3200\text{ }^\circ\text{C}$) and melts a continuously fed spray wire, "wire flame spraying". The layer material is propelled onto the component by the addition of a compressed gas. Apart from various steel grades, the most important materials of wire flame spraying are aluminium and zinc for corrosion protection and molybdenum for wear protection [2.39/].

By sintering ceramic powders into rods and slow feed in the wire flame spraying gun, these can also be spray-coated. In all commonly used wire guns, powdered metallic hard alloys or ceramic powders can also be processed in flux-cored wires of plastic material.

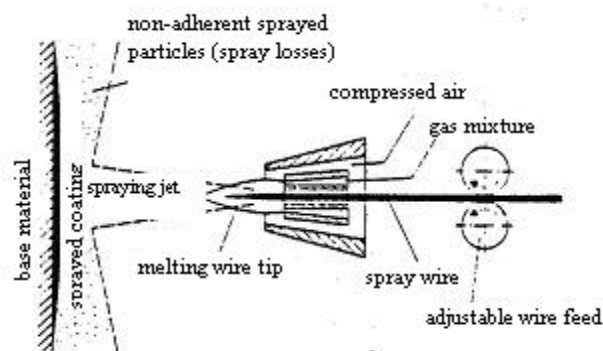


Fig. 2.17: Schematic representation of wire flame spraying [2.40/]

Another variant of flame spraying is "powder flame spraying". A distinction is made here between

- powder flame spraying without fusing
- powder flame spraying with simultaneous fusing
- powder flame spraying with subsequent fusing.

The powder additive is melted by the gas flame and accelerated by the expansion of the fuel gases. Apart from pure metals and oxides, carbides, nitrides, borides and silicides, powders of the group of self-fluxing Ni-Cr-B-Si-base alloys are primarily used as spray additives.

By means of (simultaneous or subsequent) fusing at process temperatures of 1000 - 1150 °C the material increases the property of self-fluxing due to the boron and Si additions. The confluent spray particles form a more homogenous layer with reduced porosity, without oxide inclusions, with a cast structure. The adhesive strength due to diffusion processes is increased and is thus above the non-fused coating.

The highly wear resistant surface finish thus produced at room temperature must be paid for with the disadvantage of high temperature load on the base material.

Electric arc spraying

Under an angle of about 60 to 90°, two continuously fed spray wires are burning in the electrically generated arc ($T \approx 4000^\circ\text{C}$) [2.40/].

The wires are continuously melting and are atomized and accelerated by compressed air. Apart from the wire materials of flame spraying, so-called pseudoalloys can also be processed.

By spraying in an inert chamber under protective gas, wires of special metals and refractory metals such as Ti, Zr, Nb or Ta can be sprayed.

In comparison to flame spraying, the process of electric arc spraying has the advantage of producing higher adhesive strengths and higher melting efficiencies.

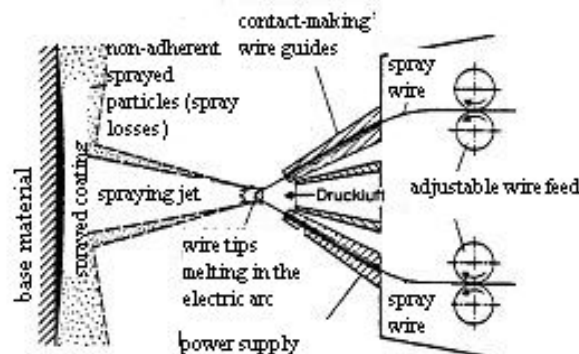


Fig. 2.18: Schematic representation of electric arc spraying [2.40/].

Plasma spraying

In plasma spraying, an electric arc is generated between a centred tungsten cathode and an annular-shaped copper anode. By the addition of gases such as Ar/H₂, N₂/H₂ or Ar/He or liquids (water) the plasma is produced in the electric arc and leaves the torch nozzle in an electrically neutral state by expansion with temperatures of 5000 - 20,000 °C and high outflow rates. The powdered spray material is introduced into the plasma jet by means of carrier gas, begins to melt and is melted and propelled onto the material surface. Plasma spraying is above all suited for high-melting carbides, nitrides, oxides and silicides [2.39/ 2.40/ 2.42/.

Since the electric arc in plasma spraying is not transferred to the workpiece, the component remains relatively cold (up to approx. 250 °C).

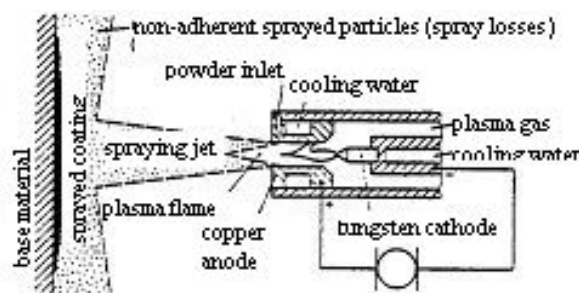


Fig. 2.19: Schematic representation of plasma spraying [2.40/.

The disadvantage in atmospheric plasma spraying (APS) is that intensive metallurgical reactions with the air constituents already occur on the flight path to the workpiece. This can be circumvented by low-pressure plasma spraying (LPPS).

This takes place in a low-pressure chamber in which a pressure of 50 - 70 mbars is maintained during spraying. Exhaust-air filters clean the gases enriched with spray powder. The enclosure in a chamber has made automated coating indispensable.

Due to the fact that gas/metal reactions hardly take place any more, alloy burn-out, oxidation and nitride formation are largely prevented, adhesive tensile strength and layer thickness increase.

This low-pressure process is suitable for the production of hot-gas-corrosion-resistant NiCrAlY alloys or corrosion-resistant layers of special or refractory metals.

Detonation spraying

In detonation spraying, reaction gases such as acetylene/oxygen and spray powder are introduced into the reaction chamber of a detonation gun and electrically ignited. The gas jet produced by the detonation begins to melt the powder, accelerates it to approx. 800 - 900 m/s and propels it onto the workpiece. Layers with very high adhesive strengths and relatively low porosities are normally produced between 0.03 and 0.5 mm [2.42/.

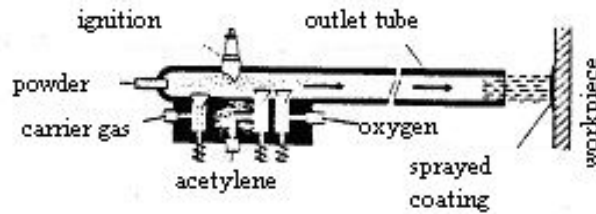


Fig. 2.20: Schematic representation of detonation spraying /2.42/

Hypersonic flame spraying

On the basis of the relatively simple principle of flame spraying, hypersonic flame spraying, also called Jet Kote process, has been developed.

In this process, an expansion nozzle is installed behind the torch, in which the escaping gas jet is further accelerated /2.43/.

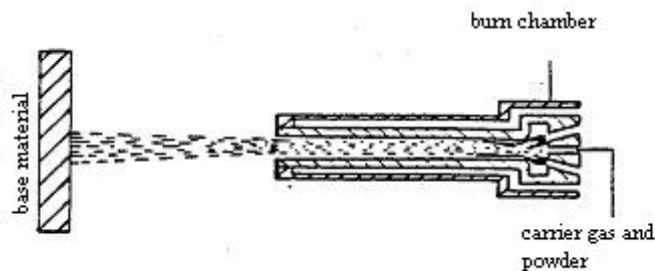


Fig. 2.21: Principle of hypersonic flame spraying /2.43/.

High pressure of the fuel gas and a relatively long distance traversed by the coating powder through the flame ensures that the powder undergoes the necessary heating and has a higher impact velocity onto the substrate than is the case in plasma spraying /2.44/.

Laser spraying

In this process, the coating powder is laterally transported through a laser beam onto a substrate material. The energy of the laser causes the coating material to melt even before impinging on the workpiece surfaces. In a thin surface region, the substrate material simultaneously begins to melt due to the laser action.

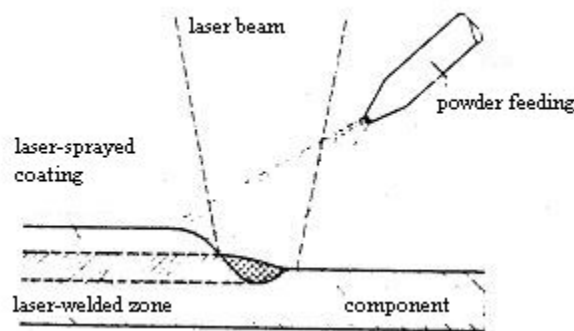


Fig. 2.22: Principle of laser spraying /2.45/.

The surface layer produced exhibits high adhesive strength on the substrate material with exact control of the process parameters /2.45/.

2.10.2 Goals of Thermal Spraying

	Thermal spraying
Goals	<ul style="list-style-type: none"> • wear protection • corrosion protection • thermal insulation • electrical insulation • anti-stick coating • shaped-body production from ultrahigh-melting materials • production of porous layers • improvement of sliding properties • repair of worn parts • decoration

2.10.3 Materials Used

Nearly all substrate materials comprising plastics, metals, sintered materials and ceramics, which can withstand a temperature load of 100 - 250 °C, can be coated by thermal spraying. An exception is spraying with simultaneous or subsequent fusing, where the temperature load is significantly higher.

In principle, all materials that do not decompose or sublime can be thermally sprayed /2.45/. High-melting materials (oxide ceramics and carbides) with melting temperatures above 2000 °C are primarily processed with plasma spraying facilities and detonation guns.

	Thermal spraying
Substrate materials	Suitable substrate materials: plastics steels special metals cast materials

	sintered materials ceramics
Sprayed materials	<p>In principle, all materials that do not decompose or sublime</p> <ul style="list-style-type: none"> • wear protection: <ul style="list-style-type: none"> - tungsten, molybdenum, self-fluxing alloys (Ni Cr B Si), oxides, carbides, mixtures • corrosion protection: <ul style="list-style-type: none"> - zinc, aluminium, lead, copper, nickel, chromium, cobalt, tantalum, titanium, silver, gold • corrosion and wear protection: <ul style="list-style-type: none"> - stellite, Inconel, Monel, white metal, CrNi alloys • thermal insulation: <ul style="list-style-type: none"> - oxides, mixtures • electrical insulations: <ul style="list-style-type: none"> - oxides • repair: <ul style="list-style-type: none"> - nickel, alloyed steel, nickel/chromium

2.10.4 Market Areas for Thermal Spraying

Thermal spraying has a wide field of application due to low component temperature load, the variety of material combinations, relatively high deposition rates, the large layer thicknesses attainable even on components of complicated shape, the very low plant investment costs and not least due to successful product improvement.

From the variety of possible applications, some products of the market will be specified in the following.

	Thermal spraying
Market areas	<ul style="list-style-type: none"> • <u>Protection against friction and wear</u> <ul style="list-style-type: none"> - iron and steel producing industry <ul style="list-style-type: none"> • coilers, rolls, shaft seals, inlet guides, measuring probes - mechanical engineering, automotive engineering <ul style="list-style-type: none"> • synchronizing parts for motor vehicle transmissions, shafts, bearings, spindles, pistons, bending and forming tools, wearing rollers - power plants <ul style="list-style-type: none"> • control rods, supporting surfaces, blower gyros, mill shaft bearing - components of the HTR

	<ul style="list-style-type: none"> - paper-converting industry <ul style="list-style-type: none"> • shaft seal seats, drive shafts, friction linings, winding mandrels, impellers • <u>Corrosion protection</u> <ul style="list-style-type: none"> zinc truck <ul style="list-style-type: none"> • steel structures (bridges, gates, railings), chassis, off-shore parts aluminium superheated <ul style="list-style-type: none"> • exhaust systems, off-gas stacks, steam pipes, steel engineering, apparatus construction (seawater cooler, superheater casing) chromium/nickel <ul style="list-style-type: none"> • condensate tanks, storage tanks; seawater evaporators, slag bins NiCrAlY <ul style="list-style-type: none"> • hot gas corrosion protection of superalloys • <u>Protection against corrosion and friction and wear</u> <ul style="list-style-type: none"> - pressing screws, extruders, mixing arms for ores, pump casings for the cement industry • <u>Protection against high thermal loads</u> <ul style="list-style-type: none"> - Al for superheated steam pipes, sound hoods, furnace gears $T = 100 - 700\text{ }^{\circ}\text{C}$ - self-fluxing alloys for e.g. turbine blades (application if high wear resistance with high corrosion resistance required) $T, S 500\text{ }^{\circ}\text{C}$ - WC-Co for stiffening noses on compressor blades $T = 500 \dots 1500\text{ }^{\circ}\text{C}$ - $\text{ZrO}_2\text{-MgO}$ for rocket nozzles $T > 1000\text{ }^{\circ}\text{C}$ - $\text{Al}_2\text{O}_3\text{-TiO}_2$ for industrial burners - Cr_2C_3 for turbine vanes • <u>Repair</u> <ul style="list-style-type: none"> - packing gland housings, pistons of a high-pressure pump, shaft protection sleeves, crankshafts, bearing seats, truck axles
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2.11 Chemical Vapour Deposition (CVD)

2.11.1 Processes

In these processes, easily evaporable metal compounds are deposited on the surface of heated workpieces. The process temperatures range between 500 and 1500 °C (depending on the type of coating material) /2.47/.

The facility includes supply/disposal system and deposition tank.

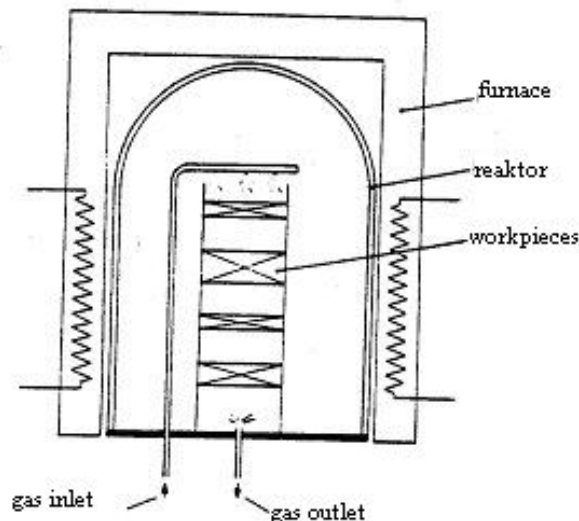


Fig. 2.23: Schematic representation of a CVD facility

The conventional CVD processes are characterized by the fact that they work at high temperatures during the reduction and conversion of metal halides into hard material precipitates and that diffusion and growth layers with strong bonding on the substrate, i.e. great adhesive strength, can be produced /2.48/.

Plasma-enhanced CVD can do with temperatures around 300 °C. The chemical reaction, which otherwise only takes place at elevated temperatures, proceeds due to an electrical discharge in the thermal plasma /2.49/.

Laser-induced CVD (LCVD) makes it possible to use a laser as the energy source for activating the chemical reaction (thermally activated process laser pyrolysis). In this way, very high deposition rates, which are higher by a factor of 100 to 10,000 than in conventional CVD processes, can be achieved by a laser beam in a narrowly localized region /2.50/.

Another possibility is to directly break up chemical compounds in the material or surrounding medium at low temperatures (non-thermal process) by the use of a laser in CVD so as to enable a deposition.

The LCVD process is at the stage of research and development.

2.11.2 Goals of CVD Coating

	Chemical vapour deposition
Goals	<ul style="list-style-type: none"> • production of wear protection layers • corrosion protection • property changes in optics and electrical engineering

2.11.3 Materials

	Chemical vapour deposition
Substrate materials	<ul style="list-style-type: none"> • all process-temperature-resistant materials • metals, sintered materials, ceramics, glass, graphite
Coating materials	<ul style="list-style-type: none"> • metals: Ta, Ti, V, Cr, Ni, Nb, W, Al • oxides: Al_2O_3 • nitrides: BN, TiN, TaN, Si_2N_4, Fe_xN • carbides: TiC, TaC, CrC, Cr_2C_3, B_4C • others: B, TaB, Si, FeSi, hard carbon (plasma CVD)

2.11.4 Market Areas for Chemical Vapour Deposition

Process temperatures and coating-gas-resistant substrate materials not prone to warping are suitable for these CVD processes. Components with close tolerances are only suitable here to a limited extent or even not at all [2.48]. Due to the high throwing power of gas deposition it is also possible to coat components of complicated shapes and restricted dimensions.

Due to the small layer thickness (approx. 1/100 mm) CVD layers are not economical for applications with high material erosion rates (e.g. building machines).

	Chemical vapour deposition
Market areas	<p>Al, Ni or Ti</p> <ul style="list-style-type: none"> • corrosion protection in mechanical engineering <p>Ta</p> <ul style="list-style-type: none"> • corrosion protection on chemical plant parts <p>TiC, TiN + Al_2O_3</p> <ul style="list-style-type: none"> • wear protection: metal cutting <ul style="list-style-type: none"> - turning tools - gear-cutting tools • wear protection: non-cutting shaping <ul style="list-style-type: none"> - deep-drawing, bending device, section rolls • wear protection <ul style="list-style-type: none"> - nozzles, knives, rollers

	<p>WC</p> <ul style="list-style-type: none"> • wear protection: textile machines <p>SiC, Nb, ZrC</p> <ul style="list-style-type: none"> • graphite protection to prevent reactions at elevated temperatures
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2.12 Deposit-Welded Layers

2.12.1 Processes

Fusion welding processes such as

- gas welding (filler rod or powdered filler material)
- plasma overlay welding
- TIG or MIG welding
- electric arc welding with rod electrodes
- fluxed-core wire welding
- submerged-arc surfacing

are primarily used as corrosion protection for low-alloyed steels or for the production of wear-resistant surfaces.

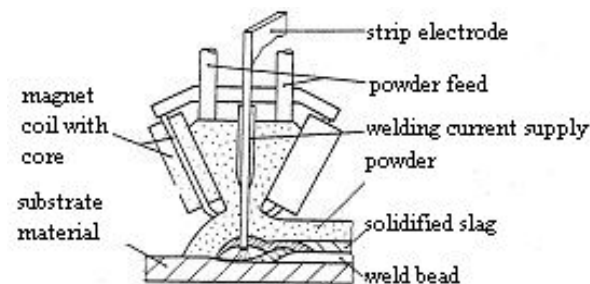


Fig. 2.24: Principle of submerged-arc surfacing with strip electrode

The processes must be related to the respective application. The lowest deposition efficiency, i.e. the slightest mixing of the filler metal with the base material, is achieved e.g. by gas welding, the highest melting rate, however, by submerged arc surfacing [2.51]. The welded-on layers are relatively thick finishing layers.

2.12.2 Goals

	Deposit-welded layers
Goals	<ul style="list-style-type: none"> corrosion protection wear protection repair, maintenance

2.12.3 Materials

	Deposit-welded layers
Substrate materials	<ul style="list-style-type: none"> mostly low-alloyed materials corrosion protection <p>nobler materials than substrate material such as copper, bronze, alloyed steels</p>
Deposit materials	<ul style="list-style-type: none"> wear protection - matrix materials based on iron, cobalt, nickel and copper with additions of carbide-boride-silicide-forming substances

2.12.4 Market Areas

Deposit welding is applied on large components as a relatively thick, highly adhesive corrosion and wear protection and on components subject to high material erosions due to wear mechanisms and for which thin hard material layers are not sufficient.

	Deposit-welded layers	
Market areas	<ul style="list-style-type: none"> corrosion protection of large containers in the chemical industry, primary components in reactor engineering (support surfaces of internals in pressure vessels) wear protection 	
	<u>Type</u>	<u>Application example</u>
	low-alloyed, Fe, Cr, Mn, Si	build-up and buffer layers, impellers
	medium-alloyed, Fe, Cr, C, Mo	excavator teeth and cutting edges, conveyor screws
	high-alloyed, Fe, Cr, C	mixer blades, blast furnace bells, slag crushers
	high-alloyed, Fe, Cr, V, C	highly scratch-stressed worms, fans
	Ni, Cr, B, Si + W ₂ C	worm, stirrer parts, grinding segments
	stellite, Co, Cr, W, C	chemistry valves, extruders, stirrers

2.13 Clad Layers

2.13.1 Processes

Overlay materials can be produced on the base material to be protected by:

- roll cladding - rolling strips onto the substrate material with subsequent diffusion annealing
- explosive cladding - the necessary pressure and temperature for cladding the substrate material is temporarily produced by the explosive charge.

In roll cladding, the maximum component dimensions of the sheets to be clad are dependent on the rolling stand and annealing furnace. The clad components are subjected to the temperature load of the annealing process. The annealing treatment restricts the possible range of materials. The whole composite material can exhibit changes in its chemical and physical properties due to annealing.

In explosive cladding, the chemical and mechanical material properties are not influenced except in a cladding zone of approx. 0.5 mm in the substrate and cladding material. Cladding materials of more than 1 mm thickness can be processed by explosive cladding [2.52].

2.13.2 Goals

	Clad layers
Goals	<ul style="list-style-type: none">• corrosion protection lining• increase in wear resistance of the component

2.13.3 Materials

	Clad layers
Base materials	<ul style="list-style-type: none">• mostly low-alloyed materials• fine grain and boilermaking steels• stainless steels
Suitable overlay materials	<ul style="list-style-type: none">• corrosion-resistant materials (Ni, NiCr, alloyed steels, Ti, Zr, Ta, Nb)• heat-resistant steels (Ni-base)• high-temperature steels• multiple claddings

2.13.4 Market Areas

In contrast to solid constructions with high-quality materials, cost savings can be achieved by the use of overlay layers on low-cost substrate materials. For this

reason, the cladding of some products has significantly increased in significance in recent years /2.53/.

	Clad layers
Market areas	<ul style="list-style-type: none"> • <i>petrochemical and chemical industry</i> <ul style="list-style-type: none"> - pipes, containers, NaCl units • <i>apparatus construction</i> <ul style="list-style-type: none"> - preheaters, shells of containers, tube plates • <i>FGD absorbers</i> • <i>off-shore technology</i> <ul style="list-style-type: none"> - shipbuilding • <i>aerospace engineering</i> (further processing of clad sheets) • <i>electrical industry</i>

2.14 Other Surface Protection Systems

In the following, coating systems will be briefly outlined, which are subject to less relevant applications in the context described here.

2.14.1 Enamel Layers

At temperatures of up to 1200 °C, inorganic protective layers mostly containing silicate are preferentially produced by hot melting. In most cases, a base enamel and a cover enamel coat are applied by dipping, brushing or spraying. Baking takes place in ovens.

In order to avoid high component temperature load, enamels can also be melted on by high-frequency electron beam or plasma jet /1.3/.

The dense, glass-like solidified enamel layers are suitable as acid, lye and high-temperature protection up to 1000 °C /25.4/.

Enamel lining is also used for lining chemical components and steel tanks for the waste water sector /2.55/.

2.14.2 Layers Produced by the Sol-Gel Method

Surfaces can be coated with a sol (organic compound) by dipping or spraying. A gel is produced by polycondensation and an inorganic layer is formed by controlled heat supply.

This process is of interest due to the low process temperature and the adjustable properties.

Gels and glasses of the silica/titania/zirconia material system can be produced, which exhibit high corrosion resistance, high softening temperatures, low thermal expansion and a high refraction of light /2.56/.

Ceramics can also be produced by the sol-gel method. Thus, for example, it has been possible to produce piezo-ceramic components of lead zirconate titanates by heat treatment at 850 °C /2.57/.

The sol-gel method is also applied in glass coating as a filter for heat and infrared radiation.

2.14.3 Lacquer Protective Coatings

Lacquer coatings of organic and inorganic polymers mixed with additives are applied as corrosion protection layers according to a multitude of processes. Application is often followed by baking. Inorganic high-temperature lacquers (Al-pigmented) can maintain their corrosion protection effect up to 600 °C /2.58/.

2.14.4 Coat-Soldered Layers

Hard material components (mostly of the carbide type) are fixed on the wear protection surface of the substrate by inorganic or organic binders.

Solders based on nickel or copper are heated to soldering temperature by simple stewing or using a solder paste and heater in a gas atmosphere /2.59/.

By changing the hard material/solder ratio, abrasive and smooth layers can be produced.

Soldered-on layers are applied for tools for removing and roughening rubber or plastics and as wear-resistant coatings of small components (brake shoes, drill rods etc.).

2.14.5 Plasma Polymerization

This process working in a vacuum from 0.1 to 1×10^{-3} bars serves for the pore-free coating of surfaces with very thin (up to 1 μm) primarily organic materials on almost any material. The glow plasma maintained by d.c. or a.c. current is "cold", i.e. the gas is practically at room temperature /2.19/. An energy transfer to an introduced monomer gas is effected by ions and electrons. After reactions in the gas phase, a condensation of the monomer on the substrate surface takes place. Polymerization is effected by further action of the plasma.

The special polymerization process leads to highly cross-linked structures, whose properties such as wettability, tightness, chemical resistance /2.60/ can be used for optics (spectacle glasses), medical engineering, the textile industry.

Plasma polymerization is at the development stage.

3. Limitation of Processes and Comparative Evaluation

3.1 Processes for the Production of Functional Protective Systems

A large number of process are available for producing surface protection systems. For some products, process variants and layer systems have become established as component protection on a technical and economic scale. These are, for example, hot-dip zinc coats commonly used for corrosion protection or electrodeposited coats for wear and corrosion protection. Further and new process technology developments, for example, by advanced heat treatment measures or the use of physical vapour deposition processes, however, raise the question as to their possible range of applications and economic efficiency.

In the following, some important parameters will be compared in order to delimit possible applications.

- **Temperature loads on substrate materials**

The temperature load of a component surface treatment can be between room temperature and melting point of the material, depending on the process used. It should be taken into consideration, however, whether the component is completely heated or whether only a relatively thin surface layer (region in which surface modification takes place) is heated. The specifications in diagrams 3.1 and 3.2 show the temperature loads to which the complete component can be exposed.

The substrate materials that can be used for the respective processes must withstand the temperature loads and the often simultaneously acting chemical reagents; they must maintain the properties necessary for their application or the properties must be restorable by suitable heat treatments (e.g. annealing and quenching). A warping of finished, tolerated components by the impact of temperature can be codetermining for the application of the process.

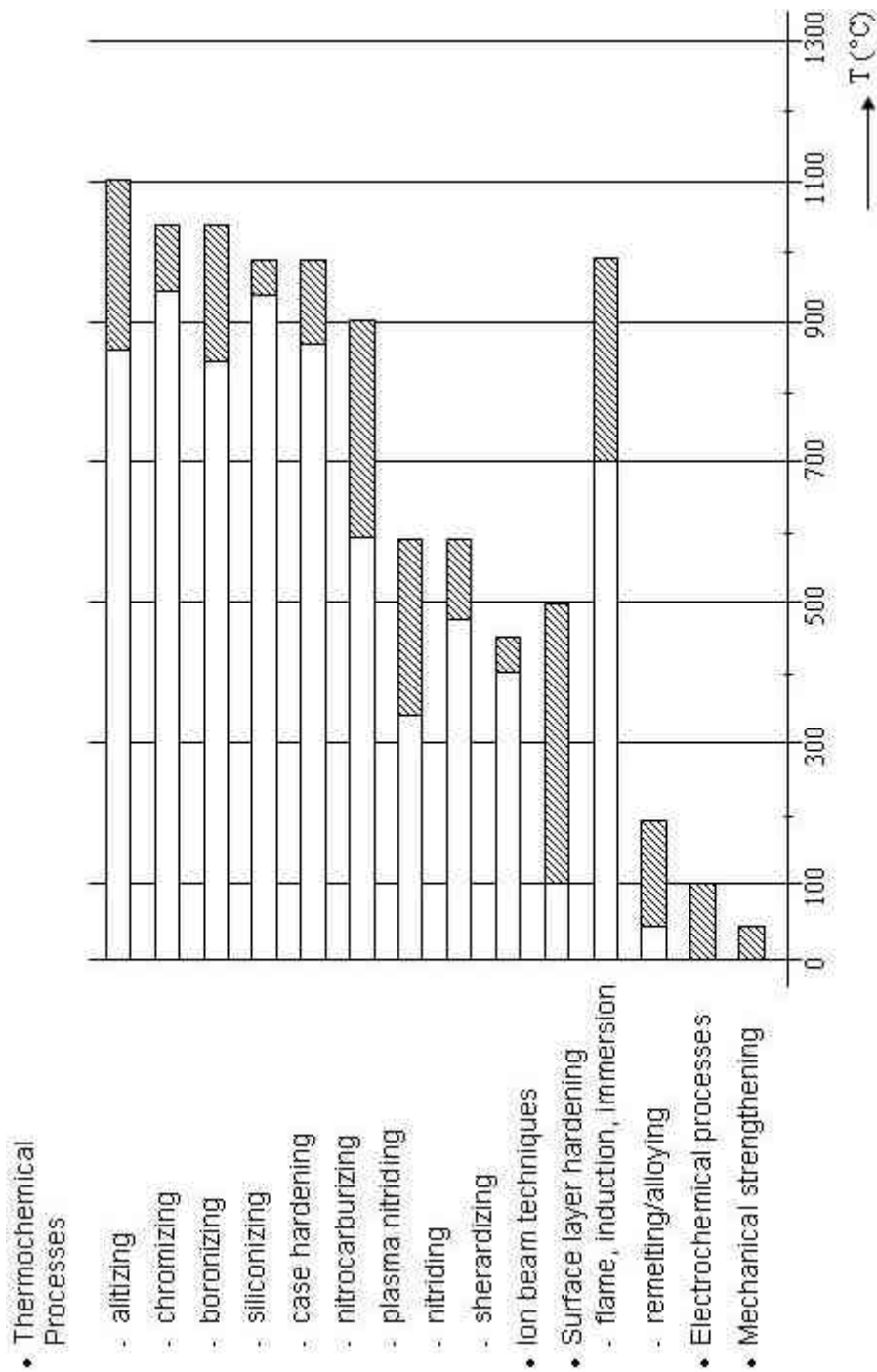


Fig. 3.1: Temperature load on the substrate material due to surface treatment

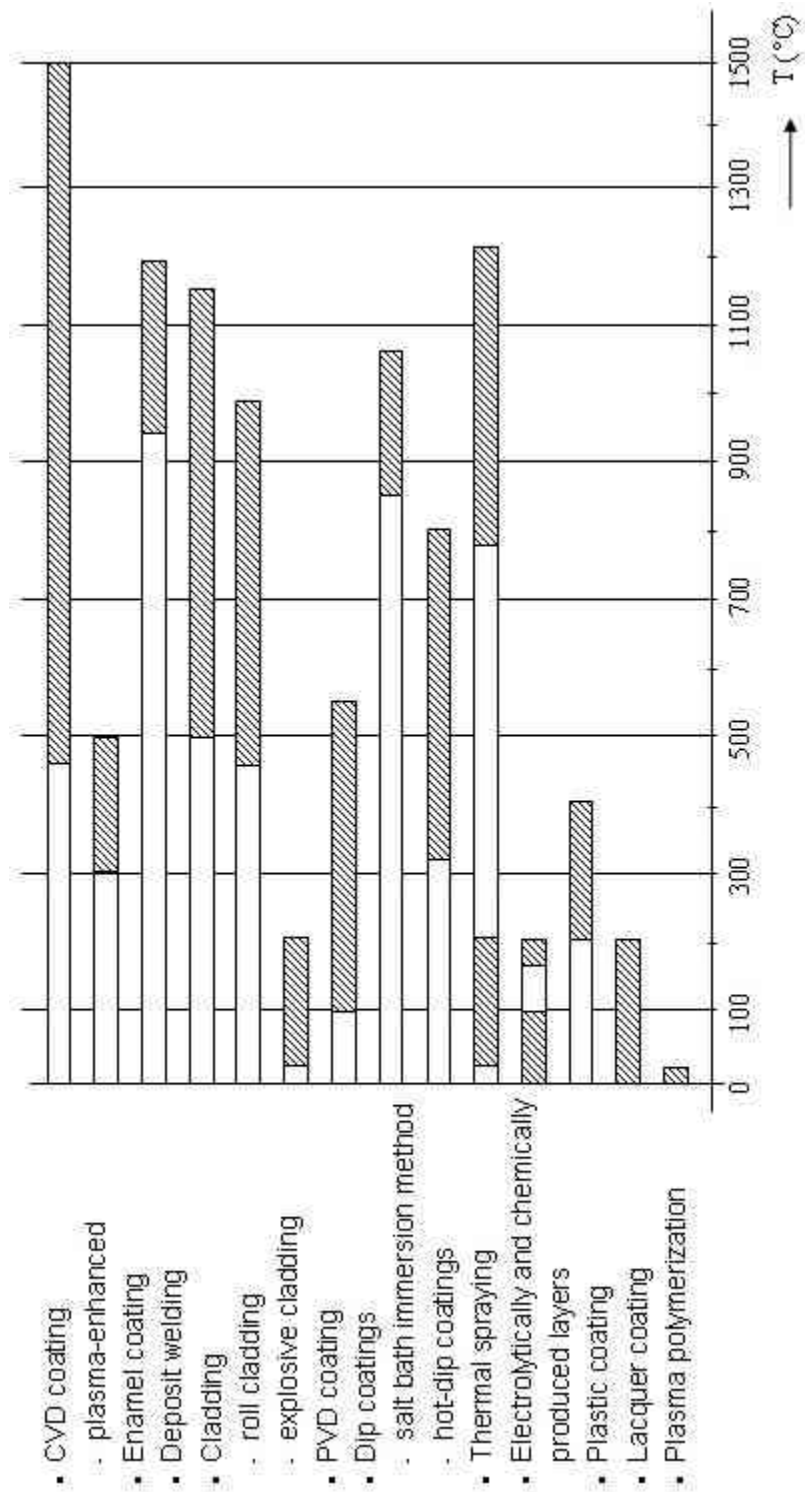


Fig. 3.2: Temperature load on the substrate material due to surface coating

- **Substrate materials and coating materials**

Nearly all substrate materials comprising plastics, metals up to ceramics are coatable. A global allocation of the substrate materials/processes can be seen from Fig. 3.3.

The range of coating materials also permits a multitude of possibilities. The processes and applicable surface protection materials are compared in Fig. 3.4.

As can be seen from the Tables, identical substrate materials can be provided with the same type of protective coating using different techniques.

The economically achievable layer thicknesses, however, and the attainable layer and composite material properties are different.

- **Layer thicknesses**

Fig. 3.5 shows economically attainable layer thicknesses as a function of the application process used. In this diagram, an approximate bandwidth is specified in which high-quality surface protection can be achieved within acceptable process times.

Processes		Substrate materials																							
		Mechanical strengthening	Electropolishing	Surface layer hardening	Ion beam techniques	Thermochemical processes							Plasma polymerization	Lacquer coating	Plastic coating/lining	Electrolytical layer production	Chemical layer production	Thermal spraying	Dip coating		PVD coating	Deposit welding, cladding	Enamelling	CVD coating	
						Nitriding	Case hardening	Chromizing	Siliconizing	Boronizing	Alitizing	Sherardizing							Plasma treatment	Salt-bath immersion					Hot dipping
plastics					+								+				+	+			+				
unalloyed steel				+	+							+	+	+	+	+	+	+		+	+	+	+	+	
low-alloyed steel		+		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
high-alloyed steel		+	+	+	+	+	+		+	+		+	+			+	+	+		+	+			+	
cast iron				+	+				+		+	+	+			+	+	+		+	+			+	
other metals		+			+	+			+				+	+	+	+	+	+		+	+	+		+	
sintered materials					+				+				+				+	+			+			+	
ceramics					+				+				+				+	+			+			+	

Fig. 3.3: Sui table substrate materials

Processes	Surface protection materials														
	Mechanical strengthening	Electropolishing	Surface layer hardening	Ion beam techniques	Thermochemical	Plasma polymerization	Chemical layer production	Plastic coating/lining	Electrolytical layer production	Thermal spraying	Dip coating		PVD coating	Deposit welding, cladding	CVD coating
											Salt bath immersion	Hot dipping			
metals				+	+	+	+		+	+		+	+	+	+
alloys	+	+	+	+		+	+		+	+			+	+	
carbon, carbides				+	+	+				+	+		+	+	+
oxides						+				+					+
borides						+				+					+
nitrides						+				+			+		+
silicides						+				+			+		+
mixtures						+				+			+	+	
conversion layers							+		+						
dispersion layers							+		+						
graphite layer													+		+
plastics						+		+		+			+		
others						+		+		+			+		

Fig. 3.4: Suitable surface protection materials

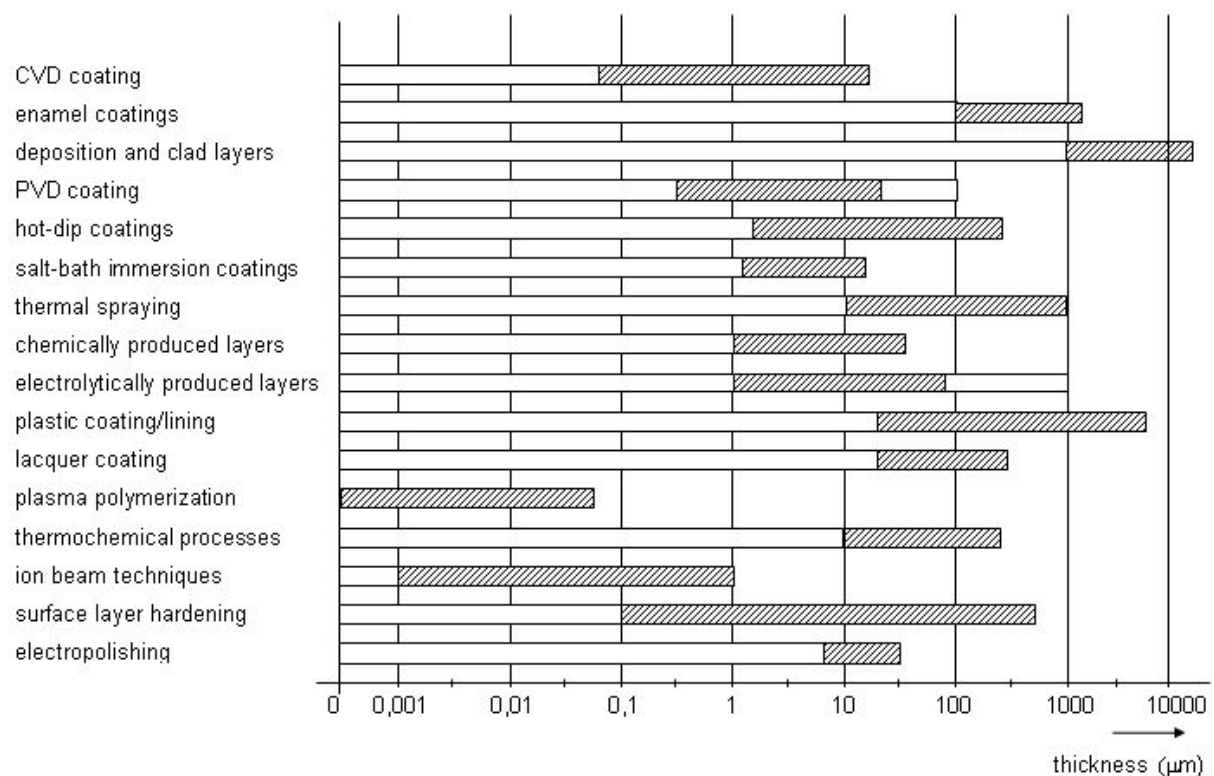


Fig. 3.5: Layer thickness ranges

Influence on component properties

Besides improving the anti-corrosion and anti-wear properties, the strength properties of substrate materials can also be influenced by surface treatment and surface coating. The fatigue strength of a material is generally determined by material strength, susceptibility to cracking and residual stress condition on the surface of a component. The fatigue strength can be increased by /3.1/:

- Mechanical strengthening of the surface layer of a component. Shot peening produces an internal compressive stress zone.
- Thermochemical treatment of a component surface for the generation of internal compressive stresses.

Tensile stresses, which negatively influence the dynamic strength of components, can arise due to coatings /3.2/. This is the case if coating material and substrate material exhibit greatly different expansion coefficients. On the other hand, the coating porosity, coating structure and adhesion to the substrate have such an effect on total performance that wide scattering ranges have been determined in experiments /3.3/.

Processes	Dynamic strength increase reduction	
• mechanical strengthening	+	
• electropolishing	+	
• thermochemically produced	+	

layers		
• electrolytically and chemically produced layers		(+)
• PVD and CVD layers		(+)
• thermal spraying		(+)

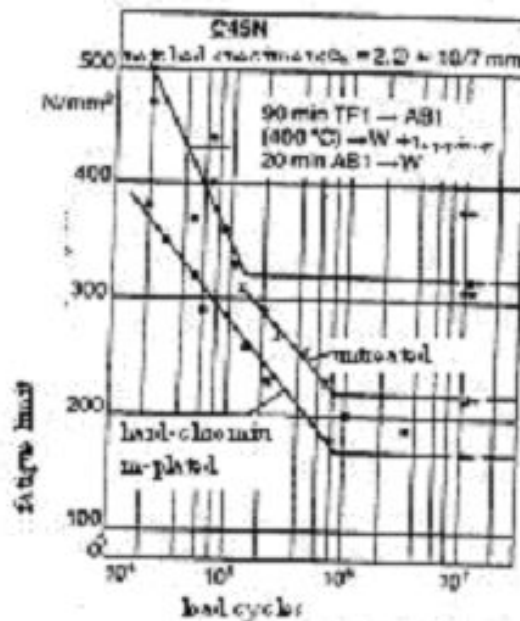


Fig. 3.6: Influence on the component properties of hard-chromium-plated and QPQ salt-bath-nitrided component surfaces /2.11/

Fatigue limit increases of the thermochemically treated sample materials are specified to be more than 50 % compared to the untreated specimens /2.11/. Hard-chromium-plated components exhibited 20 % reduced fatigue strength.

Process allocation

In the following Figs. 3.7 and 3.8, process types are allocated to their surface protection function. Technical application examples are given for the use as corrosion, friction and wear protection.

A general survey of the processes and their applicability/functional allocation, where surface protection leads to quality improvement, is given in Fig. 3.9.

Process type	Surface protection	Technical application	Remarks
lacquering	- binder plus pigment - by shot peening or baking, electr. conductivity producable, thus cathodic corrosion protection	structural steel engineering, metallurgical industry, shipbuilding, chemical industry	by combination of binder and pigment applicable for wide ranges High-temperature lacquers up to max. 600 °C
plastic coating and linings	resins, rubberizing, PA, PVDF, PTFE, FEP, PFA, E-CTFF	apparatus construction, chemical industry FGD units	non-stick, largely resistant to chemicals
electrochemical machining	electropolishing	apparatus, nuclear engineering, food industry	max. possible corrosion protection of the material attainable
electrolytically and chemically produced layers conversion layers	Al hard anodic layer Mg-HAE layer Al passivation layer Mg chromating layer browning and phosphate layer metal layers (Al, Cr, brass, bronze, Zn, Pb, Sn)	light-metal-processing industry, mechanical engineering, automobiles, aerospace engineering, printing industry, petroleum industry	conversion layers in conjunction with lacquers
thermal spraying	Al, Zn, Pb, Ni, NiCrAlY steel alloy	structural steel engineering, furnace construction, apparatus construction hot gas corrosion protection on steels	porous layers are sealed corrosion-resistant by impregnating or fusing
dip coating	Al, Zn, Pb, Sn	steel structure protection, food industry, petrochemistry, radiation protection	application primarily for simply shaped geometries
PVD and CVD	Al, Ti, TiN, Ni, NiCrAlY, Ta	mechanical engineering, components of high-strength steels, Al as CD replacement layer, hot gas corrosion	thin, dense coats, processes suitable for small components

		protection on steels structural steel parts for chem. use	
thermochemical	alutizing (Al) sherardizing (Zn)	turbine construction (high-temperature corrosion) machine and steel structure protection up to 600 °C mechanical engineering	
deposit welding, cladding	copper, bronze, alloyed steels	large containers in the chem. industry, reactor engineering	
cladding	Al, Ti, Ta, Zr, Ni, Cu alloyed steels	structural steels parts, apparatus construction, aerospace engineering, chemical industry	minimum sheet thickness required
hot melting	enamelling	chemistry plants (acids, lyes and high-temperature protection)	non-F-diffusion- proof
shot peening	blasting with globular abrasive	steam generator pipes, aircraft construction turbine blading	reduction of stress corrosion cracking
ion beam techniques	Ti, Cr, Pd, Pt, Ta, Hg, Pb	turbine blades	application for valuable cost- intensive components, processes under development

Fig. 3.7: Process allocation – corrosion protection

Process type	Surface protection	Technical application	Remarks
surface layer hardening	surface layer remelting and alloying flame induction dip hardening laser or electron beams	tool engineering, cast components punches, shaping tools camshafts, piston rings, bearing seats	conventional processes for large components, difficultly accessible and locally limited hardening for laser/electron beam hardening
thermochemical	nitriding nitrocarburizing case hardening siliconizing boronizing	spindles, bolts, forming tools toothed wheels, racks toothed wheels, anti-friction bearings, valve – pump parts, conveying equipment grinding rings, moulds for fireclay bricks	
ion beam techniques	implanting of ions	pressing and cutting tools, deep-drawing punches, extruder nozzles	N-implantation near industrial introduction
plasti coating and linings	dipping electrostatic whirl sintering vulcanizing	rolls, mixers, stirrer tanks impellers, saw blades	corrosion-resistant friction and wear protection
electrolytically and chem.produced layers	hard chromium plating nickel dispersion layers	rolls, rollers, hydraulic cylinders valve bodies, bearing bushes, extruder screws compressor parts blade coating, rotos of pumps, tappets	

thermal spraying	metals, oxides carbides, nitrides	coilers, rolls, shaft seals, bending and forming tools, friction linings, impellers	application of large layer thickness attainable even on components of complicated shape at relatively low temperature load
dip coating TD process	carbide layers	sheet-metal processing tools, forging dies	simple application of thin, hard anti- wear coatings
deposit-welding	matrix with carbide- boride-silicide- forming additives	impellers, excavator teeth, worms	for stressing with high material removal
PVD and CVD	metals, oxides carbides, nitrides	metal-cutting tools, forming tools, nozzles	thin, hard anti-wear coating on small components
soldered-on coatings	hard material solders on Cu- or Ni-base	tool industry, small components	applicable for small components

Fig. 3.8: Process allocation – friction and wear protection

Type of process	Function												
	friction and wear	corrosion protection	oxidation protection	self-lubrication/sliding propert.	non-stick protection	diffusion inhibition	adhesion primer	repair coating	increasing the fatigue strength	high-temperature protection	optics, electr. eng., medicine	shaped bodies	decoration
mechanical strengthening													
electropolishing		+		+					+				+
flame hardening	+												
induction hardening	+												
dip hardening	+												
laser/electron beam hardening	+												
surface layer remelting	+												
surface layer realloying	+												
ion implantation	+	+	+	+		+					+		
ion beam mixing	+	+	+	+		+					+		
nitriding	+	+		+					+				
nitrocarburizing	+	+							+				
case hardening	+	+											
siliconizing	+	+											
chromizing		+	+										
alutizing		+	+						+				
sherardizing		+											
plasma treatment of metals	+	+	+	+					+				
lacquer protective coatings	+	+											+
plastic coatings and linings	+	+	+	+	+	+					+		+
electrolytical deposition	+	+	+	+		+		+			+		+
chemical deposition	+	+	+	+		+		+			+		+
dispersion layers	+	+	+	+									
anodically produced conversion	+	+		+			+						+
chemically produced conversion	+	+											+
hot-dip coatings		+		+									+
salt-bath immersion	+			+									
vapour deposition		+		+							+		+
sputtering				+							+		+
ion plating	+	+		+									+
flame spraying	+	+		+	+		+	+		+	+		+
electric arc spraying	+	+		+	+		+	+		+	+		+
plasma spraying	+	+	+	+	+		+	+		+	+	+	+
hypersonic flame spraying	+	+	+	+	+		+	+		+	+	+	+
conv. CVD	+	+		+							+		+
plasma-enhanced CVD	+	+		+							+		+
laser-induced CVD	+	+		+							+		+
deposit welding	+	+						+					
cladding	+	+									+		
enamelling		+								+			
sol-gel method											+		
coat soldering	+												
plasma polymerization		+										+	+

Fig. 3.9: Processes / allocation of functions

Technical application status of processes

In Fig. 3.10 the processes are classified with respect to their technical application status. Only trends can be shown for the individual layer systems, since the treatment/coating material used is also of importance here.

Thus, for example, systems with TiN layer production are common processes in PVD. Although vapour deposition, sputtering or cladding is possible for a large number of substances /3.4/ and has been performed in the laboratory, technical application has not yet taken effect **for reasons of** demand – process gas control – process costs (economic efficiency) – know-how.

Type of process	Status of industrial use	
mechanical hardening	+	++
electropolishing	+	++
flame hardening	+	++
induction hardening	+	++
dip hardening	+	++
laser/electron beam hardening	+	(in automotive engineering ++)
surface layer remelting	+	
surface layer realloying	+	
ion implantation	+	(in electr. eng. ++)
ion beam mixing	+	
nitriding	+	++
nitrocarburizing	+	++
case hardening	+	++
siliconizing	+	++
chromizing	+	++
alutizing	+	++
sherardizing	+	++
plasma treatment of metals	+	(for nitriding ++)
lacquer protective coatings	+	++
plastic coating and linings	+++	
electrolytical deposition	+++	
chemical deposition	+++	
dispersion layers	++	
anodically produced conversion layers	+++	

chemically produced conversion layers	+++	
hot-dip coatings	+++	
salt-bath immersion	+++	
vapour deposition	+++	
sputtering	++	
ion plating	++	
flame spraying	+++	
electric arc spraying	+++	
plasma spraying	+++	
hypersonic flame spraying	++	
laser spraying	+	
conv. CVD	+++	
plasma-enhanced CVD	++	
laser-induced CVD	+	
deposit welding	+++	
cladding	+++	
enamelling	+++	
sol-gel method	+	(glass coating ++)
coat soldering	++	
plasma polymerization	+	

+ = status of research and development

++ = technical utilization, not used on a large technical scale to date for process-engineering or economic reasons

+++ = established process used

Fig. 3.10: Technical application status

3.2 Surface Finishing Areas in Apparatus Construction

The tasks of surface protection for chemical and power plant apparatus construction can be specified as follows:

- materials exposed to chemical attack are made more corrosion-resistant on one side
- low material consumption of high-grade materials
- increase in component life of components exposed to corrosion or subject to friction and wear
- increase in dynamic strength (generation of compressive stress)
- thermal protection of components

- repair of components
- ensuring the system function (reducing the friction coefficient).

The application of surface finishes in apparatus construction is determined by the demands of the market and by economic aspects.

Apparatus designs including wall thickness allowances or the use of high-grade bulk materials are conflicting with the applicability of surface protection, the costs of application and the necessary additional tests.

The following processes have largely become established as economical variants depending on the respective boundary conditions:

- electropolishing
- rubberizing
- coating with plastics
- enamelling
- galvanizing
- flame or wire spraying with CrNi steels
- plasma spraying of ceramics
- detonation spraying of carbides
- claddings

and

- deposit weldings.

Fig. 3.11 shows an extract of currently applied surface protection for heat exchangers.

The in most cases bulky components require coating processes by which protection can be applied onto the finished part or the applied protection can be further processed during apparatus construction (processing of clad sheets).

Processes that require reaction vessels or work in high vacuum are ruled out for most corrosion and erosion protection applications in apparatus construction.

Cont. No.	Apparatus	Requirements stressing, chemism, temperature	Surface finishing by:
1	heat exchanger liquid/liquid preheater cooler	corrosion by aggr. media (brackish water), 7 - 60 °C	rubberizing, plastics, tube disks, explosively clad
2	gas/gas HTR He/He IHX air preheater	adhesive wear, fretting wear, fretting in tube supports and spacers; reducing and oxidizing helium corrosion, flue gases with temperatures of up to 100 °C	APS coating ZrO ₂ ; Y ₂ O ₃ , NiCrAlY cast material or enamelling
3	liquid/gas HTR afterheat removal cooler waste heat boiler	adhesive wear in spacer, reducing He, temp. = 950 °C (fretting) corrosion	TAPS ZrO ₂ , Y ₂ O ₃ white material
4	steam/gas steam superheater in boiler	high-temperature corrosion in reducing and oxidizing atmosphere, radiant temperature 1400 - 1600 °C, protection of tubes against high temperature necessary	sprayed high-temperature ceramic
5	steam liquid/liquid condenser feedwater preheater desuperheater	corrosion, waterside (brackish water) the water boxes and reversing bonnets and tube disk, max. temperature = 150 °C erosion, U-tube tube plate (HP) welding temperature 180 - 280 °C, coil apparatus baffle	hard rubberizing, epoxy resin or plastocore plastic (also with flame-spr. NiCr linings or explosively clad)
6	steam liquid/gas preheater (e.g. hall)	corrosion of the tubes	hot-galvanized
7	liquid steam/liquid evaporator steam generator PWR	tube plate and box, temperature 530 °C	clad
8	liquid steam/gas HTR steam generator	abrasive wear and fretting spacer, red. He temperature 750 °C	D-gun, plasma spraying
9	liquid steam/steam liquid water separator reheater column evaporator	erosion inlet of separators of "cold reheater" water inlet rate = 50 m/s, X – 13 X i temperature – 190 °C corrosion, medium	clad, or wire spraying with CrNi

Fig. 3.11: Practised surface protection applied to heat exchangers

3.3 Surface Finishing Processes for Application in Plants for Nuclear Process Heat Generation

From the finishing processes available, a large number are ruled out through criteria that preclude a fulfilment of the functions of the surface finish. The surface protection goals possible for PNP components require adapted finishing systems. Thus, for example, permeation inhibition and corrosion protection are aimed at producing layers as dense as possible, so that the surrounding atmosphere cannot act on the substrate material. In contrast, thermal barrier coatings with high pore fractions can fulfil the function. Anti-friction and anti-wear coatings can exhibit both dense and porous protection systems. Of significance for function fulfilment is therefore not only the layer chemism, but also the coating condition. In the following table, Figs. 3.12 and 3.13, process types with delimiting process parameters are shown.

Type of process	Possible finishing			Influence on substrate			Dimensional restr.		chamber necessary	reproducible process *2	Finishing time		Repair of coating possible in situ		Application range for nuclear process heat					Further developments for high-temperature applications worth pursuing	
Surface treatment	metallic	ceramic	others *1	strength	warping-prone	warping not to be expected	apparatus components	small components			high *3	low *4	no	yes	friction and wear	corrosion	permeation	thermal insulation	not suitable	no	yes
mechanical strengthening			+	↑		+	+			+		+		+		+				+	
electrochemical machining			+	↑		+	+		(+)	+		+		+		+				+	
surface layer hardening, conv.			+	↑	+		+			+	+		+						+	+	
surface layer remelting	+	+				+		+		+		+	+		+					+	
electron/laser beam hardening	+	+				+		+		+		+	+		+					+	
surface layer redispersing	+	+	+			+		+				+	+		+						+
ion implanting and ion beam mixing	+	+	+			+		+	+	+		+	+		+		+			+	
plasma treatment		+	+		(+)	+		+	+	+	+	+	+		+					+	
thermochemical processes		+	+	↑	+		+		+	+	+		+		+		+				(+)

*1 removing, inorganic or organic materials

*2 operation possible

compressing,
automated

*3 hours
*4 minutes
() restricted statement

↑
↓

increase
decrease

Fig. 3.12: Process parameters delimiting surface treatment for PNP applications

3.4 Application-Oriented Process Features

3.4.1 Apparatus Construction

Surface finishes in apparatus construction primarily have the task of protecting the base material from corrosion. In order to achieve this goal, the surface protection must be of such a nature that the corrosion-initiating medium does not act on the substrate material or only to a minor extent during the design period of the apparatus.

This requires above all dense coatings firmly bonded to the surface of the base material.

In addition to corrosion, erosion, friction and wear also occur in some locations of the apparatus.

Processes applied with their specific advantages and drawbacks are shown in Fig. 3.14.

Due to the versatility of component shapes and operational load types, the selection of a protective system must be individually matched.

The processes and layer systems that are established and available largely cover the interests of apparatus construction.

Further developments or improvements of corrosion protection coatings for chemical loads at high media temperatures are advanced by the production of dense, low-pore layers according to the hypersonic process or according to low-pressure plasma spraying (LPPS).

Type of process	Possible finishing			Influence on substrate			Dimensional restr.		chamber necessary	reproducible process *2	Finishing time		Repair of coating possible in situ		Application range for nuclear process heat					Further developments for high-temperature applications worth pursuing	
Surface treatment	metallic	ceramic	others *1	strength	warping-prone	warping not to be expected	apparatus components	small components			high *3	low *4	no	yes	friction and wear	corrosion	permeation	thermal insulation	not suitable	no	yes
plastic coating and linings			+	→		+	+		(+)	+		+		(+)					+	+	
electrolytical and chemical deposition	+			↓		+	+		(+)	+		+	+							+	
dispersion layers	+		+	↓		+	+		(+)	+		+	+		+					+	
conversion layers	+		+	↓ →		+	+		(+)	+		+	+						+	+	
hot-dip coatings	+				+			+	(+)	+		+	+						+	+	
salt-bath immersion TD process		+			+			+	(+)	+	+		+						+	+	
vapour deposition PVD	+		+			+		+	+	+		+	+			+	+				(+)
sputtering PVD	+	+	+			+		+	+	+		+	+			+	+				(+)
ion plating PVD	+	+	+	↓ →		+		+	+	+		+	+		+	+	+				(+)
flame spraying	+	+		↓	+		+					+		+					+	+	
electric arc spraying	+			↓		+			(+)	+		+	+						+	+	
detonation spraying	+	+	+	↓ →		+	+		(+)	+		+	+		+						+
plasma spraying	+	+	+	↓ →		+	+		(+)	+		+	+		+	+		+			+

hypersonic flame spraying	+	+				+	+			+		+	+		+	+					+
conventional CVD	+	+		↓ →	+			+	+	+		+	+		+					+	
laser-induced and plasma-enhanced CVD	+	+				+		+	+	+		+	+		+	(+)	(+)			+	
deposit welding	+			↓	+		+			+		+		+	+					+	
roll and explosive cladding	+				(+)	+	+		(+)	+		+	+						+	+	
enamelling		+			+		+			+		+		(+)		(+)			+	+	(+)
sol-gel		+				+				+		+		(+)	(+)	(+)		(+)			
cquer protection			+	→		+	+			+		+		+		(+)				+	
coat soldering	+				+			+		+		+		+					+	+	
plasma polymerization			+	→		+		+		+		+	+						+	+	

*1 other inorganic or organic materials

*2 automated operation possible

*3 hours

*4 minutes

() restricted statement

↑

↓

→

increase

decrease

primarily unchanged

Fig. 3.13: Process parameters delimiting surface coating for PNP applications

Application • examples	Process	Advantages	Disadvantages	Development required	
				Yes	no
apparatus construction • chamber linings	plastic coating/lining	<ul style="list-style-type: none"> • dense anti-corrosion layer • non-stick properties • suitable for "large" and "small" components • chemically resistant to a large number of substances 	<ul style="list-style-type: none"> • application temperature below 300 °C • coating can only withstand minor mechanical actions • often not vapour-diffusion-resistant 		+
• pressure vessels	• lacquer coating	<ul style="list-style-type: none"> • good corrosion protection of less stressed parts • simple application 	<ul style="list-style-type: none"> • damage due to mech. actions easily possible 		+
• waste water treatment	• hot melting of enamel	<ul style="list-style-type: none"> • good corrosion protection for acids and lyes; up to high temperatures • vapour-diffusion-resistant • smooth surface (cleaning) 	<ul style="list-style-type: none"> • chipping due to mech. action easily possible • low thermal conductivity 		+
• heat exchanger tubes for dry cooling	• hot-dip coatings	<ul style="list-style-type: none"> • good corrosion protection under atmospheric load (Zn) 	<ul style="list-style-type: none"> • limited to atmospheric stressing 		
• piping	• thermal spraying	<ul style="list-style-type: none"> • production of resistant anti-friction and anti-wear coatings • processing of high-melting materials possible • parts of complicated shape and large parts coatable • refractory 	<ul style="list-style-type: none"> • the layers are porous without thermal recompression or impregnation • inner surface coating limited • - relatively poor adhesion 	+	

		metals sprayable in chambers			
• vessel lining	• cladding	<ul style="list-style-type: none"> • corrosion and wear protection lining of medium wall thicknesses • variety of metallic materials • suitability for pressure vessels 	<ul style="list-style-type: none"> • minimum plate thickness required • restricted to substrate shapes suitable for cladding 		+
• nozzle lining/ steam inlet	• deposit welding	<ul style="list-style-type: none"> • production of thick anti-wear coatings, anti-corrosion coatings • best layer adhesion to base material • application for in-situ repairs 			+
• screw connections	• electroplating	<ul style="list-style-type: none"> • corrosion protection of small components 	<ul style="list-style-type: none"> • not suitable for component segments that are welded together 		+

Fig. 3.14: Process features of coatings in apparatus construction

By thermal spraying at subatmospheric pressure (chamber sizes up to 2000 mm diameter) it becomes possible to process refractory metals such as Ta, Zr, Ti etc. according to requirements.

3.4.2 Tool Engineering

By means of surface finishing, the base material, the tool, is protected against premature wearing. This and the reduced corroding of the tool due to surface protection causes significant increases in tool life depending on the application (see Section 4). Fig. 3.15 compares the advantages and drawbacks of applied processes by means of application examples.

Application process - examples	Advantages	Disadvantages	Further development required	
			yes	no
tool engineering - metal-cutting – • cutting plates CVD	production of thin coatings with • high hardness with • high resistance to adhesive wear and • low tendency to cold welding • highest coating adhesion • good control of coating properties	due to high process temperature • decrease in strength of the base material • danger of warping • temperature resistance of base material required • relatively sophisticated process • not for large components		+
milling cutters PVD	• properties similar to the CVD processes, but • the process temperatures are relatively low, therefore • no danger of base material warping • wide range of materials coatable	• due to the relatively low process temperature, in practice, only a few coating systems can be deposited • relatively sophisticated process • not for large components		+
- non-cutting - forming tools in sheet-metal processing for TD process CVD	see above • friction and wear protection simple production by • immersion coating in salt baths • superior to chromium-plated, nitrided steels and hard metals	see above • the high bath temperatures lead to the danger of tool warping	+	
• die-forging tools	• friction and wear protection by boronizing the tool best properties for die forging • relatively thick weld deposit against friction and wear • friction and wear protection • suitability for tools with surface areas primarily perpendicular to metal working	• deposit material hardens cold during application • limited application • thin coating is destroyed by forging	+	

Fig. 3.15: Process features of tool coatings

3.4.3 Power Plant Engineering and Others

Figs. 3.16 and 3.17 will illustrate once more the processes used with their advantages and drawbacks.

Application - examples	Process	Advantages	Disadvantages	Further development necessary	
				yes	no
	Deposit welding	<ul style="list-style-type: none"> thick, adequately adhesive coatings 	<ul style="list-style-type: none"> Co-containing alloys anti-wear coating causes high dose rates in the nuclear reactor plant due to abrasion and corrosion high heat input into substrate 	+	
<ul style="list-style-type: none"> control rod drive 	thermal spraying	<ul style="list-style-type: none"> Co-free highly wear-resistant coatings low heat load and thus not warping-prone 			+
<ul style="list-style-type: none"> gas turbine blades 	thermal spraying	<ul style="list-style-type: none"> oxidation and hot gas corrosion protection a small pore fraction is produced by heat treatment up to 1000 °C 	<ul style="list-style-type: none"> subsequent heat treatment for adhesion strength increase required vacuum chamber for low-pressure processing required 	+	
<ul style="list-style-type: none"> boiler surface 	thermal spraying	<ul style="list-style-type: none"> abrasion and corrosion protection against dusts and highly fluid slag 	<ul style="list-style-type: none"> deterioration of heat transfer 	+	

Fig. 3.16: Process features of coatings from power plant engineering

Application - examples	Process	Advantages	Disadvantages	Further development necessary	
				yes	no
other gas turbines	HAE anodizing	corrosion protection of Mg alloys in combination with lacquers	since coating grows half into the base material; multiple coating causes <ul style="list-style-type: none"> dimensional compliance problems 		+
- Cr steels	lacquer coating (pigmented)	corrosion protection of low-alloyed chromium steels <ul style="list-style-type: none"> by baking cathodic protection 	<ul style="list-style-type: none"> cathodic protection deteriorates with time 	(+)	
- cams	- D gun	<ul style="list-style-type: none"> wear protection supporting cams high-strength, dense layers 	<ul style="list-style-type: none"> reworking of the coating required 		+
- toothed wheels and shafts	thermochemical (nitriding)	<ul style="list-style-type: none"> wear protection with exact surface hardness high geometrical accuracy 	<ul style="list-style-type: none"> closely tolerated process temperatures 	+	
- gap seal	plasma spraying	<ul style="list-style-type: none"> inlet (wear) at 1 ag requirement combination due to multilayer coating of different composition exact reproducibility of application 			+
- blade roots	CVD, PVD galvanic, dispersion coating	<ul style="list-style-type: none"> fretting and erosion protection thin, hard protective coating fretting and erosion protection 	<ul style="list-style-type: none"> sophisticated process less expensive than CVD, PVD 	+	+
- turbine blade	alizing	<ul style="list-style-type: none"> hot gas corrosion protection 	<ul style="list-style-type: none"> influence on component strength 		
	plasma spraying APS	<ul style="list-style-type: none"> hot gas corrosion protection 	<ul style="list-style-type: none"> after spraying, fusing of the coating in a kiln is required 		
	plasma spraying LPPS	<ul style="list-style-type: none"> hot gas corrosion protection 	<ul style="list-style-type: none"> increased 		

	plasma spraying	<ul style="list-style-type: none"> • low-pressure plasma spraying improves the adhesion, density and purity of the coating • thermal insulation • temperature lowering in the metal surface 	apparatus expenditure compared to APS <ul style="list-style-type: none"> • adhesion problems in using ceramics 		
--	-----------------	--	--	--	--

Fig. 3.17: Process features of 'other' coating applications

4. Development Status of Application-Oriented Surface Protection

4.1 Conventional Surface Finishes

Tool engineering

Tools are provided with different protective materials with the aim of reducing friction and wear.

The substrate accommodates the mechanical loads – the protective coating deters wearing attack.

Apart from the processes of

- nitriding and
 - hard chromium plating already applied for some time
 - boronizing and the
 - physical vapour deposition of nitrides and carbides /4.1/
 - salt-bath coating according to the TD process
- are being applied.

Suitable surface protection coatings must fulfil the following requirements /4.2/:

- reducing the tendency to adhesion
- improving the sliding properties
- good adhesion to the base material
- sufficient elastic properties
- high hardness.

Additional condition: sufficient supporting effect of the base material is necessary.

Performance of coated tools

Cutting and forming tools with protective coatings were tested in a large number of studies /4.1 – 4.23/.

Depending on the application conditions, surface coating systems and treatment, the following properties were identified:

- increase of the cutting speed and feed rate in the material
- shortening the machine times (up to 90 %)
- reducing the cutting forces (reduced friction coefficient due to the coating)
- reducing the cutting temperature
- reducing the tendency to welding between workpiece and tool (coating as diffusion barrier)
- improving the geometry of the chip flow, clean cut of the surface
- reducing crater and flank wear
- improving the corrosion behaviour of the tool
- increasing the applications of the cutting material (material diversity)
- extending the service life
 - tool life increase metal cutting 200 - 1000 °C
 - tool life increase forming 50 - 400 %

State of the Art

The coating of cutting tools is state of the art today in certain areas of the metal-processing industry. Thus, for example, 70 - 80 % of the precision hobs are coated with TiN layers /2.34/.

In gear-cutting technology, coating has become most widely spread in percentage terms. At least 80 % of the gear-cutting tools are coated with TiN /4.25/.

The coating of drilling tools, end mills, taps, reamers and forming tools is increasingly gaining significance. In shape cutting, coated hard-metal disposable inserts have become more and more established in recent years and conquered a market share of approx. 60 % /4.3/ /4.22/. However, the development is not yet completed, and new improvements are to be continually expected.

Coating systems for tool engineering

Hard-metal plates (composites of hard materials and binders/sintered materials) are primarily coated with hard materials such as

- | | |
|-------------------------|----------------------------------|
| • titanium carbide | TiC |
| • titanium nitride | TiN |
| • titanium carbonitride | Ti(C, N) and |
| • aluminium oxide | Al ₂ O ₃ . |

The toughness of the hard-metal core and the wear resistance of the surface layer can be largely adapted to the material to be machined. The ceramically coated plates are improved by

- multilayer systems (multiple coating)

so that the advantages of the nitrides and carbides take effect /4.24/. Additional Al_2O_3 overlays led to considerable tool life increases in the machining of cast materials /2.48/.

If hard metals are chiefly coated according to the CVD process, steel parts can also be finished according to the PVD process, which involves considerably lower process temperatures.

As an example of metal-cutting machining, Fig. 4.1 shows the efficiency of coated in comparison to uncoated drills made of high-speed steel (HSS).

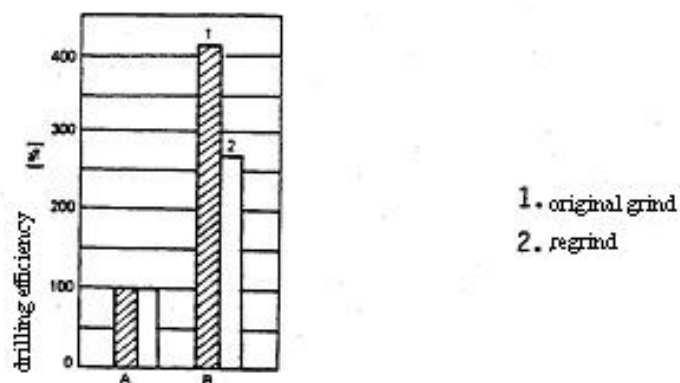


Fig. 4.1: Comparison of drilling efficiency
HSS drill (A) with TiN-coated drills (B) /4.3/

Even the reground TiN-coated drills exhibit clear efficiency improvements. Original tools, i.e. without regrind, allow higher cutting speeds and feeds with prolonged tool life travel and better surface finish. Fig. 4.2 illustrates this interplay. For the titanium-nitride-coated and the black-oxidized standard drills compared, the increased cutting speed did not only increase the drill efficiency but total productivity.

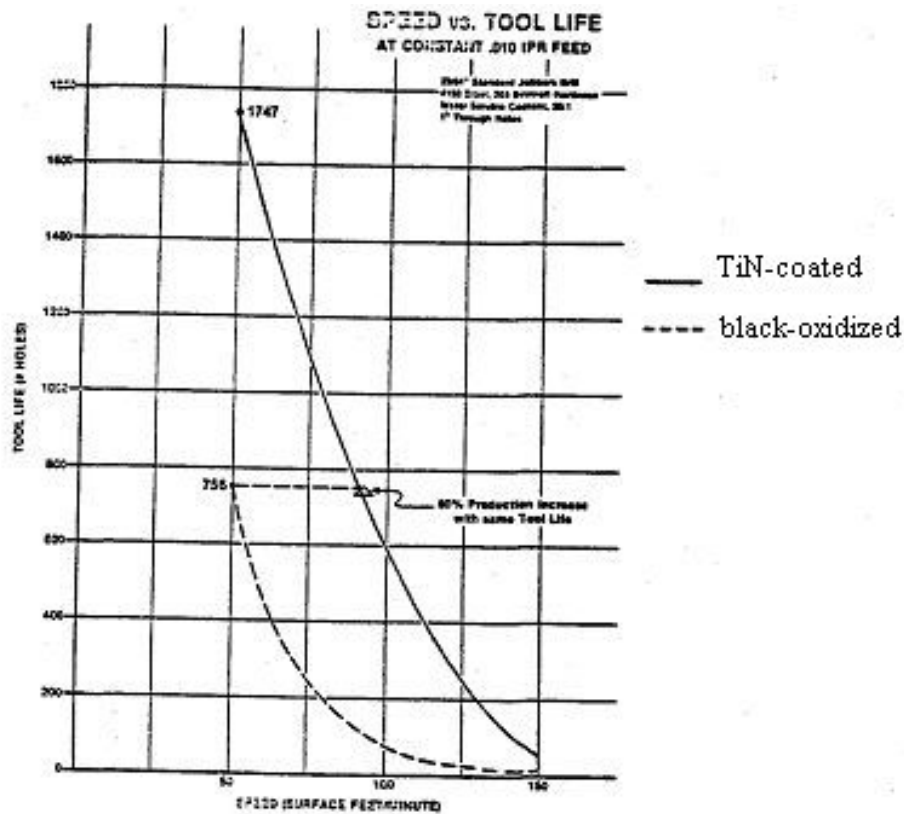


Fig. 4.2: Comparison with TiN-coated drills (constant feed) /4.18/

At present, steel tools are primarily coated with

- titanium nitride - TiN /4.22/ and also
- titanium carbide - TiC.

New materials are nitrides, carbides, oxides and borides of metals TiCN; CrN; Cr/CrN; TaN; W:N; TiAlN; AlON; BN:TiN; WC; Al_2O_3 ; Cr_2O_3 ; T:B₂; ZrB₂; W₂B₅.

Coatings are also increasingly used in non-cutting shaping in addition shape cutting.

Typical materials for cold working tools and their suitable surface coating are specified according to /4.1/.

typical materials for cold working tools			surface coating						
material class	DIN designation	material no.	CVD technique			PVD technique	bath nitriding	boronizing	vanadizing
			TiC	TiN	Cr ₂ C ₃	TiN			VC
high-speed steels	S 6-5-2	1.3343	X	X	x	X	x		X
	S18-1-2-10	1.3265	X	x	X	x	X		x
cold-work steels	X 165CrMoV12	1.2601	X	X	X	x	X	X	X
	X 155Cr VMo 12 1	1.2379	X	X	X	X	X	X	X
	X 210Cr W 12	1.2346	X	X	X	X	X	X	X
	X210 Cr 12	1.2080	X	X	X	X	X	X	X
	X 100Cr Mo V 5 1	1.2363	X	X	X		X	X	X
	145 Cr 6	1.2063	X	X	X		X	X	X
	100 Cr 6	1.2067	X	X	X		X	X	X
	90 Mn V 8	1.2842	X	X	X		X	X	X
hot-work steels	C 110 W 2	1.1650	x	X	X		X	X	X
	X 40CrMo V 51	1.2344			X		X	x	X
	X 32CrMo V 33	1.2365			X		X	X	X
hard metals	P 10 bis P 30		x	x	X	x	x	X	x

Fig. 4.3: Typical materials for cold working tools and their suitable surface coatings after /4.1/.

An increase of the tool life quantity is to be observed for all surface-coated tools. Fig. 4.4 is presented here as an example. The CVD-coated HSS and HWS tools led to the largest increase in tool life quantity.

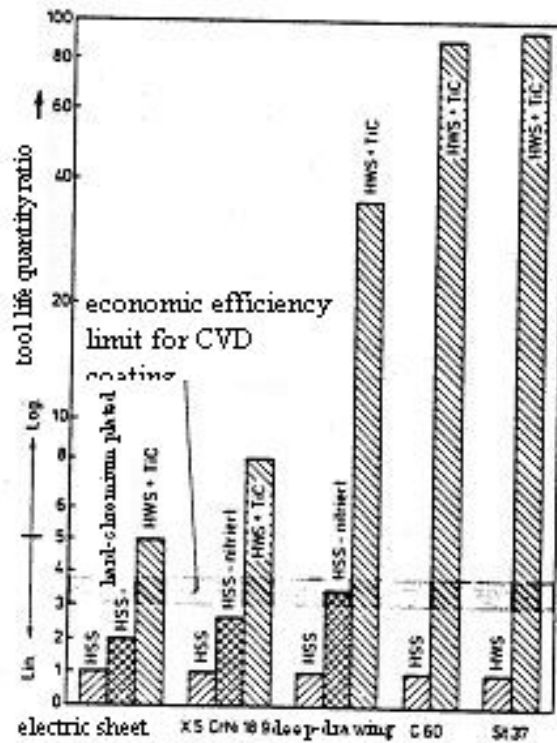


Fig. 4.4: Tool life quantity comparison of surface-treated punches after /4.2/.

According to Japanese studies /1.9/, in addition to CVD coatings, the salt-bath coatings according to the TD process of forming tools are shown to be suitable for the sheet fabricating industry.

In this context, forming tools are coated with hard carbide layers such as

- vanadium carbide - VC
- niobium carbide - NbC and
- chromium carbide - Cr_7C_3 .

According to the Japanese studies, the carbide coating is superior to

- chromium-plated and
- nitrided steels, and to
- hard metals.

Concerning the applicability of coated and surface-treated die-forging tools,

- thermochemically produced
- deposit-welded and sprayed CVD and
- galvanically produced coatings were investigated /4.16/.

The results showed here as well that a tool life improvement was achieved by all the protective systems applied.

The author specifies the following allocation:

Protection	Result
thermochemically produced	best suitability; good bonding to the base material due to diffusion boronizing better properties than nitriding
deposit-welded and sprayed	no general statement; deposit material hardens cold during application D-gun spraying meaningful for tools with surface areas predominantly perpendicular to the forming direction
CVD-produced	suitability only limited; shattering of the thin coating by forging
galvanically produced	hard-chromium plated meaningful for tools with surface areas predominantly perpendicular to forming

In Fig. 4.6, the amount of wear is plotted over the number of forgings of a partial investigation. The boronized tool showed the lowest wear.

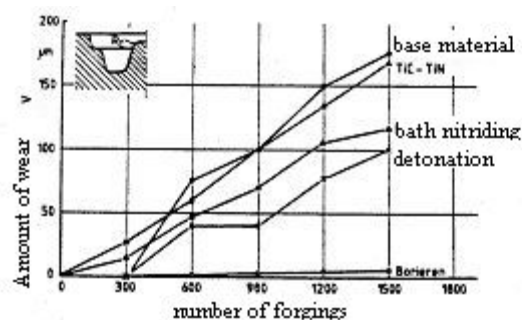


Fig. 4.6: Wear on forging tool over the number of forgings after /4.16/.

Investigations with surface-layer-remelted tools and high-speed steel, especially concerning the impacts on wear behaviour, are under way /2.6/.

The tool life was doubled by surface layer remelt alloying for turning chisels /2.6/, where it was tried to weld tungsten carbide into high-speed steel to combine the favourable strength of high-speed steel with the favourable wear resistance of the (quasi-) hard metals.

Tool life increases by a factor of 3 to 10 were achieved by implanting nitrogen into pressing and cutting materials using ion beam techniques /2.8/. Cutting edges of WC with Co as the binder were applicable 8 to 12 times longer, drawing nozzles for wires of WC achieved the 5-fold tool life.

Metal ion implantation of

- rare earths or
- yttrium

in tool steel improved wear behaviour considerably /2.7/.

Power plant engineering

Corrosion protection, wear and erosion protection measures on parts of the component surfaces used in power plant engineering are chiefly covered by established processes. Workpiece surfaces are finished here by

- shot peening
- electropolishing
- plastic coating and lining
- cladding
- deposit welding and
- thermal spraying with its process variants.

Fig. 4.7 gives a survey of possible protective applications.

Stress corrosion cracking is reduced by generating compressed stresses in the material surface on e.g. steam generator pipes or blades of the turbine by shot peening, so that the service life of the parts can be effectively prolonged.

Type	Function
COALING	
drum motors (belt conveying)	- adhesive coating
conveyor belt rollers	- adhesive coating
raw coal bunkers (Supralen)	- corrosion, sliding surfaces, wear
coal chutes (Supralen)	- corrosion, sliding surfaces, wear
coaling hopper cars	- corrosion, sliding surfaces
dust coal bunkers	- corrosion
explosion pipe - dust coal bunker	- corrosion
dust allotters - worm troughs	- wear
dust allotters - conveyor worms	- corrosion, wear
casing of coal discharging belts	- corrosion
refuse charging hopper	- minor wear
	corrosion, sliding surfaces
coal inlet funnels	- corrosion, sliding surfaces
coal drop shafts	- corrosion, sliding surfaces
mill beater heads	- wear
mill shaft bearings	- slide bearing, shaft seat
blower gyros (carbon dust)	- erosion, sliding surface

FUEL STORAGE fuel oil tank bottom protection (more than 20,000 l contents) fuel oil floating-roof tank/inner slide surfaces fuel oil tank outer surfaces plant parts refuse storage and conditioning	- corrosion - corrosion, slide surfaces - corrosion - corrosion by chemical attack wear, sliding surfaces
TURBINE AREA turbine parting lines in the high-, medium- and low-pressure range turbine guide bottom plates turbine blades of the low-pressure end stage steam turbine reducing valve steam turbine valve spindle bolts for intercept valve turbine shaft condenser, steam side	- sealing surfaces - erosion - cavitation (test coating) - cavitation - sealing seat - sealing seat - bearing seat - corrosion, erosion
BOILER AREA high-pressure steam boiler tubes in the furnace (smooth, unstudded tubes) collecting grate tubes edge tubes burner array bottom tubes boiler tubes in the secondary region cyclone boiler tubes, studded, under ramming mix tubes of the large and small shells tubes in the air and dust nozzle region tubes cyclone tip tubes cyclone collar tubes secondary and tertiary region superheater tubes, reheater and end superheaters stoker-fired boiler tubes in the front region, side wall tubes refuse boiler tubes in the firing region and in the gas passes burner cooling tubes burner tips and nozzle tubes ash handling plants worms, belts, pipes etc. ash bunker slag bunker immersion frame of the slag trough	- high-temperature corrosion - high-temperature corrosion, stud adhesion, (protection of tube walling – welding of high-alloyed studs is to be avoided) - high-temperature corrosion, salt-melt corrosion (test coatings) - high-temperature corrosion (red. atmosphere) - corrosion due to chemical attack at high temperature (test coating) - erosion - scaling

wet slag removal equipment casing boiler start-up flash tank boiler starting and shutdown vessel vertical tube boiler drum steam exhaust pipes with safety valve high-pressure steam sound absorbers incl. internals	<ul style="list-style-type: none"> - wear, corrosion - sliding surfaces, corrosion, wear - erosion - corrosion - corrosion - corrosion - corrosion - corrosion (water hammer hazard) - corrosion
REACTOR AREA steel structure support for austenitic base material of the cover bricks - reactor pressure vessel water treatment treatment hold-up tank for condensate collection tank supporting frame for refuelling machine support surfaces of RPV internals control rod drive (latches of the magnetic jack) Application possibilities for boiling-water, pressurized-water and ship propulsion reactors containment steel structure containment with expansion system vent pipes fuel storage pool and racks transport cask for fuel elements fuel element pond shield water tank reactor pressure vessel wet steam turbine casing pump casing guide rods tube plate and chamber for steam generators	<ul style="list-style-type: none"> - corrosion - corrosion - corrosion - corrosion - friction and wear - friction and wear - corrosion (atmospheric) - corrosion (deionized water) - corrosion (deionized water) - corrosion (deionized water) - corrosion (deionized water) - corrosion (deionized water) - corrosion (deionized water) - material substitute for deposit - welding - cavitation - cladding - material substitute - cladding
SEALING SURFACES, BEARINGS, SHAFTS sealing surfaces of seats starting nozzles, cones in the high-pressure, water and steam region etc. bearings for fans suction droughts, air preheaters, mills	<ul style="list-style-type: none"> - repair (reject recovery) and equivalent or high-grade material substitute - repair (reject recovery) and equivalent or high-grade material substitute

discharge belts, pumps etc. sewage water, cooled bearings turbine bearings electric filters, slide bearings shaft seats for fans suction draughts, air preheaters, mills, discharging belts, pumps etc. turbine shafts sliding ring seals and bearings for pumps	- repair (reject recovery) and equivalent or high-grade material substitute - repair (reject recovery) and high-grade material substitute
--	--

Fig.4.7: A survey of possible protective applications.

Electropolishing of nuclear components does not only lead to the highest possible corrosion resistance of the base material, but it also reduces the build-up of radioactive contamination on the workpiece surface, or surfaces already contaminated are cleaned. In decommissioned power plants, electropolishing of nuclear components is used as a means of decontamination, so that the materials can be handled without risk /2.4/.

Plastic coatings are increasingly used as a protective overlay on low-alloyed steels, so that high-grade, i.e. cost-intensive, metallic materials can be avoided. The coatings applied here primarily in apparatus and pipes at temperatures below 200 °C have become established as an economically efficient corrosion protection measure /4.26/.

For increased stressing of the surface by friction/wear and/or corrosion at elevated temperatures, metal-material claddings, deposit-weldings or thermally sprayed overlay layers are practised protective measures.

Corrosion protection is produced by the deposition of CrNi steels; hard alloys are used for friction and wear protection /4.27/. For nuclear applications, above all, cobalt-free protective layers are applied /4.28/.

Further fields of application for the surface protection of components from **power plant engineering** can be covered by thermal spraying. In the 1990s, thermal spraying was the surface coating technique with the widest application range /2.40/. Apart from deposit welding, the spraying technique provides coatings for repair and maintenance. The application of these spraying techniques for corrosion protection is primarily directed to the layer densities to be achieved. Sprayed layers exhibit pores; they do not reach the resistance of bulk materials. The attainable coating porosity is primarily dependent on the deposition process. Fig. 4.8 shows an order of magnitude that can be achieved for coating densities obtained by spraying.

Process	Relatively attainable density %	Impact velocity of sprayed particles m/s
vacuum plasma	100	1000
detonation spraying	85	700
hypersonic flame spraying	80	500
plasma spraying	50	300
flame spraying	0 ^{*1}	150

^{*1} without fusing

Fig. 4.8: Relatively attainable coating densities by thermal spray processes /4.30/.

Flame spraying with fusing of the coating at approx. 1050 °C leads to dense overlay surfaces. However, the high substrate temperature loads restrict the application to robust components.

The further development of the flame spraying process, hypersonic flame spraying, provides the possibility of producing compact layers with high adhesive bond using a spray gun which is relatively easy to handle /4.33/. Coatings with porosities of approx. 1 % can be achieved according to the present status of development /3.32/. Compact coatings can be produced by vacuum plasma and detonation processes; however, the components must be brought to the coating facility (not usable in situ) or in the case of vacuum plasma coating must be enclosed in a vacuum tank.

Thermal spraying for friction and wear protection on control rod drives, conveyor worms, sealing surfaces or pump shafts etc. provides the possibility of producing partial, highly resistant wear overlays not least due to the large variety of layer systems. The spraying technique provides advantageous applications due to low substrate temperature load and the possibility of component repair and reject recovery. Limitations to thermal spraying are the process-induced relatively low adhesive tensile strengths of the layers.

In conventional power plant engineering, boiler surfaces have been increasingly coated in recent times. Sprayed Ni alloys have been successfully used here against erosion of finned tubes /4.33/. Plasma-sprayed nickel aluminium forms corrosion-resistant protective coatings on boiler walls due to the generation of an alloy layer/diffusion layer of nickel-aluminium iron /4.34/. Protection against abrasion and corrosion caused by dusts and slags is to be obtained by sprayed duplex coatings composed of metal bond coat (NiCr) and ceramic top coats (Al₂O₃ or ZrO₃). The operating experiences acquired have turned out to be positive /4.30/.

Aeronautical industry

Surface finishing has become largely established in the aeronautical industry. Processes such as

- shot peening
- thermochemical treatment
- thermal spraying and
- electroplating

are chiefly applied. Aircraft parts are of complicated geometrical shapes and consist of materials with high strength or other high-quality technological properties. The high component costs do not permit scrapping after expiry of the service life. If the expenditure for overhauling a component by surface finishing amounts to less than 60 % of the price of a new component, overhauling is carried out /4.35/. This overhauling can lead to quality improvement and prolonged service life of a component due to coating. Approx. 30,000 material positions per passenger aircraft are treated by electroplating alone. An overhaul without the application of galvanic layers would be technically and economically impossible /4.36/.

The main applications of surface finishing in the aeronautical industry are corrosion protection, wear protection and thermal insulation.

The following is used for corrosion protection:

- cadmium
- nickel cadmium
- chromium and copper
- silver
- anodizing of aluminium
- chromating and phosphating
- lacquers
- aluminizing, chromium aluminizing
- NiCrAlY

for friction and wear protection:

- hard chromium
- nickel sulfamate
- electroless nickel
- copper
- silver
- titanium nitride
- hard material – tungsten carbide, cobalt
- dispersion coating cobalt + chromium oxide
- nitriding

and for thermal insulation

- ceramics

Fig. 4.9 gives a survey of the protective systems used for structural and engine part coatings.

Coating goal	Protection obtained by:	Component example
corrosion protection of low-alloyed, high-strength steel parts	multiple coating <ul style="list-style-type: none"> - cadmium-plated - chromated - zinc chromate primer - polyurethane top coat 	landing gear axles and crossmembers
corrosion protection of aluminium	anodizing	structural parts
corrosion protection of magnesium alloys	spinel coatings of Mg, Al and manganese compounds in combination with lacquers	combustion chamber casing
corrosion protection of low-alloyed chromium steels applicable up to 600 °C	Al-pigmented lacquers	engine
corrosion protection of steels exposable up to 500 °C	nickel-cadmium diffusion layer	engine, compressor region, tie rods, blades
hot gas corrosion of Ni-base alloys	aluminized layer chromium-aluminized layers	engine blades
hot gas corrosion	M Cr AlY (low-pressure plasma-sprayed)	turbine blades
wear protection	hard chromium coating	slide bearing surfaces landing gear axles
wear protection applicable up to 600 °C	tungsten carbide / cobalt	support contact surfaces of compressor blades
wear protection	nitriding	toothed wheels, shafts
wear protection for temperatures above 500 °C	silver coating	engine parts
running-in and start-up coats	multilayer plasma-sprayed coatings	gap loss limitation between rotor and casing
abrasive wear and erosion-prone positions of titanium alloys	titanium nitride	roots of vanes and moving blades
thermal insulation	plasma-sprayed ceramics	hot part of gas turbine, blades

Fig. 4.9: Coatings of structural and engine parts

High-temperature technology

For the protection of parts subject to corrosion, wear and erosion at high temperatures, processes such as

- chemical vapour deposition
 - pack cementation
- thermal spraying
 - flame spraying
 - plasma spraying (APS and VPS)
 - detonation coating
- physical vapour deposition
 - electron beam vapour deposition
 - sputtering
- electroplating
 - dispersion coating
- cladding
- enamelling

have been used.

In order to ensure protection, surface finishes must fulfil the following functional requirements /4.38/ /4.39/:

- high thermal stability in the operating environment
- high mechanical stability in the operating environment
- low self-diffusion rate
- low interaction with chemical and mechanical properties of the base material
- high adherence to the base material
- sufficient thermal stability of the coating.

Fig. 4.10: Functional requirements to be fulfilled by a high-temperature coating

Some coatings addressed in the previous sections are shown in Figs. 4.11 and 4.12 in terms of order of magnitude according to the specified maximum temperature-induced application possibilities. The limits are determined by the oxidation, decomposition or softening of the coating.

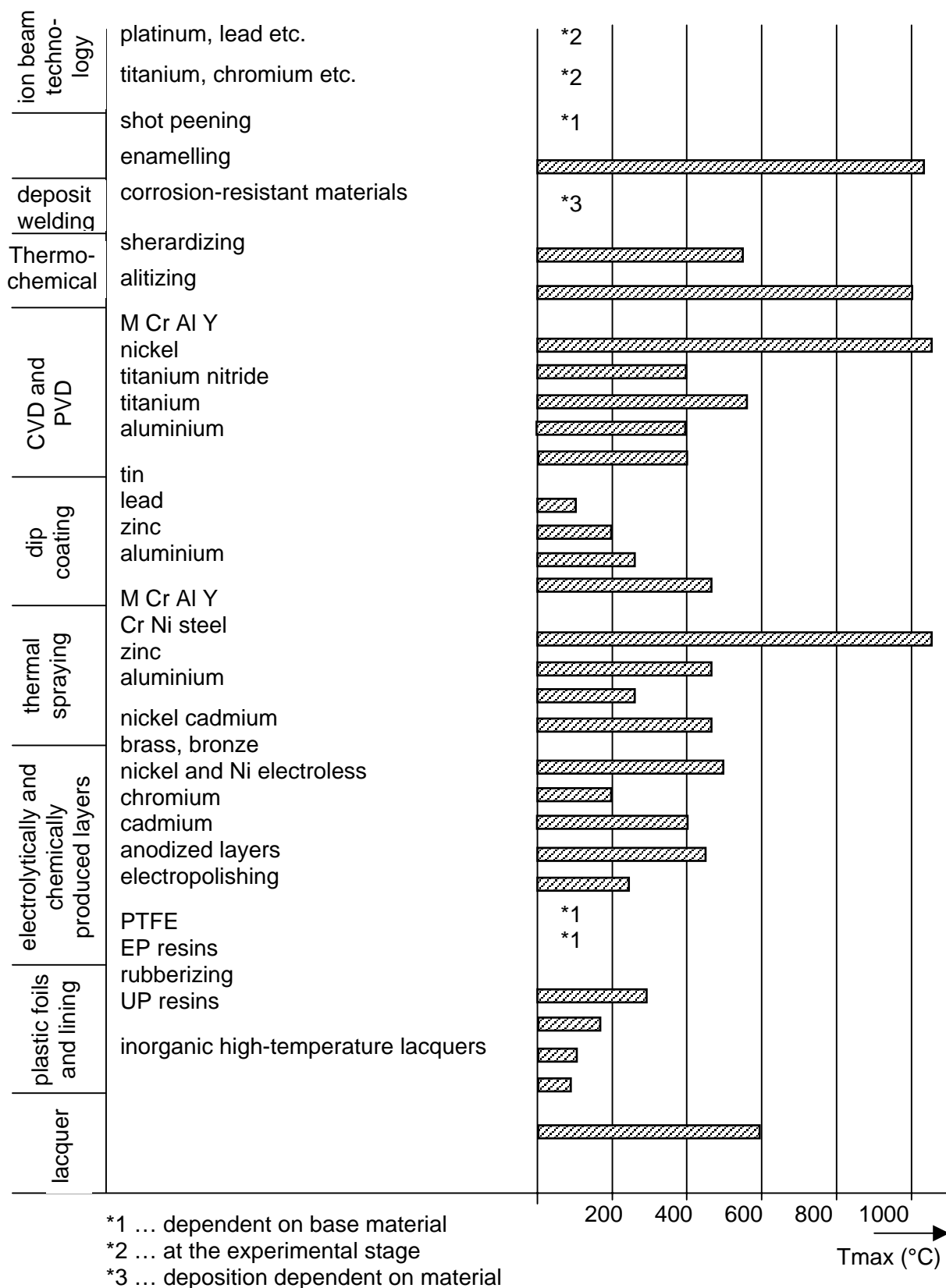


Fig. 4.11: Max. temperature load on the coating
 - corrosion protection -

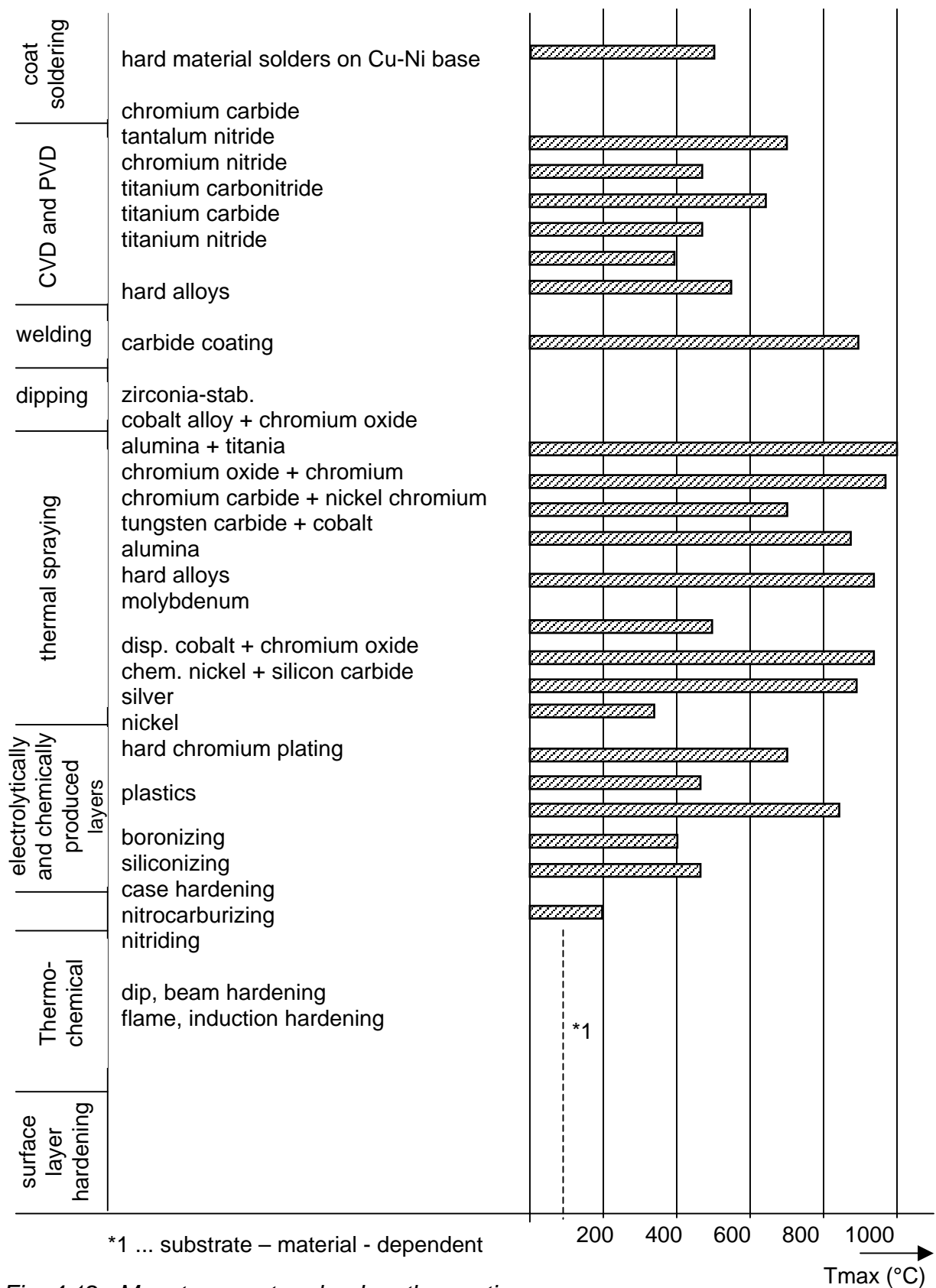


Fig. 4.12: Max. temperature load on the coating
- friction and wear protection -

Corrosion protection layers suitable for high-temperature protection

- form preferentially oxidic surface layers
- form in many instances impermeable layers on the substrate material /4.49/.

Primarily

- metallic layer systems

are used, which provide aluminium, chromium and/or silicon in sufficient concentrations as effective elements. Both single-component and multicomponent protective coatings are applied.

Multicomponent coating	Top coat
M-Cr-Al; Ni-Cr-Al, Pt-Al	Al ₂ O ₃ , spinels
M-Cr; M-Cr-Al; Ni-Cr-Al-A	Cr ₂ O ₃ , spinels
M-Cr-Si; M-Cr-Si-A	SiO ₂ , where appropriate, silicates

M = Ni, Fe, Co

A = active elements such as Y, Ta, Zr, Ti, Hf, Ca, Ce, Sc or additions of Y₂O₃; La₂O₃; ThO₂, CeO₂

Fig. 4.13: Hot gas corrosion and high-temperature oxidation protection systems after /4.39/ /4.50/.

After the application of metallic layers, there is the possibility of applying

- ceramic layer systems (enamel)

especially high-temperature enamel as protection on components. In Fig. 4.14 some high-temperature enamels are specified, which were developed as corrosion protection for chromium-nickel steels and nickel alloys /4.49/.

SiO ₂ - B ₂ O ₅ - Al ₂ O ₃ - CaO - BaO - ZnO - ZrO ₂
SiO ₂ - B ₂ O ₃ - Al ₂ O ₃ - CaO - BaO - ZnO
SiO ₂ - CaO - BaO - ZnO - MoO ₃ - BeO

Fig. 4.14: Examples of high-temperature enamels after /4.49/.

Candidate friction and wear protection systems are

- composite coatings with hard material or oxide dispersions

in a metal matrix of nickel-chromium or cobalt-chromium alloys.

Wear-resistant layers of the alloy systems

- Co – Cr – W – C (stellite) and
- Co – Mo – Si (Triballoy)

are also of great significance /4.39/.

Resistance to erosion, as required for hot gas flows with high ash content, has been found with the hot gas corrosion protection coating M Cr AlY.

Thermal barrier coatings for protection against excessive heat acting on metallic component surfaces are achieved by ceramic layers. Partially or completely stabilized ZrO₂ layers are predominantly applied onto a bond coat mostly of Ni-Cr, Ni-Al or M Cr AlY /4.51/.

Fig. 4.14 below specifies some high-temperature protection effects achieved /2.40/ /4.45/ - /4.46/ /4.49/ - /4.52/.

Type of Coating	Application / Effect
aluminizing by spraying or dipping	<ul style="list-style-type: none"> • corrosion protection of furnaces and hearth parts, exhaust pipe lifetime extension 2- to 20-fold
enamelling	<ul style="list-style-type: none"> • scaling protection of exhaust pipes and stacks, heating boiler protection
alitized and hot-dip-aluminized layer or Colmonoy-sprayed	<ul style="list-style-type: none"> • protection against SO₂, SO₃, H₂S at 600 °C on iron or nickel alloys in heat exchangers
Ni-Cr-Al-Mo-Fe spray coating	<ul style="list-style-type: none"> • protection against oxygen attack and chem. substance up to 600 °C for heat exchanger surfaces in steam boilers
4-layered spray coating 1. NiCr 2. NiCr + ZrO ₂ -MgO 3. ZrO ₂ -MgO 4. silicone resin	<ul style="list-style-type: none"> • protection of industrial burners against hot gas corrosion for operating loads, T approx. 1200 to 1500 °C
M Cr AlY spray coating	<ul style="list-style-type: none"> • hot gas corrosion protection in turbines at approx. 1100 °C

Ni-Al ₂ O ₃ (cermet)	• corrosion protection for blowers in blast furnaces
zirconium or chromium oxide sprayed	• protection against attack by slags and molten metals
oxide layers sprayed Al ₂ O ₃ + TiO ₂ /Al ₂ O ₃ -Ni A1	• corrosion protection on casting moulds
sprayed Al ₂ O ₃ or carbide coatings	• erosion protection of moulds
boronizing or nitriding	• corrosion protection of titanium and titanium alloys by Al melts up to 800 °C
ZrO ₂ -Y ₂ O ₃ sprayed	• corrosion protection from vanadium-containing combustion gases
ZrO ₂ -Y ₂ O ₃ + NiCoCrAlY sprayed	• thermal insulation on gas turbine blades
Mo-Cr ₂ O ₃ + CeO ₂ sprayed or Ni-SiC dispersion coatings	• thermal insulation and increase of service life in engine combustion chambers
CrNi weld deposit or spraying of stellite	• outlet valves of combustion engines
aluminizing or chromizing	• corrosion protection of exhaust systems
Cr ₃ C ₂ -NiCr	• wear protection in nuclear installations
oxide layers produced in situ on workpieces by selective thermochemical pretreatment	• permeation hardening of hydrogen, deuterium, tritium

Fig. 4.14: Effect of high-temperature protective coatings

4.2 Friction and Wear Protection Surface Finishes for PNP Applications

Investigations on the tribological system of the contact areas of components contacting each other under HTR conditions have been performed in laboratory experiments and also on operational components.

The factors influencing the tribological system are

- atmosphere (oxidizing, reducing)
- component materials
- geometric ratios
- surface condition
- surface pressure
- motion characteristics
- temperature /transient processes, and
- time behaviour /load cycles

In order to assess the suitability of the respective surface protection, it is necessary to know the factors of influence. Laboratory test results that predefine restricted boundary conditions (e.g. simplified test geometry or motion characteristics) for the feasibility of measurements, may easily lead to faulty statements. It is also common lab-scale practice to obtain information about "time behaviour" by predefining elevated load values. This involves the danger of overtesting, and operationally functionable protective systems could be discarded.

The investigations referred to in the literature are only comparable to a limited extent with respect to the boundary conditions imposed. Deviations due to coating techniques, the composition of the contaminated helium test atmosphere, specimen geometries, surface pressures, different friction rates and overall friction travels, thermal shock tests and the static exposures performed at the different surface pressures only permit comparative evaluations pointing in certain directions.

The development basis was protective systems for which experience was available concerning adequate properties in the low temperature range and coatings applied above all for heat and corrosion protection (TBC) in gas turbine construction.

Friction and wear protection for PNP boundary conditions below 700 °C

Significantly elevated friction coefficients can already occur at HTR helium temperatures below 600 °C depending on the material pairing, the component load, the strain-induced friction travels and friction rates as well as the time of application. According to investigations by A. Eiermann et al. /1.15/, for example, the material Nimocast 713 LC together with the material Nimonic 75 has already led to a steady increase of the friction coefficient at a component surface pressure of 10 N/mm² and a friction rate of 2 mm/min. even in the heating phase. At 600 °C the approx. 2.8-fold force had to be applied for rubbing the specimen bodies compared to the initial state at room temperature. It cannot be seen from these studies whether the friction coefficient continues to increase under steady-state operating conditions in 600 °C HTR helium.

Nimonic 75	Ni balance; 20.5 Cr; 3.8 Fe; 0.45 Mn; 0.45 Si; 0.35 Ti and 0.2 Al; 0.1 C
Nimocast 713 LC	Ni balance; 11-13 Cr; 5.5-6.5 Al; 3.8-5.2 Mo; 1 Co; 0.4-1 Ti; 0.5 Fe and others

As another metallic pairing which, however, remained at a constant friction coefficient of $\mu = 0.5 - 0.6$, Colmonoy 6 had been tested against Colmonoy 6 with 50 N/mm² surface pressure at 600 °C. After an overall friction travel of 5.2 m, the surfaces were smooth and no traces of wear were present.

The following Fig. 4.15 gives a survey of the behaviour of investigated metallic material pairings /1.14/ /1.15/ /4.54/ - /4.56/.

material pairing	static load						dynamic load					
	temp. °C	surface pr. N/mm ²	atmosph.	corros.	not welded	welded	temp. °C	surface pr. N/mm ²	atmosph.	friction level in	friction coefficient μ	remarks
Nimocast 713 LC/ Nimonic 75	-	-	-	-	-	-	600	10	HHT	0,1	0,7	welded at T = 870 °C
Colmonoy 6 / Colmonoy 6	-	-	-	-	-	-	600	50	HHT	5,2	0,5-0,6	friction surface smooth
Nimocast 713 LC/ X 20 Cr Mo V 22L	-	-	-	-	-	-	350	10	HHT	2,5	0,7	welded friction surface smooth
Nimocast 713 LC/ 17 Cr Mo 55	-	-	-	-	-	-	480	10	HHT	2,5	0,75	friction
Mo-T2M/ 17 Cr Mo 55	-	-	-	-	-	-	400	10	HHT	1,5	1,2	local welding
Inconel 625/ Inconel 625	700	20	HHT	X	-	1	-	-	-	-	-	-
NiAg/ Inconel 625	700	20	HHT	-	X	1	-	-	-	-	-	-
boiler plate	H II/ H II	400	0,06	HHT	1	-	2	-	-	-	-	-
Inconel 617/ Inconel 617	-	-	-	-	-	-	650	5	HHT	0,38	>1	welded
Stellite 6/ Stellite 6 als Spreitzkelle	-	-	-	-	-	-	25	ca. 2000	He	150	0,25	local welding
St 37/St 37	-	-	-	-	-	-	RT	-	HTR	1 mm/min = 0,038	>1	friction, oxidation, transfer
Hast.X/Hast.X	-	-	-	-	-	-	RT	-	HTR	0,008	>1	friction, oxidation, transfer
WLeg/WLeg	-	-	-	-	-	-	RT	-	HTR	0,050	>1	friction, oxidation, transfer

Fig. 4.15: Metallic material pairings and behaviour under HTR conditions at temperatures below 700 °C

Colmonoy 6 ... 71 Ni; 17 Cr; 4.5 Si; 3.5 Fe; 3.1 B; 1 C

In fretting wear studies /4.57/ typical materials for boiler tubes were tested in a fretting test facility under helium atmosphere. Tubes in tube supports were loaded with a static load of 110 N on the test piece at a vibration frequency of 50 Hz and a vibration amplitude of ± 0.5 mm. Testing at temperatures of up to 600 °C led to pronounced local wear and noticeable transfers of material for all metal pairings, in individual cases even to a poorer result.

Tube	Plate	Temp. °C	Wear depth mm	Assessment
St 35.8	H II	350	80	local
13 Cr Mo 44	13 Cr Mo 44	500	4	wear
H T 9	H T 9	520	220	and
18/8	18/8/2	600	20	Transfer of
Incoloy. 800	Incoloy. 800	600	20	material
Hastelloy. B	H T 9	500	10	
Nimonic. 80 A	Incoloy. 800	600	10	

Fig. 4.16: Fretting tests under helium after /4.57/.

St 35.8 high-temperature carbon steel
H II boiler plate
H T 9 12 % Cr, 1 % Mo steel
18/8 austenitic steel
18/8/2 austenitic steel
Inc. 800 Incoloy 800
Hast. B Hastelloy B
Nim. 80 A Nimonic 80 A

The test results show that for many unprotected metallic materials wear phenomena can already occur under helium atmosphere at low temperatures.

Friction and wear protection for PNP boundary conditions in the temperature range below 850 °C

The necessary surface protection has also been confirmed by General Atomic tests /1.17/ at temperatures of 800 °C and under dry contaminated helium atmosphere.

Austenitic materials such as Alloy 800 and Hastelloy X were rubbed on each other in a test arrangement at a surface pressure of 0.7 N/mm². At the beginning of the friction tests, a friction coefficient of 1.75 was established. This value increased up to 2.5 with increasing friction travel. The influence of the friction rate on the coefficient was insignificant. The surfaces after testing showed plastic deformations beside the locations of friction.

In Japan, various metals and alloys were examined for their behaviour under He atmosphere /4.58/.

Alloy	Material	Hastelloy-X		Incoloy-800		Inconel-601		Inconel-625		Ta	Mo	Nb	W
	°C hrs	800	1000	800	1000	800	1000	800	1000	800	1000	800	1000
Hastelloy X	100	x	x	x	x	0	x	x	x				
	500	x	x	x	x		x	x	x			x	
	1000		x				x		x				
Incoloy 800	100			x	x	x	x	x	x				
	500			x	x	x	x	x	x	x			
	1000				x		x		x				
Inconel 601	100					x	x						
	500					x	x						
	1000						x						
Inconel 625	100							x	x				
	500							x	x				
	1000								x				

X ... bonding, ... weak bonding, 0 ... no bonding

Fig. 4.17: Behaviour of alloys and metals at 800 and 1000 °C under helium atmosphere

It becomes apparent here, too, that material bonding already occurs after 100 h exposure at 800 °C helium temperature.

In the following Figure /4.18/ the results of an exposure with 50 N/mm² area load are shown. With the aid of the tests, three zones can be classified:

- zone with "no adhesion"
- zone with "weak adhesion"
- zone with "strong bonding".

The extrapolation to 100,000 h of operation shows that for the three material pairings

- ... Hastelloy X with Hastelloy X
- ... Incoloy 600 with Incoloy 600
- ◇ ... Incoloy 800 with Hastelloy X

the adhesive forces remain < 50 N below an operating temperature of 690 °C.

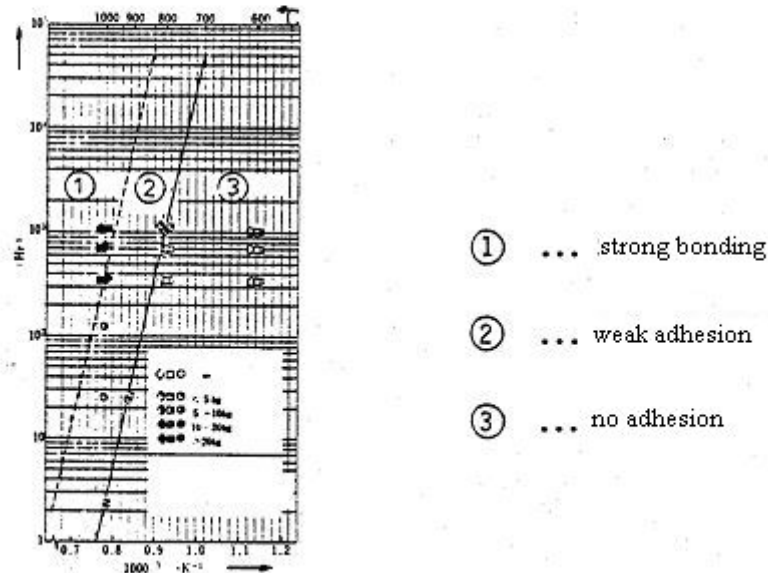


Fig. 4.18: Behaviour of alloys under He atmosphere /4.57/.

A 20 m friction test with the material pairing Hastelloy X - Hastelloy X has shown an increase of the friction coefficient from

$\mu = 0.88$ at 200 °C
through $\mu = 0.63$ at 500 °C
to $\mu = 0.88$ at 800 °C.

In this case, too, a material limiting temperature of 690 °C has been fixed, beyond which a protective coating becomes necessary.

Friction and wear protection for PNP boundary conditions in the temperature range above 850 C

In order to take protective systems for PNP boundary conditions in the high-temperature range for a component life of 140,000 operating hours into consideration, the following conditions must be fulfilled:

Supplemented protective system boundary conditions after /4.59/:

1. melting point or sublimation point or decomposition temperature must be sufficiently far above 1000 °C

2. phase stability, sufficient strength and hardness up to 1000 °C
3. chemical compatibility with HTR helium and component materials; no alloy formation
4. no internal or external diffusion of individual layer constituents
5. sufficient adhesion to the base material especially in temperature-transient operation
6. no or only slight activability of individual layer systems.

Taking the high quality requirements to be met by the protective systems into consideration, applicability with respect to the possible materials is as follows:

Proceeding from the possible metals specified in the periodic table, elements are found which have a melting point above the maximum possible operating temperatures of high-temperature facilities for nuclear process heat generation.

Metals	Melting point °C
chromium	1800
hafnium	2207
iridium	2454
molybdenum	2610
niobium	2500
osmium	2700
platinum	1773
rhodium	3147
rhodium	1966
ruthenium	2500
tantalum	2977
thorium	1827
titanium	1812
vanadium	1720
tungsten	3380
zirconium	1860

Fig. 4.19: Metals with melting points > 600 K above the max. possible operating temperature

Despite a relatively great distance from the melting temperature and operating point, pure metals and metal alloys are not suitable as wear resistance due to their high diffusivity and their relatively ready plasticizability [4.59/ 4.60]. Friction tests performed with rhodium-coated specimens at high temperatures in both air and helium atmosphere confirm this behaviour (test report see Annex). The use of metallic coatings in conventional application ends between 400 and 700 °C, depending on the application boundary conditions.

For metallic material pairings this limit had also been confirmed under helium atmosphere (Figs. 4.15, 4.16, 4.18).

Intermetallic phases

Compounds of a metallic nature are characterized by the fact that they form a specific lattice structure typical of the compound. In contrast to solid solutions, phases can exhibit fairly high hardnesses in conjunction with considerable brittleness. Of a few thousand known intermetallic phases, the following can be deposited as coatings by APS and VPS after /4.46/:

- Ni Al
 - Triballoy
 - Co - Mo - Cr - Si
 - Ni - Mo - Cr - Si
 - Ni Cr AlY M2
 - Ni Cr AlY
 - Co Cr AlY
 - Ni - Co Cr AlY
 - superalloys
- M1= Fe or Co or Ni
 - M2= W; Ta; Hf; Pt; Si; C

According to /12/ further intermetallic phases are specified that exhibit very high heat resistance.

- Cr Be₂; Mo Be₁₂, Ta Be₁₂, Zr Be₁₃.

The melting temperatures range between 1600 and 1800 °C.

NiAl and NiCrAlY layers have been repeatedly used as interlayers (bonding and compensating layer between base material and top coat) in tests after the HRB investigation results from the HHT and PNP project. Exposure tests have demonstrated the general suitability of some compounds for the high-temperature range /4.61/. Diffusion processes have been observed after 3,000 h of application as an interlayer on Inconel 625 at 950 °C /4.62/. Aluminium from the intermetallic interlayer diffused into the substrate material and Mo, Fe and Nb diffused into the Ni Cr AlY. After these relatively short test times, however, the diffusion on both sides did not lead to spalling due to the formation of brittle phases.

Due to the high diffusivity of the metal fractions, a self-welding protection is not to be expected in reducing atmosphere at high temperatures.

Friction and wear tests with Triballoy 700 (50 Ni 15 Cr - 32 Mo - 3 Si) showed /4.61/ fretting and wear phenomena after short friction travels (s = 0.1 m) at a test temperature of 850 °C.

Hard alloys

Hard alloys based on nickel, cobalt and iron partially consist of a metal matrix to which certain amounts of hard materials (borides, carbides and silicides) have been admixed. The hardness of such hard alloys ranges between 20 and 60 HRC at room temperatures.

Test with the alloy of the Ni-CY-B-Si + CY-A1 type under HTR conditions (1,000 °C) showed that a welding of the specimens could in part be prevented /4.58/. However, little significance was attached to this coating as wear protection.

The melting point of the alloy, which is only slightly above the max. operating temperature, and the high diffusivity at high temperatures speak against a suitability as long-time applicable wear protection system.

Hard materials

The group of the hard materials includes solids of high inherent hardness. On the basis of the most important physical properties, these materials can be subdivided into metallic and non-metallic hard materials /4.63/. Metallic hard materials are understood to be binary compounds of the transition metals with carbon, nitrogen, boron and silicon.

Ti;	Zr	Hf;	V;	Nb;	Ta;	Cr;	Mo;
with							
carbon		nitrogen		boron		silicon	
↓		↓		↓		↓	
carbides		nitrides		borides		silicides	
and							
mixed carbides							

and some intermetallic compounds such as W-Co or Mo-Be.

These compounds are characterized by good thermal and electrical conductivity, high melting point, high hardness and high corrosion resistance. As an example of the resistance of hard materials, the tool performance of hard-clad cutting edges should be mentioned. The edges remain sharp even if heated up to red heat /4.64/.

hard material	melting temperature in °C	hard material	melting temperature in °C
TiSi ₂	1540	Mo C	2690
TiB ₂	2980	HfSi ₂	1750
TiC	3140	HfB ₂	3250
Ti N	2950	Hf C	3980
CrSi ₂	1550	HfN	2980
CrB ₂	1960	TaSi ₂	2200

Cr ₃ C ₂	1890	TaB ₂	3100
CrN	decomp.	TaC	3880
ZrSi ₂	1700	TaN	3090
ZrB ₂	3060	WSi ₂	2160
ZrC	3530	W ₂ B ₅	2300
ZrN	2980	WC	2870
NbSi ₂	1950	VSi ₂	1670
NbB ₂	3000	VB ₂	2400
NbC	3480	VC	2830
NbN	2050	VN	2050
MoSi ₂	2030		
Mo ₂ B ₅	2100	TaC + Hf C	4215

Fig. 4.22: Metallic hard materials with high melting temperature /4.49/.

Metallic hard materials can be applied onto the substrate by thermochemical processes, chemical and in part also physical vapour deposition and thermal spraying. The last-mentioned process also provides the possibility of processing mixtures of metallic hard materials /2.41/.

The non-metallic hard materials include ceramic-like layers of compounds of B, C, N and Si as well as other high-melting solid solutions and mixtures with other oxides. The non-metallic hard materials are characterized by high heat and wear resistance. Oxides (oxide ceramics) can also be assigned to this group.

hard material	melting temperature in °C	hard material	melting temperature in °C
Z-SiC	2830	Al ₂ O ₃	2000
B ₄ C	2450	Al ₂ O ₃ + TiO ₂	1950
A ₁₄ C ₃	2200	Cr ₂ O ₃	2200
BN	3000	ZrO ₂ + 5 % CaO	2500
Si ₃ N ₄	1900	ZrSiO ₄	1670
AlN	2400	CeO ₂	2600*
Be ₃ N ₂	2200	NiO	1990
SiB ₃	2750	Mg Al ₂ O ₄	2135
SiB ₆	2000	CaZrO ₃	2350
BNC	3000	HfO ₂	2780

* transition to Ce₂O₃

Fig. 4.23: Non-metallic hard materials /4.46/.

The production of such protective coatings is possible by thermochemical diffusion processes, CVD or in part by PVD and by thermal spraying.

Hard materials are promising material combinations for friction and wear protection in the high-temperature range.

Protective coatings of metal -nonmetal components

Compositions of ceramic and metallic components are called cermets (ceramic + metal).

Ceramic components are: non-metallic hard materials and oxides, silicides.

Metallic components are: heavy metals, metals.

A composite of metal and ceramic material provides impact-resistant overlay layers. In this way, ceramics of mechanical strength for applications at high temperatures are obtained.

Type	Ceramic part	Metallic part
oxides	Al ₂ O ₃ Cr ₂ O ₃ Mg O Si O ₂	Al;Be;Co;Cr Cr-Ni-Fe Cr Al; Be;Co;Mg Zr
carbides	CrC	Ni-Cr
	TiC	Mo;W;Fe;Co
		superalloys
borides	Cr B ₂ Ti B ₂ Zr B ₂	Ni Fe;Ni Co Fe; Ni Co
nitrides	Ti N	Ni
silicides	Mo Si ₂	Ni; Co, Cr; Pt

Fig. 4.24: Examples of some cermets /4.63/

Multicomponents and multilayers

A composition of several components in one layer is intended to increase the temperature resistance and reliability of layer systems. Additions stabilize lattice structures, so that they do not undergo any transformation even at high temperatures or a volume extraction that may lead, for example, to spalling.

The application of interlayers for friction and wear protection has the purpose of

- producing an improved bond coat
- separating top coat and substrate by a dense bottom layer (corrosion protection)
- adaptation to the different thermal expansion coefficients.

Two-stage (duplex) coatings and multilayer coatings as well as graded coatings with stepless transitions of individual layers are possible.

Promising layers

Due to the not very regular crystal lattice structure of ceramic coating materials /4.63/ and the relatively low diffusibility of individual elements of the lattice /4.59/, the chemical resistance and strength at high temperatures, the ceramic-like materials fulfil important prerequisites for application as friction and wear protection. Improvements in thermal cycling behaviour and strength under impact stress can be achieved by metallic fractions.

Layer systems tested under HTR conditions

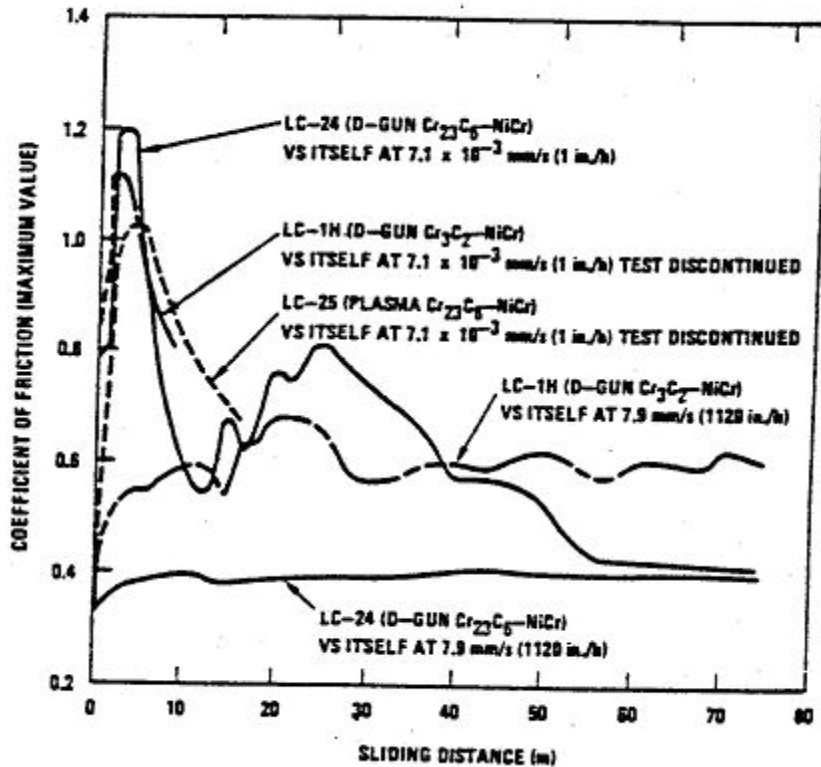
Carbide layer systems

The General Atomic Company concerned itself with carbide protective layers and presented the results on sliding and wear coatings in 1979 /1.12/. Cr_{23}C_6 -NiCr and Cr_3C_2 -NiCr plasma and D-gun sprayed coatings were applied onto Hastelloy X material.

Specimens placed on top of each other were dynamically tested in a test apparatus under simulated HTGR atmosphere (He with 200 μatm H_2 ; 20 μatm CH_4 ; 10 μatm Co and 1 μatm H_2O) at 816 °C at a surface pressure of 3.45 N/mm² and a friction rate of 7.1×10^{-3} or 7.9 mm/s.

The following results were obtained:

1. Coatings with 75 or 80 % chromium carbide provide excellent wear protection under HTGR conditions.
2. Cr_{23}C_6 -NiCr and Cr_3C_2 -NiCr show similar friction and wear behaviour.
3. At the beginning of the tests, the friction coefficient of the LC-1H, LC 24 and LC 25 layers is relatively high (in the range of $V_s = 7.1 \times 10^{-3}$ mm/s, $\mu_{\text{max}} = 1.2$). With increasing friction travel, the friction coefficient decreases and assumes an almost constant value (see Figure 4.25 below).
4. The test results show that in the coatings with a hardness of 650 - 900 VHN 30 flatters (flow-induced vibrations) do not cause any significant damage.



0

Fig. 4.25: Friction coefficient as a function of sliding distance /1.12/.

In further studies C.C. Li /1.12/ investigated the adhesive strength of plasma- and D-gun-sprayed layers. The simulated high-temperature reactor conditions were increased up to temperatures of 982 °C. The substrate material was Hastelloy X and Alloy 800 H.

The following conclusions are drawn:

1. Plasma-sprayed layers chip off faster than D-gun coatings.
2. $\text{Cr}_{23}\text{C}_6\text{-(NiCr)}$ layers are more resistant to chipping than *1 $\text{Cr}_3\text{C}_2\text{-(NiCr)}$ layers.
3. Layers on the Alloy 800 H material chip off earlier than layers on Hastelloy X.

Figure 4.26 a+b illustrates the behaviour of sprayed-on layers. After 20,000 h only the D-gun $\text{Cr}_{23}\text{C}_6\text{-NiCr}$ layer has remained undamaged in all temperature ranges. If the performance of the D-gun- Cr_3C_2 layer were extrapolated to 140,000 h of exposure, the maximum possible operating temperature would remain limited to 750 °C for the Alloy 800 H material.

However, the dependence of the substrate material is unmistakable here. The fact that even the plasma-sprayed layers have not failed in connection with Hastelloy X material is explained by the higher oxidation resistance.

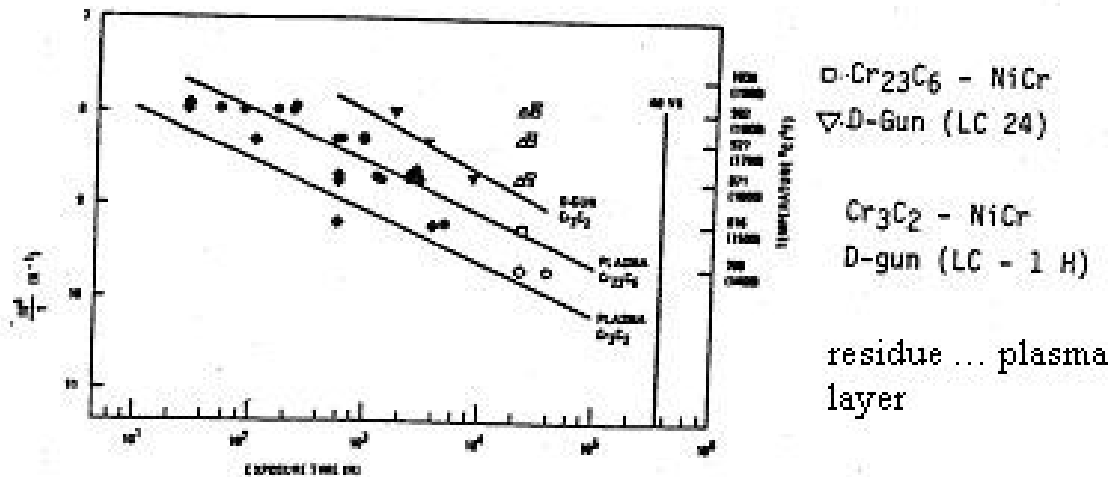


Diagram a, substrate material Alloy 800 h

One reason: phase change of $\text{Cr}_3\text{C}_2 \sim \text{Cr}_7\text{C}_3 \sim \text{Cr}_{23}\text{C}_6$ during high-temperature exposure. The phase change involves a volume contraction.

- open symbols tests continue
- closed symbols layer chipped off

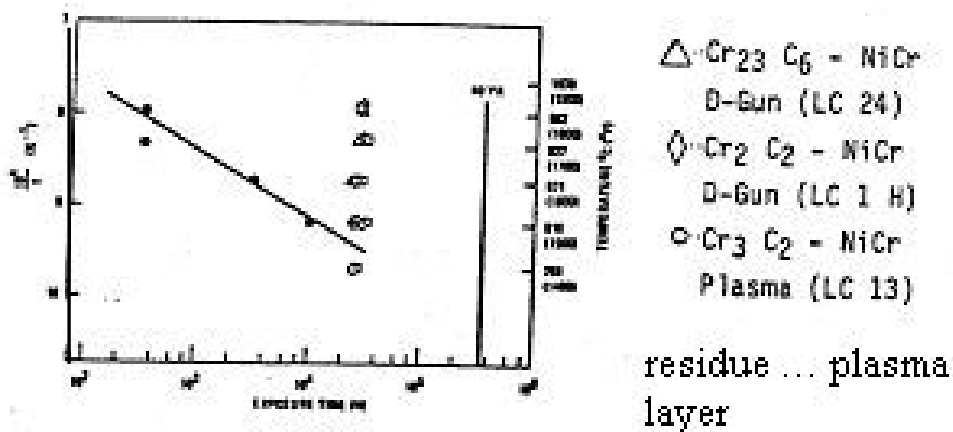


Diagram b, substrate material Hastelloy X

Fig. 4.26: Chipping performance of chromium-carbide layers [1.12].

Since 1978 HRB has also selected candidate layer systems for high-temperature application and tested them experimentally by subjecting specimens to

- friction tests
- static welding tests
- thermal shock tests and thermal cycling
- exposure tests.

The selection of the systems coming into consideration was made via selection phase, data backup phase and demonstration phase. Some characteristic results are mentioned.

The following carbidic layer systems were placed on a short list and examined /4.61/:

- $\text{Cr}_3\text{C}_2 + (\text{Cr}_3\text{C}_2 + \text{Ni Cr})$
 - $\text{Cr}_3\text{C}_2 + \text{NiCr}$
 - $\text{Cr}_{23}\text{C}_6 + (\text{Ni Cr AlY})$
 - $\text{Cr}_{23}\text{C}_6 + \text{Ni Cr} \dots$
 - $\text{Cr}_{23}\text{C}_6 + \text{NiCr} + (\text{NiCr})$ or (Ni CrY)
 - $\text{Cr}_{23}\text{C}_6 / \text{Cr}_{23}\text{C}_6 + \text{NiCr} + (\text{NiCr}) \dots$ duplex coating
 - NbC
 - NbC + Ni
 - NbC + (NbC + Ni Cr)duplex 1 and triplex coating
 - TiC + (Ni₃Ti)
 - TiC + (TiC + TiN + Ni₃Ti); triplex 1 coating
 - TiC + TiN
-
- $\text{Mo}_2\text{C} + \text{Mo}$
-
- W_2C

The layers were applied by thermal spraying and chemical vapour deposition. The test specimens were tested against similar or uncoated high-temperature materials under simulated HHT or PNP atmosphere.

According to /4.56/ /4.59/ /4.60/ /4.61/ the tests yielded the following results:

() ... bottom layer, bond coat
 1 ... with different interlayers

Chromium carbide layers

- Cr_3C_2 layers:

Type	Layer	Friction coefficient μ	Surface pressure N/mm^2	Temp. $^{\circ}\text{C}$	Time/Travel h m	Assessment pos.. / .neg.	
friction stat.	Cr_3C_2 duplex	0.98	5	950	5	X	
	$\text{Cr}_3\text{C}_2 + \text{NiCr}$	0.5 - 0.8	1 - 5	700	5	X	
	$\text{Cr}_3\text{C}_2 + \text{NiCr}$	0.5	20	700	20	X	
	Cr_3C_2 duplex	-	10	850	$3 \cdot 10^3$	X	

Experience from CO_2 -cooled reactors showed that the Cr_3C_2 layer already developed into Cr_{23}C_6 layers after relatively short application times, so that Cr_{23}C_6 layer systems were used instead of Cr_3C_2 layers.

The D-gun-sprayed $\text{Cr}_3\text{C}_2/18\%$ NiCr cermet layer was limited to operating temperatures of 700°C on account of the results from static and friction tests /4.64/.

- Cr_{23}C_6 layers

Type	Layer	Friction coefficient μ	Surface pressure N/mm^2	Temp. $^{\circ}\text{C}$	Time/Travel h m	Assessment Pos. / neg.	
friction	cermet	> 1	5	950	9		X
	cermet	> 1	3.4	900	0.09		X
	duplex	0.7	5	950	20	X	
	cermet	0.83	5	850	20	X	
	cermet	> 1	20	850	1-2		X
	duplex	0.8	20	850	20	X	
	cermet	> 1	5	700	1.8		X
stat.	cermet	-	7	900	2-103	X	
	duplex	-	10	950	3-103	X	
	duplex	-	0.8	1050	100		X
thermal shock	cermet	-	-	$\downarrow \uparrow$	-	X	
	duplex	-	-	$\downarrow \uparrow$	-	X	
long	cermet			950	6-103	X	
	duplex			850	2-104	X	
	duplex			950	6.5-10		X
	duplex			950	9-103	X	

The Cr_{23}C_6 layers with NiCr interlayers produced according to the D-gun technique can be used up to 850°C on account of the selection tests /4.64/; in long-time 950°C friction tests (> 5 m) the friction coefficient rapidly increased to $\mu > 1$, which is attributable to partial welding of the metallic matrix material /4.59/.

Niobium-carbide layers

Type	Layer	Friction coefficient	Surface pressure N/mm ²	Temp. °C	Time/Travel h m	Assessment pos. / neg.	
friction	NbC-Triplex-(NbC-NiCr)	spalling	5	950	approx. 5		X
	NbC-duplex-(NbC-NiCr)	0.75	5	950	5	X	
	NbC	spalling	5	950	5		X
	NbC	0.78	20	850	5.3	X	
stat.	NbC-triplex (NbC-NiCr)	spalling	0.8	1050	100		X
	NbC + Ni	spalling	1	1050	100		X
thermal shock	niobium carbide	-	-	↓↑	2 cyc. 1.		X
long	niobium carbide	-	-	950	3*10 ³	X	

The niobium-carbide samples sprayed according to the APS process show above all failure in layer bonding. Spalling already occurred after relatively short times in static welding tests and above all in thermal shock tests.

Thermal shock behaviour was improved by parameter variations. Some friction tests yielded positive results. In the selection phase it was found that a reliable production of a certain layer quality is not ensured /4.59/. Although long-time behaviour was found to be positive up to 3000 h /4.60/, the thermal stability of the layer is said to be too low /4.64/.

Titanium carbide layers

In the Swiss studies on anti-wear layers /4.6/, among other things, CVD-TiC layers were also tested with respect to the friction coefficient in helium atmosphere at high temperatures.

It becomes apparent in Fig. 4.27 that the friction coefficient is remarkably low with rising temperature. Above 600 °C, however, the coefficient increases, which may be attributable to softening of the TiC layer.

friction coefficient μ
TiC versus TiC

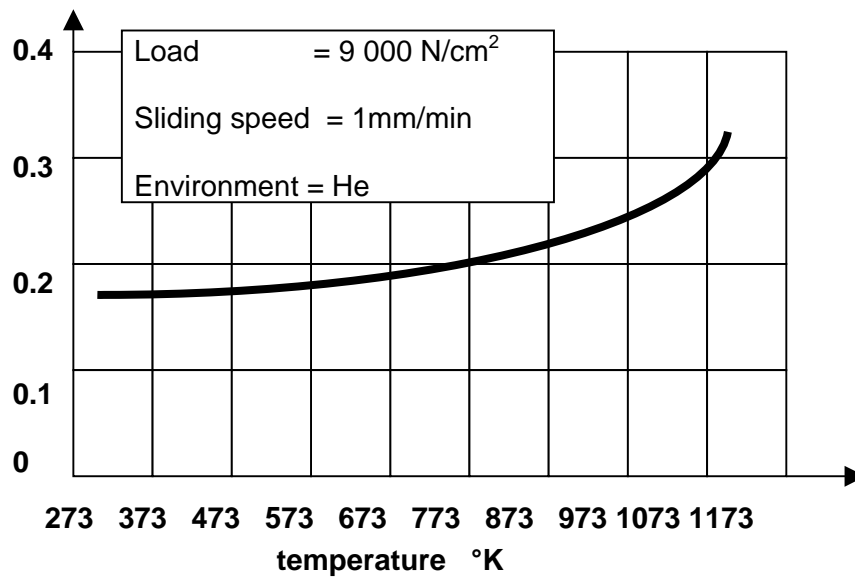


Fig. 4.27: Friction behaviour of TiC/TiC under helium after /4.6/.

The testing of titanium carbide layers at HRB yielded the following results:

Type	Layer	Friction coefficient μ	Surface pressure N/mm ²	Temp. °C	Time/Travel h m	Assessment pos. / neg	
friction	TiC-triplex-(TiC-TiN-Ni Ti)	spalling	5	950	20		X
	Ti -triplex-(TiC-TiN-Ni ₃ Ti)	spalling 1.	5	950	5		X
	TiC-triplex-(TiC-TiN-Ni ₃ Ti)	0.8-1	5	950	1 - 3		X
	TiC (Ni ₃ Ti)	0.3-0.6	5	950	5	X	
	TiC (Ni ₃ Ti)	0.5	20	850	5	X	
	Ti C + Ti N	>1	5	850	~1		X
stat.	TiC-triplex (TiC-TiN Ni Ti)	-	0.8	1050	100	X	
	TiC (Ni ₃ Ti)	-	0.8	1050	100	X	
	TiC + TiN	-	0.8	1050	100	X	
long	TiC triplex (TiC-TiN Ni Ti)	-	-	950	3*10 ³		X
	TiC (Ni ₃ Ti)	-	-	950	3*10 ³		X

The protective layers applied according to the CVD process did not prove efficient in friction tests. Welding protection is given for short periods of time under static load.

The negative results of long-time exposures showed that the titanium carbide layers turned out to be chemically and thermally unstable /4.59/. The low oxygen partial pressure ensured that the top coat fractions transformed into soft Ti_2O_3 after prolonged exposure at 950 °C under HTR atmosphere.

Mo₂ + Mo layer and W₂C layer

Type	Layer	Friction coefficient μ	Surface pressure N/mm ²	Temp. °C	Time/Travel h m	Assessment pos. / neg.	
friction	Mo ₂ C + Mo	1.5	5	850	0.25		X
stat.	Mo ₂ C + Mo	-	10	1050	100		X
friction	W ₂ C	1.2	10	850	0.6		X

This behaviour precludes a suitability.

Nitridic layer systems

The following nitride layers were tested in the investigations by HRB:

- TiN
- TiN (Ni₃Ti)

Type	Layer	Friction coefficient μ	Surface pressure N/mm ²	Temp. °C	Time/Travel h m	Assessment pos. / neg.	
friction	TiN	>1	5	950	3		X
	TiN	1.5	10	850	0.2		X
	TiN (Ni ₃ Ti)	>1	5	950	2.19		X
stat.	TiN (Ni ₃ Ti)		0.8	1050	100	X	
	TiN (Ni ₃ Ti)		5	950	3•10 ³	X	
long	TiN			950	3•10 ³		X (1)
	TiN (Ni ₃ Ti)			950	3•10 ³	X	

(1) ... coating partially oxidized forming Ti_2O_3

The layers applied by CVD are not suitable for abrasive wear protection in the high-temperature range. The interlayer (intermetallic phase Ni₃Ti) showed a diffusion-inhibiting effect. According to investigations by Koichi Murasa /4.58/ it is possible to produce good sliding properties on the substrate material by the use of BN for limited applications.

Boridic layer systems

HRB test results on CVD layer

- Static welding tests

Type	Layer	Friction coefficient μ	Surface pressure N/mm^2	Temp. $^{\circ}\text{C}$	Time/Travel h m	Assessment pos. / neg.	
stat.	Ti B ₂ (Mo)	-	0.8	1050	10		X
thermal shock	Ti B ₂ (Mo)	-	-		-		X

The titanium boride protective system did not lead to a suitable surface protection.

W.W. Ssytschew /4.65/ carried out investigations concerning the temperature influence on friction and wear of the boride coats deposited on molybdenum. A 40 to 50 μm thick molybdenum-boride layer was deposited on molybdenum specimens for 3 - 4 hours at a temperature of 1000 $^{\circ}\text{C}$ using boride powder. The layer system

-MoB (Mo₂B₅) was obtained.

Friction and wear testing was performed under helium in a high-temperature facility. The following results were obtained.

- Friction test

$\mu = 0.3$, $F = 1 - 10/\text{Nmm}^2$, $T = 900^{\circ}\text{C}$, $s = \text{low}$ \longrightarrow result negative.

In the case of very short friction travel

- cracks in the coating
- tearing and slipping from the boride layer

were observed.

Oxidic layers

In Japanese investigations ZrO₂ and Al₂O₃ were selected for further studies from various ceramic coatings /4.58/. The top coats applied onto 80 Ni 20 Cr substrate showed after evaluation of the tests that the zirconia coating is superior to the alumina coating.

Temp. $^{\circ}\text{C}$ cycled flat specimen	Temp. cycled cylinder		Exposure in He atmosphere	Friction test	Long-time 800 $^{\circ}\text{C}$ He atmosphere
0	0	ZrO ₂ plasma	0	0	0
X		Al ₂ O ₃ plasma	0	X	

0 ... without defects

X ... cracks and detachment

Fig. 4.28: Comparative study of oxide ceramics /4.58/.

The influence on the friction coefficient by a ZrO_2 coating in the 20-m friction test is shown in Fig. 4.29.

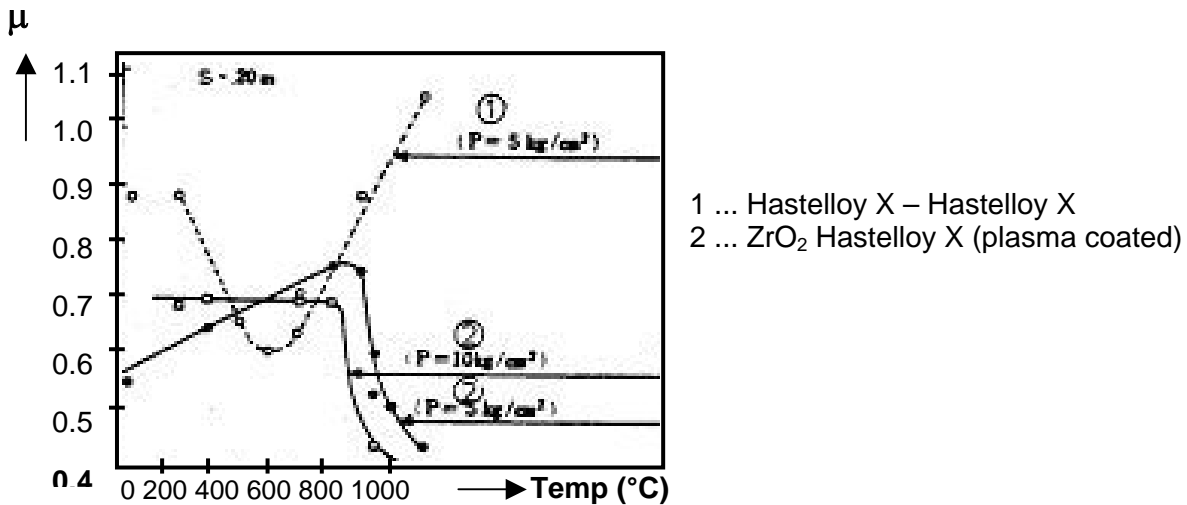


Fig. 4.29: Relationship between friction coefficient and temperature in helium gas $s = 20 \text{ mm}$) after /4.58/.

The CaO -stabilized ZrO_2 layer applied by the plasma technique is referred to as a very good and the Y_2O_3 -stabilized ZrO_2 layer as a good (investigations not yet completed) countermeasure.

For the sliding connections between graphite and metal components, according to /4.58/, a coating against "baking" is not necessary in the temperature range below 1020 $^{\circ}\text{C}$ of the multi-purpose high-temperature gas reactor. It is recommended, however, that the ZrO_2 layer should be used as a barrier to carburization.

A large number of oxidic layers were investigated by HRB. The protective layers were applied by thermal spraying in air and at low pressure in a vacuum chamber.

The following layer systems, in which the individual fractions were still varied in different mixing ratios, were tested:

- Mo_2O_3
- Al_2O_3
- $\text{Al}_2\text{O}_3 + \text{ZrO}_2$
- $\text{Al}_2\text{O}_3 + \text{Y}_2\text{O}_3$
- $\text{Al}_2\text{O}_3 + \text{TiO}_2 (\text{NiCr})$
- $\text{Al}_2\text{O}_3 + \text{MgO}$
- Cr_2O_3
- $\text{CrO}_2 + \text{Al}_2\text{O}_3$
- $\text{CaO} + \text{ZrO}_2$
- MgZrO_3
- $\text{MgO} + \text{ZrO}_2$
- ZrO_2 cermet ($\text{ZrO}_2 + \text{Y}_2\text{O}_3 + \text{NiCrAlY}$)
- $\text{ZrO}_2 + \text{NiO} - \text{ZrO}_2 + \text{Cr}_2\text{O}_3$
(NiCr)
- or ($\text{ZrO}_2 + \text{CaO} + \text{NiO}$)

- $ZrO_2 + Y_2O_3 - ZrO_2 + Y_2O_3$ (Ni Cr AlY) also graded coating; electron-beam-treated (Ni Cr AlY + Al_2O_3)
- $ZrO_2 + Y_2O_3 / Yb_2O_3$ (Ni Cr AlY)
- $ZrO_2 + CaO$ (Ni Cr)
- $ZrO_2 + CaO + NiO$
- $ZrO_2 + CaO + NiAl(Ni Al)$ or (Ni Cr)
- $ZrO_2 + NiAl$ (Ni Cr)
- $ZrO_2 + ZrSi$
- $ZrSiO_4$

Based on available layer systems of thermal protection against high temperatures, oxidic layer systems were selected and tested as friction and wear protection for HTR requirements. Some layer systems had to be changed in their parameters for special PNP requirements. The characteristic results of the oxidic coatings are as follows:

Type	Layer	Friction coefficient μ	Surface pressure N/mm^2	Temp. $^{\circ}C$	Time/Travel h m	Assessment pos. / neg.	
stat.	Mo_2O_3 pure	-	10	850	100		X
friction	Al_2O_3 pure	abrasion	5	950	0.68		X
	$Al_2O_3 + TiO_2$	spalled	5	950	-		X
	$Al_2O_3 + TiO_2$ (Ni Cr)	abrasion	5	950	-		X
stat.	Al_2O_3 pure	-	0.8	1050	100	X	
	Al_2O_3 pure	-	1	950	3-103	X	
	Al_2O_3 rein	-	10	850	100	X	
	$Al_2O_3 + TiO_2$	-	0.8	1050	3-103	X	
	$Al_2O_3 + MgO$	-	0.8	1050	100		X
long	Al_2O_3 - pure	-	-	950	3•103		X
	Al_2O_3 - Y_2O_3	-	-	950	3•103	X	
	Al_2O_3 - ZrO_2	-	-	950	6•103		X
thermal shock	Al_2O_3 (NiCr)	-	-	↓ ↑	100 cyc.	X	
friction	Cr_2O_3 pure	spalled	0.8	1050	100		X
	Cr_2O_3 pure	spalled	10	950	100		X
	$Cr_2O_3 + Al_2O_3$	spalled	10	850	5		X
stat.	$CaO + ZrO_2$	spalled	0.8	1050	100		X
friction	$MgZrO_3$	- 0.7	5	950	20	X	
	$MgO + ZrO_2$	- 0.58	5	950	5	X	
	$MgO + ZrO_2$	- 0.6	5	950	20	X	
	$MgO + ZrO_2$	- 0.74	20	850	20	x	
stat.	$MgO + ZrO_2$	-	0.8	1050	100	X	
	$MgO + ZrO_2$	-	5	950	10-103		
	$MgO ZrO_3$	-		850	1-104	X	X
thermal shock	$Mg ZrO_3$	-	-		30 cyc.	(X)	

Type	Layer	Friction coefficient μ	Surface pressure N/mm^2	Temp. $^{\circ}\text{C}$	Time/Travel h m	Assessment pos. / neg.	
friction	ZrO ₂ cermet (ZrO ₂ +Y ₂ O ₃ + NiCrAlY)	abrasion	20	850	0.5		X
	ZrO ₂ + NiO	- 0.9	5	950	20	X	
	ZrO ₂ + Cr ₂ O ₃ (Ni Cr)	spalled	5	950	3.3		X
	ZrO ₂ + Y ₂ O ₃	- 0.71	5	950	5	X	
	ZrO ₂ + Y ₂ O ₃ (NiCrAlY~ Z ₂ + Y ₂ O ₃)	- 0.8	5	950	20	X	X
	(Ni AlY) ZrO ₂ + Y ₂ O ₃ (NiCrAlY + Al ₂ O ₃)	- 0.54	20	850	20.2	X	
	ZrO ₂ + Y ₂ O ₃ (graded coating NiAlY)	abrasion	20	850	1.4		X
	ZrO ₂ + Y ₂ O ₃ (graded coating Ni AlY)	0.58	5	950	20.2	X	
	ZrO ₂ + Y ₂ O ₃ (graded coating Ni AlY)	abrasion	20	850	20.2		X
	ZrO ₂ + Y ₂ O ₃ (Ni Cr AlY)	0.5	5	950	100.7	X	
	ZrO ₂ + Y ₂ O ₃ Yb ₂ O ₃ (NiCrAlY)	abrasion	5	950	58		X
	ZrO ₂ + Ca O (Ni Cr)	- 0.77	5	950	5	X	
	ZrO ₂ + Ca O + NiO	0.86	5	950	5	X	
	ZrO ₂ + CaO + Ni AL	0.88	5	950	20	X	
	ZrO ₂ + Ni AL (Ni Cr)	0.83	5	950	5	X	
	ZrO ₂ + ZrSi		5	950	0.3		X
	ZrSi O ₄	abrasion	10	950	1.2		X

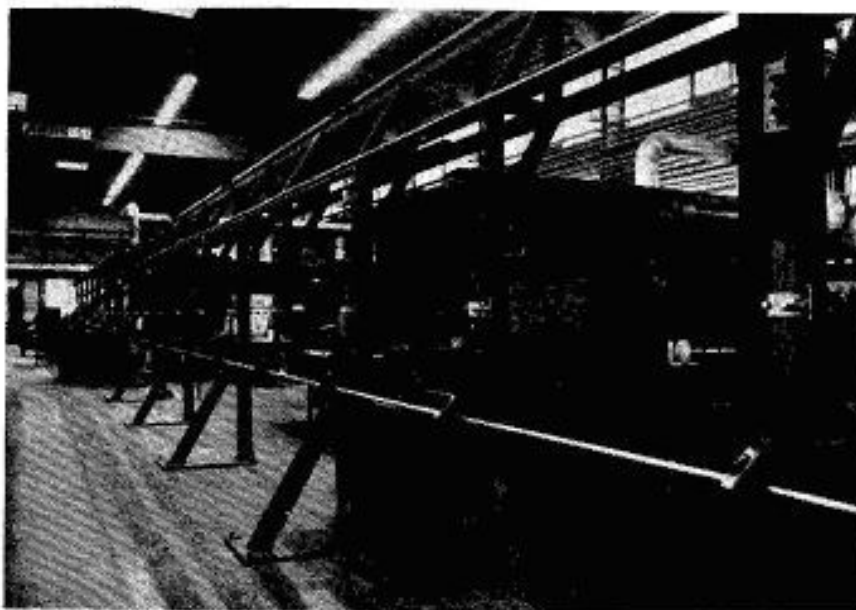
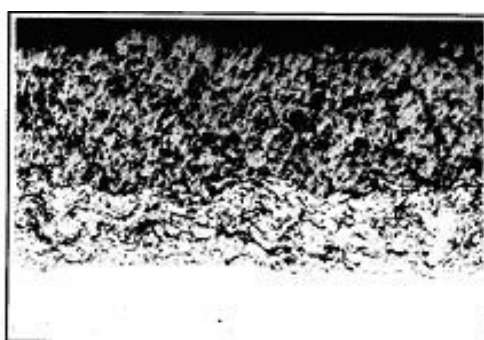


Fig 4: Coating facility for zirconia layers on approx. 18 m long heat exchanger tubes (shop photograph from BERNEX GmbH)



top coat
bond coat
200 : 1
etched, V2A pickle
Fig 5: Zirconia layer in
the as-sprayed
condition



Transition bond coat -
base material (fluid
limit due to diffusion

Figure 6: Zirconia layer
after annealing

Fig 5: Zirconia layer in the as-sprayed condition

Fig 6: Zirconia layer after annealing

Type	Layer	Friction coefficient μ	Surface pressure N/mm^2	Temp. $^{\circ}\text{C}$	Time/Travel h m	Assessment pos. / neg.	
stat.	ZrO ₂ + Cr ₂ O ₃ (Ni Cr) or (ZrO + CaO + Ni O)	spalled	0.8	1050	100		X
	ZrO ₂ + Y ₂ O ₃	-	0.8	1050	100	X	
	ZrO ₂ + Y ₂ O	-	0.8	1050	100	X	
	(Ni Cr AlY~ ZrO ₂ + Y ₂ O	-	5	950	9*10 ³	X	
	(Ni Cr AlY1 ZrO ₂ + Ca O	spalled	1	950	3* 10 ³		X
	ZrO ₂ + Ca O + Ni Al	-	1	950	3*10 ³	X	
long thermal shock	ZrO ₂ Y ₂ O ₃ (Ni Cr AlY)	-	-	950	6*10 ³	X	
	ZrO ₂ Y ₂ O ₃ (graded coat.) Ni Cr AlY)	-	-	950	6*10 ³	X	
	ZrO ₂ Y ₂ O ₃ (Ni Cr AlY)	-	-	950	1.2.10*10 ³	X	
	ZrO ₂ (Ni Cr)	-	-		300 cycles	X	
	ZrO ₂ + Cr ₂ O ₃ (Ni Cr)	-	-		300 cycles	X	
	ZrO ₂ + Y ₂ O (Ni Cr AlY~	-	-		300 cycles	X	

The Y₂O₃-stabilized ZrO₂ with a bond coat of NiCrAlY produced by APS or VPS fulfils the requirements for friction and wear in the high-temperature range.

Surface finishes referred to as friction and wear protection under the PNP project

According to the then state of the art

- metallic friction and wear layers up to max. 600 °C
- carbide friction and wear layers up to max. 850 °C

- oxidic friction and wear layers up to max. 950 °C

were suitable for high-temperature conditions under PNP atmosphere.

coating system	coating method	Max temp in HTR helium				
		200	400	600	800	1000 °C
Colmonoy 6	APS					
Triballoy 700	D-Gun					
Chromium carbide cermet	D-Gun					
Chromium carbide duplex	D-Gun					
Zirkonoxid duplex	APS					
	VPS					

Fig. 4.30: Suitable friction and wear protection layers in PNP helium atmosphere

Data in support of the high-temperature coatings as per 1986 are to be taken from Fig. 4.31.

Layer	Test temperature in °C and type of load	Time / Travel h m	Assessment
Zr ₂ O ₃ + Y ₂ O ₃ (NiCrAlY)	850 static load	19 - 22000	without damage
	950 static load	19 - 25000	without damage
	950 loadless exposure	28000	without damage
	950 friction test	100 m	friction values not increased

Fig. 4.31: Backup status of the zirconia duplex layer in PNP helium atmosphere

The exposure and friction test results of the zirconia duplex layers indicate the applicability of this layer system [4.66]. However, an extrapolation of the samples after 30,000 h exposure to the planned operating life of the layer was not made.

The influence of component geometry on layer performance – deviation from flat specimens to cylinder geometry – did not lead to any inadmissible change in performance.

A further backup of the chromium carbide duplex layer towards longer exposure times and friction travels was not made because the project was discontinued.

A long-term backup under PNP boundary conditions for layers referred to as being suitable up to 700 °C was not made.

5. Requirements to be Met by the Wear Protection System for PNP Components

In a PNP plant, problems of friction and wear are encountered on different components both on the

- primary gas side and on the
- secondary gas side

in the temperature range from 200 to 1000 °C.

This is caused, on the one hand, by different component elongations due to

- temperature exposure of thin-walled and thick-walled components
- dissimilar component materials
- temperature changes due to given plant operation.

Another reason is that the fulfilment of functions in pipes with shut-off elements must be ensured.

In this connection, friction welding in the closed position of the fitting must be prevented.

In addition to the friction loads caused by thermal expansion and contraction, movements are generated by coolant flows or pump vibrations. This fretting motion sequence must be taken into account in the requirements.

Although a summation of thermally induced sliding motions corresponding to plant operation (load cycles) is possible for individual component parts, however, the influence on fretting behaviour can only be estimated.

In investigations concerning the performance of heat exchangers subjected to fretting wear /5.1/ it was found that there are dependences on

- material hardening
- clearance between support and tube
- amplitude and frequency of vibration and
- reaction forces (tube support).

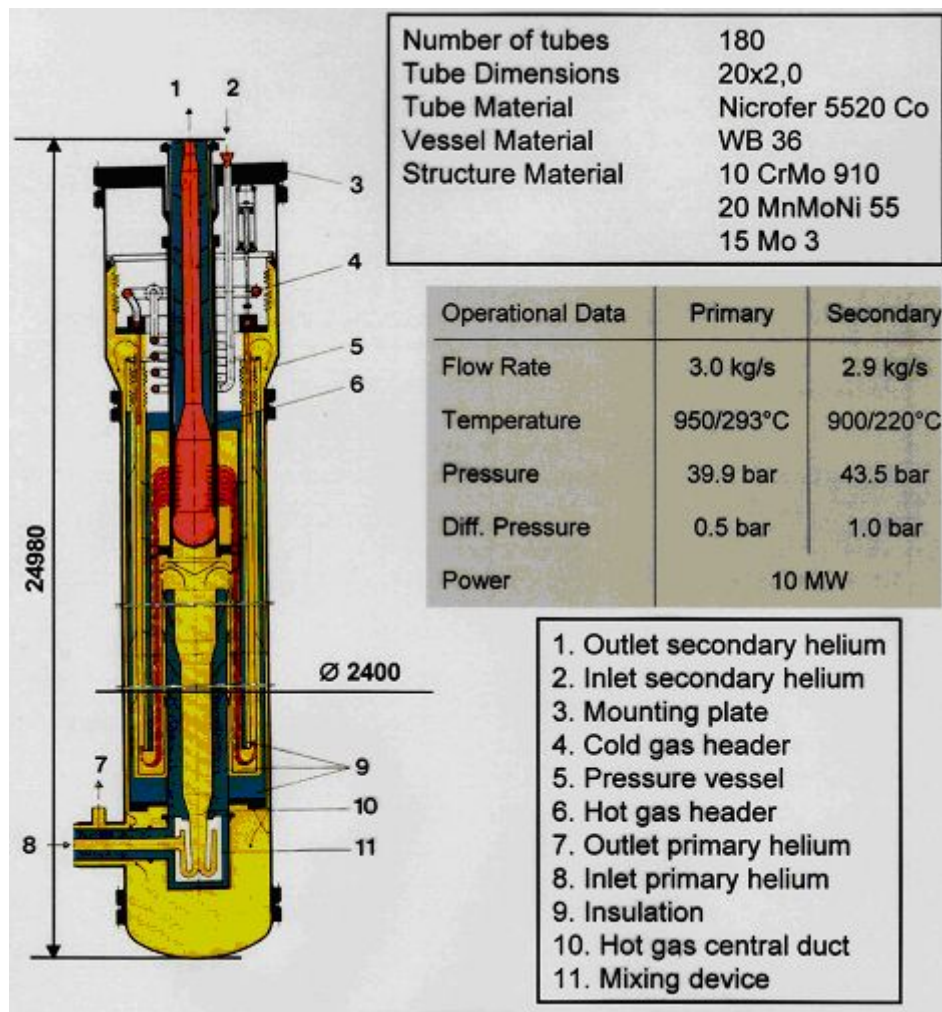
The surrounding atmosphere and the high temperatures certainly also influence the performance.

The reactor helium with its impurities has primarily a reducing effect. This affects or prevents the formation of oxide scales normally acting as a diffusion barrier and thus welding protection on the base material.

Unless a component can be designed so that damage due to friction and wear processes remains without negative consequences, it is necessary to selectively apply layers to achieve a protective effect.

5.1 Intermediate Heat Exchanger

In the following, the exposure to friction and wear of the tribopairing of tube and tube support caused by plant operation in the URKO-IHX (U-tube intermediate heat exchanger) will be dealt with.



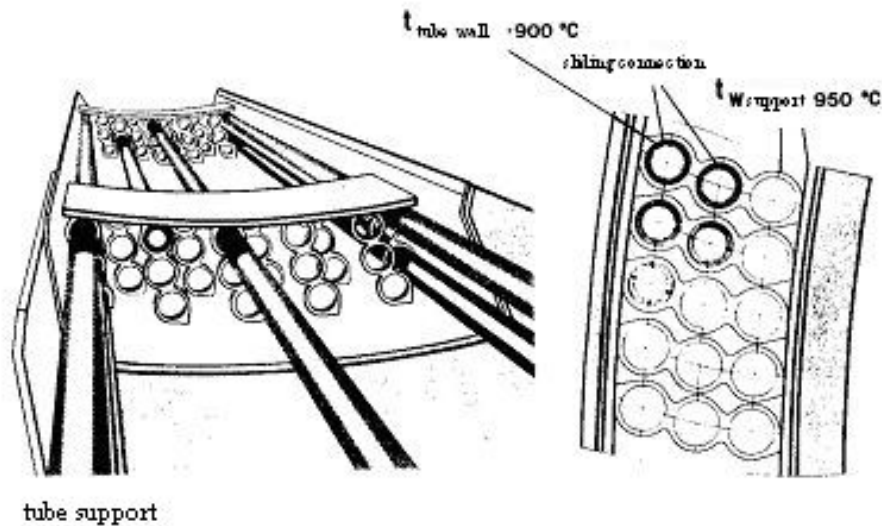
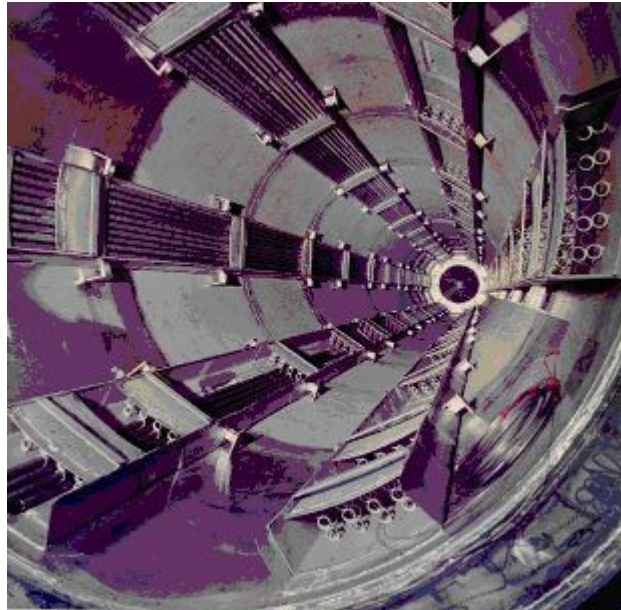


Fig 3: Tubes with tube supports in the duct

The assumed operating conditions and collective loads are taken from the planning sheets of PNP 500 /5.2/ and PNP Module with SGC /5.3/.

The reaction forces exerted by the tube on the support are caused by the tube displacements between "cold and hot branch" = $U_{diff.} - F_{x^*}$ with $F_{x^*} = 54.28 \text{ N}$ /5.4/.

The relative displacements in normal operation are taken from the finite-element calculations of the URKO /5.5 /5.6/. The numbers of events of the individual load histograms are combined so that a conservative statement on the friction travel between tube and support is obtained.

F_{x^*} ... reaction force due to unit displacement

Operating condition / collective load	Total number of events		Reaction force Fx N	Travel mm	Total friction m	
	PNP 500	Module (HTR 100)			PNP 500	Module (HTR 100)
Normal operation • cold start • complete cooling • warm start • normal shutdown • emergency shutdown	254			10.05	2.6	
or						
• power cold start • transition power to steam operation • running up from steam operation • transition power		492				5.0
control fluctuation	105	104		0.72	72	7.2
abnormal operation	28	136		15 (2)	0.4	2.0
accidents or	44			15 (2)	0.66	
emergencies and failures		42		15 (2)		0.63
Total					75.6	14.8

(1) 100 % load Fx = 175 N; complete cooling = Fx = 192 N

control fluctuation Fx = 208 N

(2) conservative estimate

Fig. 5.1: Friction travel loads URKO He/He intermediate heat exchanger

Valuation of total friction travels

The friction travels shown here are maximum friction travels occurring in the hot/cold branch deflection area. The operating temperature is here approx. 680 °C.

In the temperature range from 850 to 950 °C the relative displacement is about 1/3 as much.

	Temp.	Integral friction travel	
	°C	PNP 500	Module HTR (100)
friction location	> 850 °C	25 m	5 m
friction location	< 850 °C	76 m	15 m

Fig. 5.2: Thermally induced sliding motions

In addition to the thermally induced sliding motions, relative motions occur between tube and support due to vibration.

Elongations that occur have been determined in measurements on the URKO flow test model /5.7/.

At a frequency of 500 Hz and a flow rate of $w = 50$ m the maximum elongation of the tubes was determined at the frequency of 120 Hz.

Loads on the clamping of tube and support depend on damping factors such as

aerodynamic damping (surrounding gas)
material damping
Coulomb damping (dry friction).

The movements that occur between tube and support are small and constantly change their direction. The bending vibrations constantly cause angular and transverse motions. Integral friction travel load due to thermally induced sliding motion plus stressing by fretting describe the load system of tube and support.

A detailed verification of surface protection is of particular significance here, since a failure of protection may lead to a failure of the heat-exchanging component due to the thin walls of the tubes.

Further locations in the intermediate heat exchanger of straight-tube or helical design (HELIX) need to be protected against friction and wear, since a coating failure will essentially impair the life of the component.

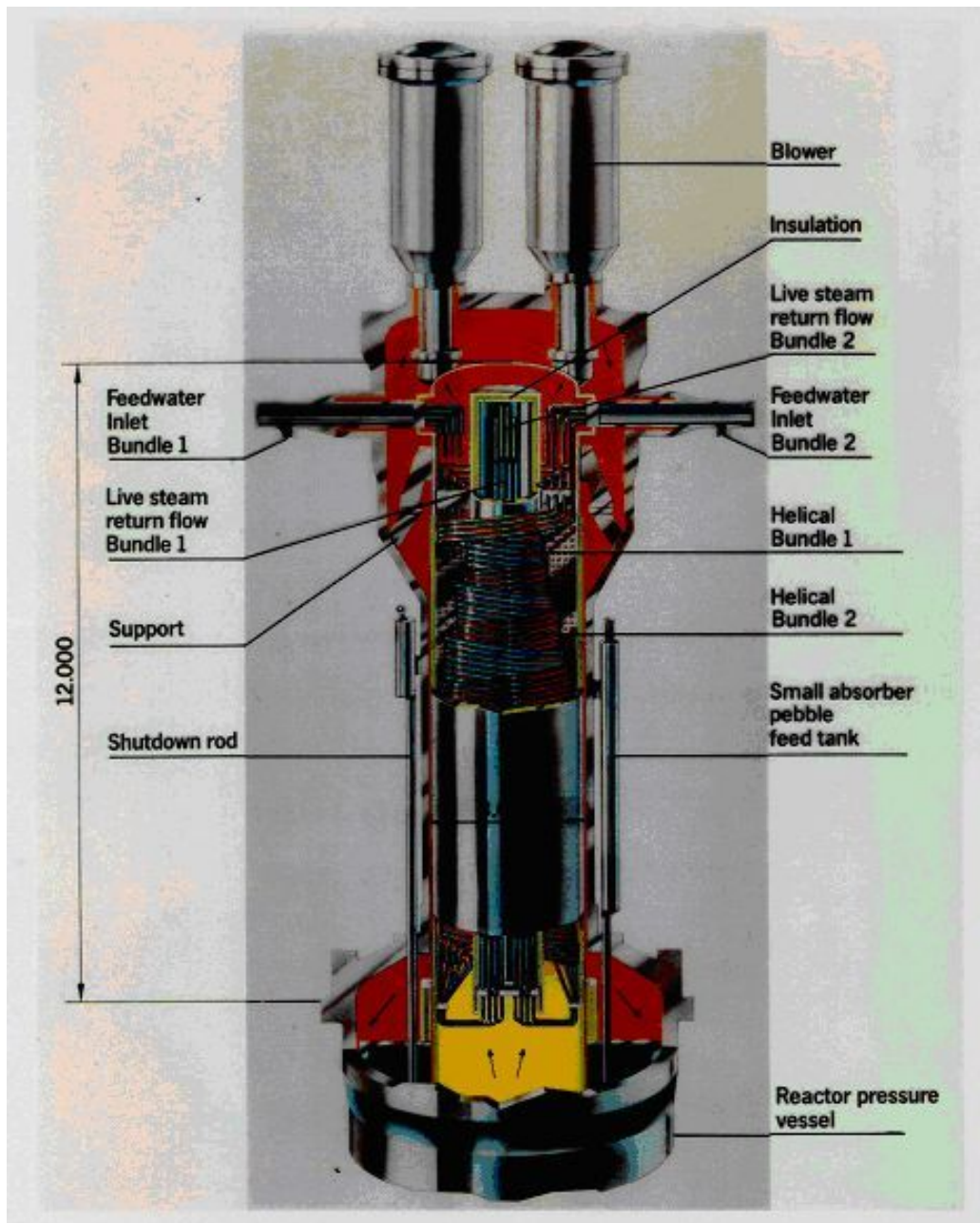
Requirements to be fulfilled by welding and wear protection for PNP high-temperature application are shown in Fig. 5.4 for components representative in shape and load with reference to /5.8/ /5.9/ and /5.10/.

		Load					
Components mass in mm	Atmosphere prim. sec.		Surface pressure	Type	Integral friction travel m	Nominal temp. °C	Max. temp. transient K/min
tube guide plate tube diam. 20x2 support bore diam. 20x30	+		normal force up to 210 N	sliding and fretting	76 and fretting	up to 950	10
tube guide plate sleeve diam. 27/22x30	+		normal force up to 350 N	rolling/ tilting	-	up to 950	10
spacing of tubes centring diam. 820- 2900 and flat material	+		< 5 N/mm'	sliding	up to 200 m	up to 950	10
insulating rings, end of insulating basket		+	< 5 N/mm'	sliding	up to 130 mm	900	1

Fig. 5.4: Requirements for the wear protection system in the He/He IHX

5.2 Steam Generator (Modular HTR)

During start-up and shutdown and during load changes relative motions occur between tube support and guide shell. The sliding connections are subjected to a temperature load of 700 °C. Helium-flow-induced vibrations lead to fretting loads of the guide locations.

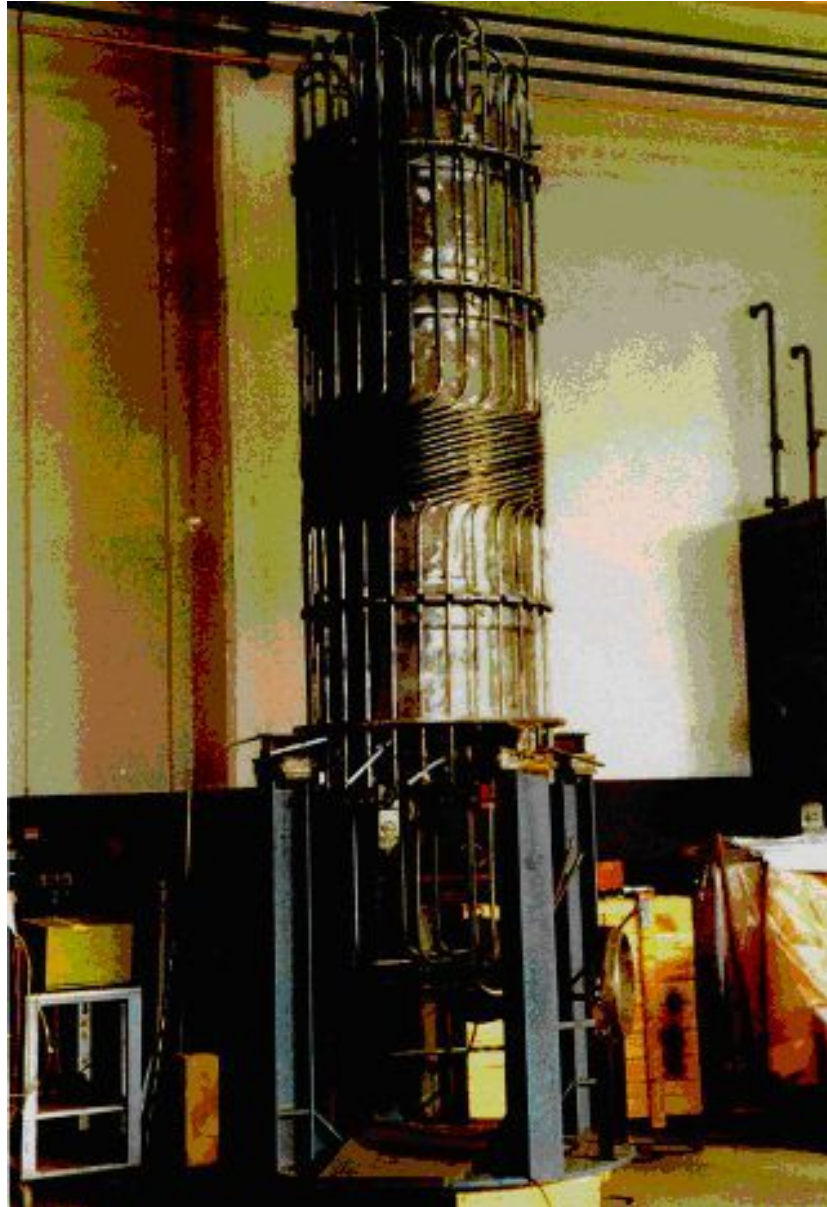


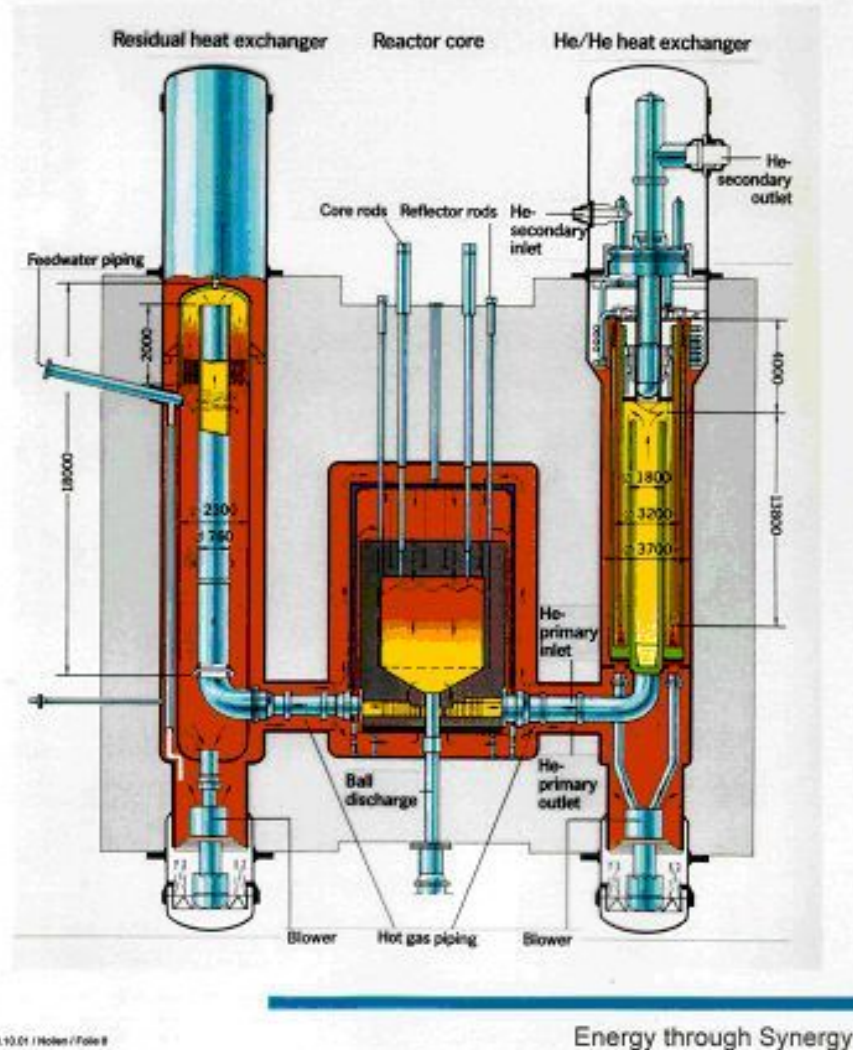
Component	Load						
	Atmosphere prim. sec.		Surface pressure	Type	Integral travel m	Nominal temp. °C	Max. temp transient K/min.
tube support							
guide shell	+		5/Nmm ²	sliding and fretting	15 and fretting	700	-

Service life: $300 \cdot 10^3$ h

Fig. 5.5: Requirements for the wear protection system in the steam generator

5.3 Afterheat Removal Cooler





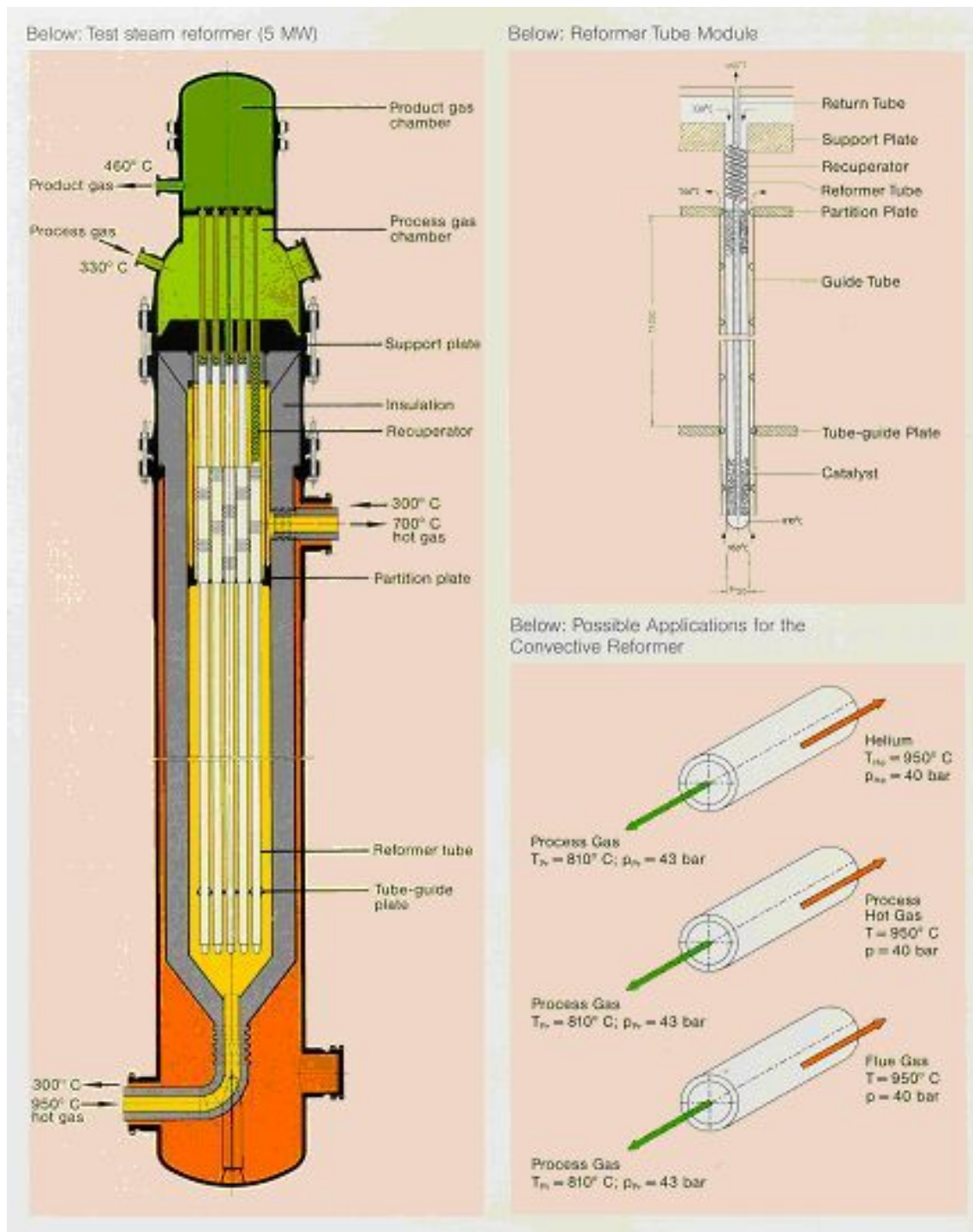
At operating temperatures of up to 950 °C, as for the above-mentioned components, relative motions caused by plant operation and fretting loads due to helium-flow-induced vibrations occur between tube supports and guide shell. The load on the cooler as the emergency system can lead to high temperature gradients between substrate material and coatings.

Component	Load						
	Atmosphere prim. sec.		Surface pressure	Type	Integral travel m	Nominal temp. °C	Max. tem. transient K/min.
tube support							
guide shell	+		5/Nmm ²	sliding and fretting	20 and fretting	950	-

Service life: 140 • 10³ h

Fig. 5.6: Requirements for the wear protection system afterheat removal cooler

5.4 Steam Reformer



During start-up and shutdown and during load changes relative motions occur between reformer tube and jacket.

Component	Load						
	Atmosphere prim. sec.		Surface pressure	Type	Integral travel m	Nominal temp. °C	Max. tem. transient K/min.
cams / jacket	+		normal force 500 N	sliding and fretting	5 and fretting	700 to 950	10

Service life: $140 \cdot 10^3$ h

5.5 Hot Gas Ducts

Between the individual sections of the gas ducts there are sliding connections which undergo relative motions during start-up and shutdown and during load changes.

Component	Load						
	Atmosphere		Surface pressure	Type	Integral travel m	Nominal temp.	Max. temp. transient
	prim.	sec.				°C	K/min.
tube guide plate	+		5 N/mm ²	sliding and fretting	75 and fretting	900	10

Service life: $140 \cdot 10^3$ h

5.6 Hot Gas Armature

In the closing armature of the intermediate circuit, welding of the sealing surfaces must be prevented.

Component	Load						
	Atmosphere prim. sec.		Surface pressure	Type	Integral travel m	Nominal temp. °C	Max. tem. transient K/min.
outer cone / inner cone	+		average 15 N/mm ²	quasi- static	-	900	10

Service life: $140 \cdot 10^3$ h

5.7 Influence of Finishing on Component Design

Structural adaptation

It should be basically endeavoured to minimize locations of friction and wear by structural measures on a component, to displace sliding connections to structural parts not exposed to high loads or design the arrangement in such a way that differential expansions do not take effect in hot-going sections.

However, this reaches its limits, since load diversions take place via the "cold component end" for reasons of strength, so that the relative displacement must be made in the hot gas region.

As a possibility of transferring the friction and wear of endangered components to thick-walled wearing parts, reference should be made here to the cotter/sleeve arrangement /1.17/ /5.11/ or to the tube support bar (groove-and-tongue joint) solution /5.12/. Both designs displace the wearing zone so that a failure of the coating cannot lead to a failure of the component.

If a component has to be coated and if representative composite properties are to be produced, the component design must be adapted to the process applied.

If layers are to be produced by CVD or PVD processes, the component must be designed so that it fits into the closely limited reaction vessel. For heat-exchanging component parts this would mean that a large number of small parts (dimensions up to approx. 300 mm diameter, approx. 800 mm length) are involved, which burdens the manufacturing costs in addition to a cost-intensive coating.

However, thermal spraying techniques are in the foreground of applications for friction and wear protection. In this case, the structural component design is not governed by small component dimensions, but is subject to quality requirements such as:

- mechanized component coating
- heat removal possible
- homogeneity in the layer thickness and
- sufficient adhesive strengths producible.

Components with openings from millimetres up to metres in diameter or component lengths of up to 20 m /5.13/ and metre-sized cylinder segments can be coated according to requirements.

If the spraying distance of the automated spraying device is not sufficient for large components, there is the possibility of phasing the layer out and restarting the coating on the offset component.

Functional protection systems are also producible by partial coating. It may be sufficient to only protect the inner surfaces of boreholes by coating the readily accessible ends. Spraying times are thus shortened and top coat materials can be saved.

The relatively low layer adhesion of sprayed wear-resistant coatings requires, however, that component edges are rounded or chamfered so that the danger of edge pressing is avoided.

Components that are thermally sprayed should be available readily machined. The design should be such that assembly weldings must not take place in the immediate vicinity of the coating.

Above all in the case of ceramic overlays, component stresses may lead to spalling.

Thermotechnical influence of the coating on the heating surface

Surface protection layers on heat exchange tubes deteriorate the heat transfer. The coating influence becomes the more noticeable

- the thicker the layer
- the larger the area of layer coverage and
- the lower the thermal conductivity

of the overlay material. The effects of the layer on the design of the heat exchanger cannot be neglected in the individual case.

He/He IHX URKO 170 MJ/s

Just over 84,800 locations on the exchanger tubes with 60 mm coating length each, i.e. slightly less than 4.5 km of tubing are covered here by a ceramic layer. A layer thickness of 0.1 mm is estimated for the $\text{ZrO}_2 + \text{Y}_2\text{O}_3$ coating. The NiCrAlY bond coat can be neglected, since the thermal conductivity is of the order of the tube material.

$$\lambda_{\text{ZrO}_2 + \text{Y}_2\text{O}_3 \text{ stab}} = 0.18 \text{ W/mK}$$

From the thermotechnical program run of heat exchanger design, the mean inner heat transfer coefficient is taken into consideration with $\alpha_i = 1474 \text{ W/m}^2\text{K}$ and the mean outer heat transfer coefficient with $\alpha_a = 995 \text{ W/m}^2\text{K}$. Assuming an average thermal conductivity of the tube of $\lambda_R = 22.5 \text{ W/m}^2\text{K}$, a value of $K = 512.23 \text{ W/m}^2\text{K}$ is obtained for the heat transfer coefficient.

Taking the surface coating into account, the transfer coefficient reads as follows:

$$\frac{1}{K_s} = \frac{1}{\alpha_i} + \frac{d_{as}}{d_i} + \ln\left(\frac{d_a}{d_i}\right) \cdot \frac{d_{as}}{2 \cdot \lambda_R} + \left(\frac{d_{as}}{d_a}\right) \cdot \frac{d_{as}}{2 \cdot \lambda_S} + \frac{1}{\alpha_a}$$

d_i ...inner tube diameter

d_a ...outer tube diameter

d_{as} ...outer tube diameter.

A value of $K_s = 396.8 \text{ W/m}^2 \text{ K}$ is obtained.

The transmission loss is consequently

$$Q = (K - K_s) \cdot A_{s \text{ total}} \cdot \Delta T \text{ m.}$$

282.7 m² of the 2772 tubes is coated with ceramic material. This thus represents a transmission loss of $Q = 2.247 \text{ MW}$ corresponding to 1.32 % of the heat exchanger power. In order to compensate this, an additional exchange surface of $A_{zus} = 63 \text{ m}^2$ of the envisaged heat exchanger surface is necessary.

Steam generator Modular HTR 202 MJ/s

If the same considerations are made for the steam generator and also considering here a 60 mm wide sprayed-on ZrO₂ coating with $s = 0.1 \text{ mm}$ on the tubes in the support region, the following is obtained:

preheater part $Q_{pre.} = 3.497 \text{ MW}$

evaporator part $Q_{ev.} = 1.571 \text{ MW}$

superheater part $Q_{super.} = 1.878 \text{ MW}$

$$Q = 6.946 \text{ MW}$$

After all, the loss to be compensated here by enlarging the heat exchanger surface would be approx. 3.4 % of the heat exchanger power.

Afterheat removal cooler 10 MJ/s

For this afterheat removal cooler, too, 3.1 % of the heat exchanger load would have to be compensated by the installation of additional heating surface. It was also taken into account here that the tubes of 22.0 mm diameter are provided with a ZrO₂ layer on all tube support locations over a length of 60 mm each and a thickness of 0.1 mm.

Valuation

If the coating has such an effect on heat transmission that a few percent of the exchange piping require considerable additional heat exchanger surface, apart from the tribological factors mentioned in the section on structural adaptation, heat

engineering should also be such that the locations of wear protection are transferred from the heat exchanger surface (tube) to external systems (support bar or sleeve).

6. Layer Specifications and Quality Assurance of Surface Protection Layers for PNP Plants

6.1 Problems

Quality-assurance measures were necessary for the reproducible production of layers. The aim was to provide nuclear components with coatings so as to comply with the results obtained in component development and testing. These measures started in the phase of component design and fabrication and accompanied the entire coating production programme.

In order to firm up these rules, it was necessary to know how the special layer is produced, how it behaves and how it can best be tested.

These specifications have been adapted to the respective state of the art.

Due regard was given here to the

- layer testing organisation
- coating producer and
- component manufacturer.

Experience with specified coatings may have repercussions on the further development and improvement of the specifications.

In-depth investigations concerning the influence of

- the component geometry to be coated
- friction travel loads
- load combinations on the composite system of layer and substrate (e.g. friction after creep pre-exposure)
- influence of the process parameter tolerances on the layer quality
- quantification of abrasion
- long-term behaviour and
- development of suitable acceptance test procedures (above all non-destructive testing)

are necessary for the further completion of the coating specifications.

6.2 Draft Technical Specifications for Surface Finishing Techniques as Friction and Wear Protection for PNP Components

Technical specifications were established for three qualified layer systems, those up to 700 °C, 850 °C and up to the nominal temperature of 950 °C.

6.2.1 Carbide layer systems

Annex 1 contains the "Technical specification for the UCAR chromium-carbide duplex and the UKAR chromium-carbide cermet coating".

6.2.2 Oxidic layer system

Annex 2 contains the zirconia duplex specification based on the HRB preliminary specification /6.1/.

7. Development Steps

7.1 Friction and Wear in PNP Components

Development at HRB

Since 1978 investigations have been carried out at HRB on the development of friction/wear protection coatings.

Four development stages were determined /7.1/ to achieve the goal:

Selection phase 1979	Testing commercial layer systems or layer systems from development primarily on simple geometrical test specimens with the aim of determining the basic suitability of a layer-base material composite.
1982	
Data backup phase: 1983	Extension of the testing programme towards longer times also on component-typical specimens with the aim of adapting the layer system to the <u>geometry</u> .
Demonstration phase : 1986	Coating of components or component-like specimens and testing with the aim of determining functionality on the component.

Quality assurance. ↓	Measures during and after production (coating) which ensure that properties from the selection, data backup and demonstration phases are guaranteed.
-------------------------	--

Goal Friction and wear protection of PNP components.

In the selection phase promising layer systems were selected and subjected to an application-oriented test programme.

Work at HRB started out from commercially available metallic and ceramic layer systems, for which suitability tests were performed under PNP boundary conditions /7.2/.

Coatings were filtered here from the following aspects:

Selection Phase

Physical and chemical requirements	Technological and commercial requirements
<p>↕</p> <p>melting point, sublimation point or decomposition temp. 1000 °C</p> <p>↕</p> <p>phase stability, strength and hardness</p> <p>↕</p> <p>chemical compatibility with HTR helium and component material</p> <p>↕</p> <p>internal or external diffusion</p> <p>↕</p> <p>activation</p>	<p>↕</p> <p>producibility according to a techn. mature process</p> <p>↕</p> <p>suitability of layer and process for component and geometry</p> <p>↕</p> <p>adequate costs including the coating expenditure</p>

The HRB selection results are as follows:

Physical and chemical requirements	Technological and commercial requirements
fulfilment by: ceramic layers	fulfilment by: thermal spraying for large components CVD process for small components

For the protective goal:

- prevention of abrasive wear
- exclusion of diffusion welding

at operating temperatures of up to 1000 °C for 40 years of operation in PNP primary coolant, tests were performed on commercially available layers and promising systems further developed.

Fig. 7.1 shows the stresses, test conditions and evaluation criteria used for determining basic suitability /7.2/.

Standardized flat specimens were used so as to preclude falsifying influences of the specimen geometry.

Type of test	Stresses in N/cm ² at test temp. in °C			Test conditions	Evaluation criteria in the selection phase	
	850	950	1050		1st step	2nd step
static test	2000	500	80		100 h 3000 h test time no welding no layer spalling	
friction test	2000	500	-	oscillating movement with 5 mm stroke, friction rate CR = 1 - 2 mm/min.	5 m m friction travel μ < 0.8	20 m
exposure test	-	x	-	minimum flow rate	3000 h	
				C = 0.075 m/s area-specific flow rate	demonstration of	

				RD = $7.54 \cdot 10^{-6}$ m/s	structural stability
thermal cycling test	-	-	-	between 200 and 90 °C heating in 3 min. cooling in 5 min.	30. 100. 300 cycles without spalling or structural change

Fig. 7.1: Boundary conditions for determining basic layer suitability /7.2/

Fig. 7.2: shows layer systems discarded in the selection phase and adopted in the data backup and demonstration phases.

Company/Institute	Coating process	Layer development	1979-1982 Selection	Application temp. range °C	1983-1986 Data backup and demonstration
TH-Aachen	APS	NbC	X		
UC	D-GUN	Al ₂ O ₃	X	< 850	X
		Cr ₂₃ C ₆	X	< 700	X
		Cr ₃ C ₂	X		X
BBC Plasma-Techn. DEVL R	APS	ZrO ₂ (Y ₂ O ₃)	X	950	X
Lurgi/BBC IFAM	LPPS APS APS	Colmonoy with changing ZrO ₂ additions and stabilizers	X	950	X
				< 600	X
AMICRON	APS	MgZrO ₃	X		
MAN-NT	CVD	TiN, TiC, Ni ₃ Ti, TiB ₂	X		

Fig. 7.3: Representation of the layers in selection, data backup and demonstration /7.2/

Initial investigations of coatings on specimens with the geometry of PNP components were performed in 1983. It was found even then that a transition from standardized flat to e.g. cylindrical geometry entails influences on the coating process/coating behaviour /7.3/ and that further analyses are required for specification.

The contact between HRB and manufacturers revealed /7.4/ that know-how must be acquired for a reliable application of layers on nuclear components going beyond the original objectives of the demonstration phase.

Evaluation

The processes and layers systems selected by HRB for the coating development programme in the selection phase were state of the art. New and further developments as shown in Figs. 3.12 and 3.13 for friction and wear protection layers worth following up have primarily remained at the development stage.

The investigations performed in 1984/1985 with respect to the coating qualification of PNP friction-wear protection systems and applicable specifications for the deposition of layers have not yet advanced to a stage where reliable component fabrication is possible from the present point of view.

In order to achieve this reliability, further investigations are required in the data backup and demonstration phases and for quality assurance.

Justification

- The preliminary specification of the only qualified high-temperature coating (ZrO_2 - (Y_2O_3) -NiCrAlY) /6.1/ has created a basis for PNP component parts. A basis because not all boundary conditions for the reproducible coating are firmed up with this preliminary specification. The coater know-how not known to the testers is too important. For a generally valid specification, according to which different coating firms can supply reproducible layer qualities in the sense of the PNP requirements, the data concerning the know-how of the coating firms must be firmed up. This is also necessary if the coating developer wants to influence the coating structure in a controlled manner to achieve property improvements. However, the approach of having variables allocated by the coating producer for ideal adjustment parameters during coating, on the basis of which the component manufacturer can then also verify the accuracy of the parameters, leads to a monopolistic position of certain advanced coaters. Overloading (deadline situation) and excessively high coating costs may be the consequence.

Furthermore, coating tests and qualifications for long-term application have not been completed. In addition to the ZrO_2 protective coatings, the carbidic systems currently used for components must also be backed up.

Apart from the possibility of changing to carbidic systems in the medium to low temperature range of PNP plants, it is also possible to change to protective layers withstanding shock loads (important for component fabrication).

The coating volume arising in PNP component fabrication can then be divided into fabrication lots.

If the whole volume of a component coating is covered by just one qualified manufacturer, production bottlenecks may arise for the coater and component producer and/or total fabrication times exceed a reasonable limit.

It is also necessary to specify a reliable coating process for the carbidic layer system.

The behaviour of surfaces that are only coated on one side is still insufficiently clarified. For component pairings subjected to static load and relative displacement it would also be possible to structurally extend the design of component parts.

A determination of quantitative abrasion, whether for unilateral or bilateral coatings, permits load-dependent, maximum permissible friction travel loads to be inferred.

Further consideration must be given to the superimposed types of load occurring in components. The accumulated friction travel load results backed up in the preliminary HRB specification are based on tests with an oscillating movement with 5 mm stroke and a friction rate of $CR = 1 - 2 \text{ mm/min}$. (see Fig. 7.1). In component operation, the friction processes caused by plant operation are superimposed on the vibrations induced by the helium loop, so that higher friction loads than backed up can occur.

Loads on coatings due to creep of the metallic, in part highly stressed structural materials or the coating behaviour during temperature changes in coated components prestressed by creep have not been taken into consideration either.

It is necessary to ensure the transferability of flat specimens to component geometries. Special features must be identified and included in the coating specification. Tests should include design-oriented loads.

An increase of the relatively low adhesive strength of plasma-sprayed ZrO_2 layers should be aimed at for the following reasons:

- increased protection against spalling due to shrinkage and creep of the substrate material
- easier handling of coated components in component fabrication.

The reflux from post-examinations of operational coatings tested in the laboratory or applied in practice to the specified data remains necessary. In the KVK component test loop, for example, coated components have been in operation for 10,000 h, including 3,300 h at 900 °C.

Diffusion processes or oxidation processes of coating and base material as well as residual lifetime tests can be performed on replaced components.

- Quality assurance measures, especially nondestructive tests of coated components have only been possible to date to a limited extent. Practicable test procedures should be included in the respective "Technical Specification" of the coating.

Not only the application of protective coatings itself, but also the basic friction/wear and welding phenomenon of suitable metals for PNP component fabrication has been insufficiently clarified. Although the investigations performed have shown that material pairings in PNP helium atmosphere are bonding together and/or are connected by non-positive action, definite statements on

- limiting temperature (beyond which coating protection is required)
- material erosion lifetime determination of the component (tearing up of bonds or abrasion of the metal)
- influence of the surrounding environment

are not sufficiently available.

In this connection, reference should be made once again to Japanese investigations /4.57/. It has been stated both for static and dynamically loaded specimens that no coating in helium atmosphere is required below 690 °C.

- The use of composite or sintered materials in component fabrication also requires a qualification or classification with respect to friction and wear behaviour. Application limiting data must be determined.

7.2 Recommendations for Continuing the Development of Friction and Wear Protection Coatings

In order to obtain results for practical application in the qualification of friction and wear protection coatings, cooperation between

- layer test organization
- component manufacturer and
- coater

is required, at the latest, after selection of the candidate coating.

The recommendations are divided into two categories.

- on the one hand,
continuation of the investigations on the basis of previously achieved results of coating development and
- on the other hand,
further necessary investigations.

The following issues should be investigated within the framework of the new HTR coating programmes:

- incorporation of chromium-carbide protective coatings into the qualification programme
- long-term backup of the layer systems
- increased friction travel load
- load superimposition in testing overlay coatings
 - friction processes with helium-loop-induced vibrations
 - creep-loaded substrate material with subsequent fretting tests
- determining the abrasion quantity
- behaviour of unilaterally coated specimens
- influence of the coating component geometry

- post-examinations on test specimens and operational coatings applied.
Reflux of results, if necessary, correction of specified data
- development of quality assurance measures
 - geometry influence
 - defining tolerances for the coating parameters
 - developing inspection test procedures, especially nondestructive tests of coatings on original components

Further necessary investigations could focus on the following:

- deriving allocatable statements on abrasive wear processes in metallic material pairings under PNP conditions
 - determining adhesive strength values
 - determining the quantitative wear and its effects
 - determining admissible load limits
 - influence of helium impurities
- determination of coating characteristics to establish generally valid specifications
- verification of the applicability of promising coating processes
 - tentative experiments with coating samples
- determination of design constraints for the application of friction and wear protection of
 - sintered ceramics and
 - CFC

7.2.1 Further investigation steps

For further backup of the wear protection layers determined, the following tests should be included in the programme:

Testable coating systems:

- A • $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ -NiCrAlY air-plasma-sprayed for test temperatures of 950 °C
- B • Cr_{23}C_6 duplex D-gun-sprayed for test temperatures of 850 °C
- C • Cr_3C_2 cermet D-gun-sprayed for test temperatures of 700 °C

- **Static specimen loading – A, B, C**

- Long-time exposure until extrapolatable statements on component life are obtained. The aim is at least 3 - 104 hours.

- **Checking the structural stability of coating/base material**

- static behaviour of unilaterally coated specimen pairs
- determination of the wear phenomenon
- post-examinations

- **Friction and wear tests – A, B, C**

- determination of the oscillating friction load behaviour by increasing the accumulated travel load from 20 to 100 and 200 m
- friction tests with unilaterally coated specimens
- determination of the abrasion quantity
- continuation of the load combination tests
 - simulation of combinations between exposure and friction
 - friction tests with specimens prestressed by creep
 - comparative determination of oscillating friction travel load CR = 1 - 2 mm/min. in comparison to flow-induced vibration load (frequency between 10 and 200 Hz, vibration amplitude 0.4 mm)
 - friction tests with internally and externally coated cylinder geometries; this test relates to the transferability of the flat specimen geometry to cylinder geometry (tubes) and provides information about the line loads arising here (diameter approx. 20 mm, clearance between coated tube and cylinder s = 0.4 mm)
- post-examinations

- **Adhesive strength investigations – A, B, C**

- thermal cycling tests on coated cylinder geometries (diameter 20 or 22 mm)
- thermal cycling tests on component test specimens prestressed by creep

- **Component-specific testing**

- Component-specific coatings and their testing as process test specimens represent the link between laboratory development and technical application. The aim should be to firm up process/coating constraints for given component geometries, to check the tribosystem for agreement with data backup and demonstration phase and to establish specific technical coating specifications. The large number of existing friction locations can be covered by combining geometry and load factors as essentially defined in Section 5 and in /5.10/.
 - post-examinations

- **Incorporation of operating experience**

Not only the testing of specimens in the laboratory, but also the operating experience with protective coatings applied are indicators for applicability and suitability. A targeted verification of the actual condition and the post-examination of removed parts will correct rules or back up the applicability.

The locations of application, the coating processes and the operating conditions of surface-protected components are shown in the following table /7.5/ /7.6/. This gives a survey of **previous experience** with surface-coated components.

Temperature range above 650

Application site	Component	Surface protection		Remarks
		Process	Type	
EVO Oberhausen	parts at the helium turbine - expansion screws - shims - baffles - sliding screws	D-gun	63 Cr ₃ C ₂ + 35 Ni-Cr (LC-1B)	
KFA Jülich	EVA II project - helium heater - fission reactor - coaxial duct - bracket plates - spacer lines - inner shell	D-gun	63 Cr ₃ C ₂ + 35 Ni-Cr (LC-1B)	T = 600 - 950 °C
	AVR - measuring probes	D-gun		
Hamm/ Schmehausen	THTR-300 - shutdown rods - tube support in SG - perforated plate - cover plate	D-gun CVD electro dep.	63 Cr ₃ C ₂ + 35 Ni-Cr (LC-1B) TiC NiAg	T < 600 °C
KVK Bensberg	IHX URKO - spacers	D-gun	Cr ₂₃ C ₆ -C ₂₃ C ₆ /NiCr (LC22/24)	T < 850 °C
	- guides	D-gun	80 Cr ₃ C ₂ + 20 NiCr	
	IHX helix - spacers	D-gun	80 Cr ₃ C ₂ + 20 NiCr	
	operational hot gas ducts - pipe connection	APS	ZrO ₂ (Y ₂ O ₃), NiCrAlY	T = 950 °C
	el. heater - heating tube connector - gaskets - spacers - collecting funnels - sealing surfaces			
	waste heat boilers - spacers			
	IHX URKO - tubes - tube supports - spacers - slide protection H.S.	APS	ZrO ₂ (Y ₂ O ₃), NiCrAlY	T = 950 °C

According to /7.1/ experience is available in the temperature range near 700 °C and down to 400 °C

Temperature range up to 700 °C

Component	Part	Issue	Type of Testing		
			Coating qualification	Component-related testing	Component test
shutdown rods	interaction rods/pebble bed	friction behaviour of steel/graphite with and without NH ₃	x	x	x
metallic internals	tube supporting elements	steel/steel-coated			x
	screw connections perforated plate in the THTR hot gas duct	steel/steel coated TiC-coated sliding connections		x	x
hot gas duct	THTR cover-plate guides	various coatings against welding	x		x
	AGRAS test rig	layer selection for welding locations	x		
ceramic internals	core bottom	friction behaviour spheres/graphite			x
steam generator	tubes in guide plate	double-sided coating with Cr ₃ C ₂ cermet	x	x	
	tube guide bearing	Incoloy 800/Deva sintered metal	x	x	
hot gas armature turbine	bearings for HHV	Colmoly 6 coating on bearing material	x		
	blade roots HHV	BN coating against static welding	x		
	cover plates of HHV blade roots	TiN coating for guide in grooves	x		
auxiliary circuits	multilayer bellows for expansion joints	inner coating against welding pressing	x		
shutdown rods	rod coupling AVR	friction behaviour steel/steel			x
	adapter sleeve coupling AVR	friction behaviour steel/steel			x
	guide bearing AVR	molycotized ball bearing		x	
	long-stroke piston in THTR drive	plastic/steel			x
	bottom guide bearing THTR	various friction pairings			x
	variants for THTR with planetary and recirculating ball rollers	friction pairing steel/steel			x
	transport and holding devices THTR	material GG 22 Cr ₃ C ₂ cermet functional demonstrations for graphite dust and NH ₃	x	x	
blower	valve bearing AVR	various friction pairings			x

	shut-off and bypass element	friction pairing steel/steel			x
auxiliary circuits	disk singularizer stressing	graphite spheres/steel			x
	transfer tube bend stressing	graphite sphere/steel			x
	double-seat shut-off valve stressing	various friction pairings			x
	spindle guide for valves	plastic/steel			x
	anti-friction bearings of different diameters	various material pairings			x

- **Development of quality-assurance measures**

- Influence of the results obtained from the tests and post-examinations on the specified data

- Component geometry influence
- Definition of data tolerances

- Development of acceptance test procedures

- The aim for the spray coatings to be applied is to upgrade testing procedures which enable unambiguous quality control of the deposited layers in practical application. A number of nondestructive and destructive testing methods are used in conventional coating technology (Fig. 7.4). The application to PNP layer systems, especially the nondestructive testing on the original component, which provides clear information about the coat layer/base material composite system, is currently not available for nuclear backup
- The development – application of ultrasound in combination with holographic interferometry – /7.7/ as a nondestructive testing method for thermally sprayed layers will certainly also provide solution approaches for relatively porous spray coatings.

Application of testing methods on components

- <i>surface condition</i>		- <i>layer thickness</i>	
optical check (standards comparison)		<ul style="list-style-type: none"> • measuring (micrometer dial gauge) • magnet-induced measuring techniques 	
<ul style="list-style-type: none"> • blisters, cracks, uncoated areas • colour and gloss deviations • roughness test 		<ul style="list-style-type: none"> • eddy-current measuring techniques • beta backscattering techniques • ultrasonic measuring techniques 	
- <i>pore testing (standards comparison)</i>		- <i>adhesion testing</i>	
immersion test		<ul style="list-style-type: none"> • thermography (dynamic method) • holography 	
<ul style="list-style-type: none"> • electrographic and electrolytic method (reference standards) 		<ul style="list-style-type: none"> • sound test • ultrasonic test 	

Application of testing methods on component test specimens
(on parts to be replaced or removed)

<ul style="list-style-type: none">- hardness test (microhardness)- layer thickness<ul style="list-style-type: none">- microscopic methods- capacitive methods- X-ray fluorescence- coulometry methods	<ul style="list-style-type: none">- metallographic testing- tribological testing<ul style="list-style-type: none">friction test
adhesive strength tests <ul style="list-style-type: none">-• <i>indirect methods</i><ul style="list-style-type: none">- chisel test- bending test- impact test- shot blasting- deep-drawing test- torsion- scratch test- thermal shock behaviour• <i>direct methods</i><ul style="list-style-type: none">- adhesive and tensile strengthadhesive and shear strength	<ul style="list-style-type: none">- component and material testing- scanning electron microscopy (SEM)- electron microprobe analyser (EMA)- electron spectroscopy methods (AES and XP)- mass spectrometry methods (SIMS and SNMS)- glow discharge spectroscopy (GDOS)- laser-induced mass spectrometry (LAMMA)

Fig. 7.5: Testing methods applied in coating technology

7.2.2 Further Investigations

Before components are coated and/or tested, the cause-determining phenomenon with its effects should be delimited. If these boundary conditions are sufficiently known, protective measures of a structural (e.g. increasing the component wall thickness, displacing sliding connections or reducing the surface pressure by large-area coats) and/or coating technology nature can be taken.

•Wear phenomenology

In order to obtain allocatable information about the process and effects of friction welding in metallic material pairings under PNP boundary conditions, further tests are recommended.

•Static tests

Exposure of test specimens with the materials

- 15 Mo 3 / 15 Mo 3
- 15 Mo 3 / Incoloy 800 H
- Incoloy 800 H / Incoloy 800 H
- 10 Cr Mo 910 / 15 Mo 3
- 10 Cr Mo 910 / 10 Cr Mo 910
- Incoloy 800 H / Inconel 617
- Inconel 617 / Inconel 617

at surface pressures from 5 to 20 N/mm² and temperature gradings up to the maximum material temperature limit in PNP helium atmosphere.

•Friction tests

It is recommended that friction tests should be carried out.

Test objectives:

- Determination of adhesive strength values. Representation of the adhesive strength values as a function of static load-exposure time. Adhesion measurements can be periodically performed by using a variety of test specimens.

In the experiments, the forces produced by friction between the test specimens is to be determined. A limitation of the friction coefficients to $\mu < 0.8$ is not to be envisaged. This means that local weldings may occur which are, however, cracked again by the displacement forces applied.

- Determination of quantitative wear. Material erosion and/or fretting traces in the material surface are to be compared with the acting load mechanisms. A validated wear extrapolation to the component life should provide information about whether effective damage can occur in the concrete case.
- Determination of admissible load limits. Extrapolated to a component life, limits determined by acting component surface pressures, operating temperatures and system loads of a static or dynamic nature are to be identified. Below this limit load no surface coating is necessary.

•Influence of helium impurities

Primary and secondary gas atmospheres in advanced HTR plants are differently contaminated by e.g. H₂, H₂O, CO, CH₄ and N₂.

A low oxidation potential is expected for the primary gas atmosphere under steady-state operating conditions. In the limit range of $100 > PH_2/PH_{20} < 1000$, however, the elements Si, Ti and Al of the suitable high-temperature alloys are always oxidized. However, the formation of Cr oxides over the entire temperature range has not been verified /7.9/.

The oxidizing additives for the secondary atmosphere have not yet been firmed up.

Since "sliding connections" must necessarily be taken into account in existing components both in the primary and the secondary helium atmosphere, the question arises as to the influence exerted by helium impurities and existing material oxide scales on friction and wear behaviour.

It should not be ruled out here either that partial coatings can be omitted if the admissible load limits are known.

According to the investigations on the "wear phenomenology", relevant investigations with appropriately doped helium impurities can reveal load limits.

•Determination of spray characteristics

In order to obtain generally valid specifications, an incorporation of the test organization is required to record the spray parameters.

If this is not possible for reasons of protecting the know-how of coating producers,

- coatings in cooperation with university institutes or
- coatings by the test organization itself

should necessarily be carried out.

•Coating techniques

Coating techniques that are possible for component coating and have been insufficiently studied up to the present are:

- hypersonic flame spraying
- surface layer remelting dispersion
- sol-gel method
- laser shock hardening

These are techniques that were in part still under development at the time of the PNP project and were hardly commercially applied.

Besides the techniques so far discussed, the above processes appear as variants that are worth testing and whose follow-up and layer testing under HTR conditions can provide promising approaches.

Hardening a sprayed surface by laser light provides a possibility of increasing the adhesive strengths between coat layers and substrate material. Increased bonding properties could thus be achieved for creep-stressed substrate materials with friction and wear protection coats.

•Ceramic materials

Changing from metallic structural materials to ceramic components for high-temperature application appears possible for some components /7.8/.

For promising materials such as

sintered ceramics
carbon-fibre-reinforced carbon

a reliable design can be achieved by answering the following questions:

- friction coefficients for the component pairing
 - ceramic/ceramic
 - ceramic/metallic material
- abrasion/lifetime of the ceramic
- influence ceramic/metal
 - diffusion processes.

Candidate ceramic materials are:

- carbon-fibre-reinforced carbon, CFC
- sintered ceramics such as
 - alumina : Al_2O_3
 - silicon carbide : SiC
 - silicon nitrate : Si_3N_4
 - boron nitride : BN
 - aluminium silicate : AS
 - magnesium-aluminium silicate: MAS
 - lithium-aluminium silicate: LAS
 - zirconium-magnesium-aluminium silicate: ZrMAS

Metallic materials as counterbodies such as
Inconel 617, Inconel 625, Hastelloy X, Incoloy 800 H

8. Cost Analysis

We can no longer imagine to obtain qualitatively high-quality component properties without the aid of surface finishes.

Factors responsible for the introduction of finishes to industrial application may be:

- economical substitution for conventional process such as
 - corrosion protection coats on low-alloyed steels or
 - the metallization of packaging material as barrier protection instead of relatively cost-intensive aluminium foils
- functional reasons such as
 - extending the application range of products by erosion protection coats or
 - reflection reduction by coats on optical lenses.

As a general rule, "economical substitution" leads to a cost reduction due to the application of surface finishes directly on the product. Finishing for "functional reasons" increases the product fabrication costs. In using the product, however, the incurred additional costs can be compensated by increased application quality or the finish can become economical by the use of the workpiece. In the following, the cost situation as per 1986 will be illustrated by the example of "friction and wear protection coatings on PNP components" and coatings from "conventional application".

8.1 Surface Coating – PNP Components

•Tube supports and tubes of the He/He IHX URKO

The essential coating costs of the U-tube compact He/He intermediate heat exchanger are caused by the bearings between U-tubes and tube supports.

In a 170-MW component more than $150 \cdot 10^3$ component locations must be coated here. Fig. 8.1 shows the design of the supports and tubes applied.

On the basis of the coating specifications, cost inquiries were addressed to qualified coating firms.

The basis was a coating run time for tubes and tube supports of 6 months along with the same lead time after placing and clarifying the order.

Clean conditions during processing and an automated production sequence were taken as a prerequisite.

The specified accompanying scope of testing and the expenditure for devices were included in the cost estimate. Accordingly, the total costs for a plasma-sprayed $\text{ZrO}_2\text{Y}_2\text{O}_3\text{-NiCrAlY}$ duplex coating of all tubes and supports amount to DM 6,670,000 (approx. €3.3 million). This corresponds to a coating cost share of approx. €20,000/MW power of the heat exchanger.

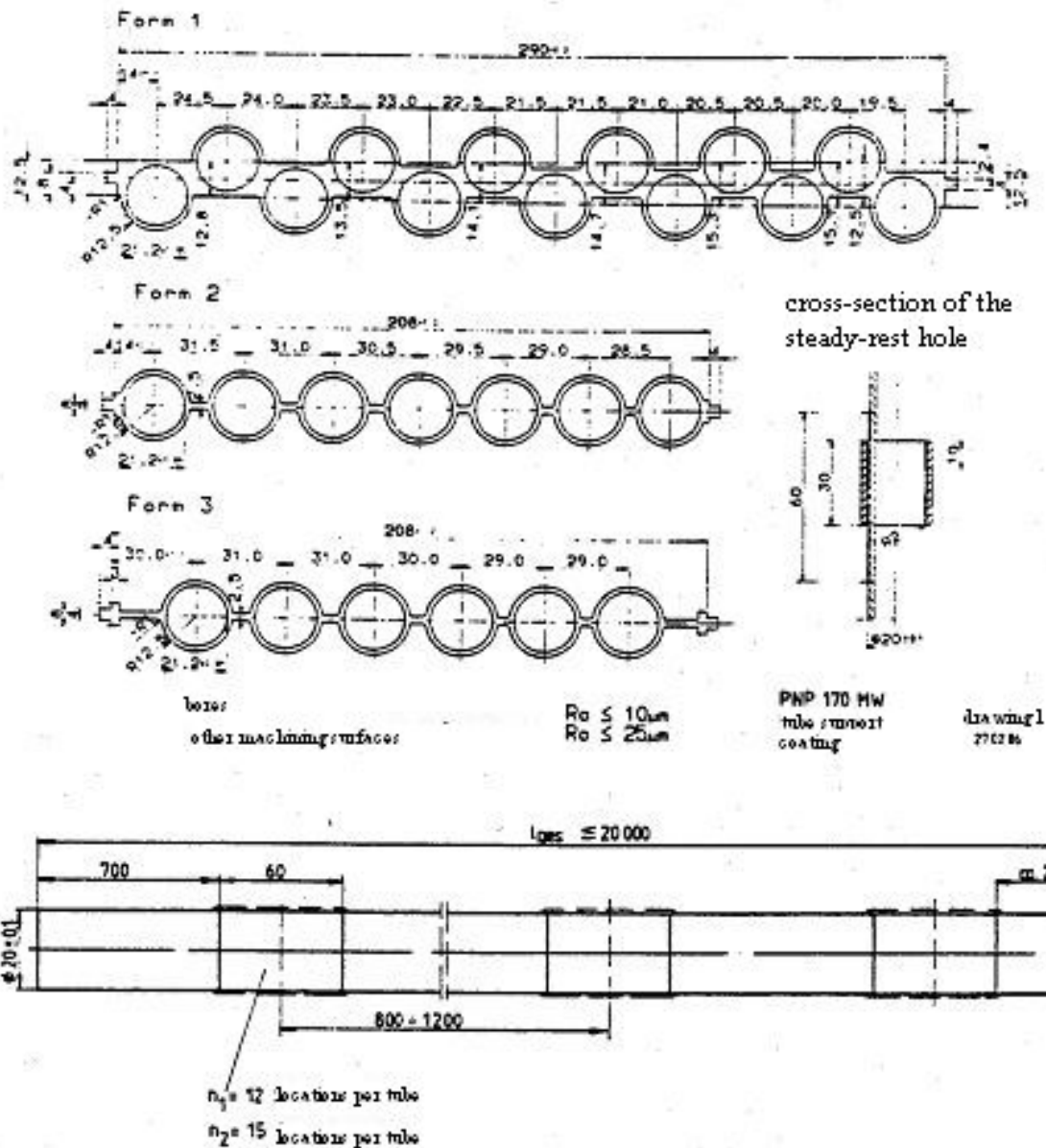


Fig. 8.1: Tube support and tube

The application of detonation-sprayed chromium-carbide duplex layers as a substitute for ZrO_2 in the temperature range below 850 °C would lead to a further cost increase of approx. 60 % of the coating costs.

•He/steam generator

The coating of the tubes and of the shell and support of the 200 MW modular steam generator concerns approx. 82,500 component locations. In accordance with the boundary conditions specified for the He/He IHX, costs of €1,900,000 would arise for a ZrO_2 duplex spray coating of the corresponding component locations. The coating costs would amount to as much as €2,400,000 with a chromium-carbide cermet coating.

It was achieved by a system modification of the steam generator modular design that the sliding connections were not between tube or shell and support. It would then be necessary, however, to coat the tube support bars on their locations of contact inside the bundle structure. Fig. 8.2 shows the form of the support bars.

The total costs for this type of high-temperature coating with the duplex ZrO_2 layer were at that time €400,000. The estimated guide prices for the chromium-carbide coatings are of the same order of magnitude.

In spite of the elevated support bar fabrication costs, the savings achieved by the cost reduction for the coating have an effect on the total price of the module. Due to the structural modification, the specific coating costs were reduced from €9,000/MW power to approx. €2,000/MW power of the heat exchanger.

This means that the coating costs were reduced from approx. 30 % to approx. 6 % of the construction costs of the steam generator by structural modifications.

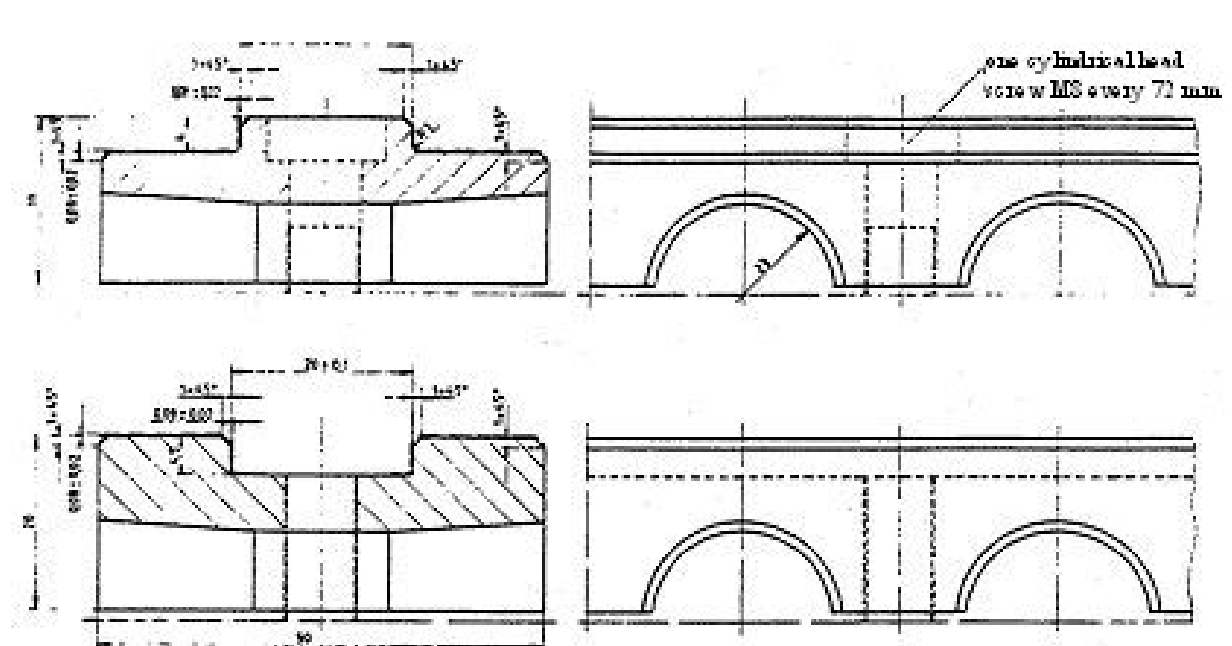


Fig. 8.2: Support bars

•Assessment

Costs running into millions arise from a friction and wear protection coating on component parts of the envisaged dimensions. From the present point of view, estimated costs are of the same order of magnitude; on the one hand, material and machine costs have decreased, on the other hand, however, labour costs have increased.

Possible savings in coating costs can hardly be achieved for the spraying costs, but rather by reducing the locations of coating.

From this perspective, it would be necessary:

- to minimize the locations of friction in component construction and
- to place emphasis on boundary conditions enabling to do without coating protection.

The latter will still require tests (see proposal in Section 7) to obtain clear information about indispensable locations of coating.

8.2 Surface Coating in Conventional Applications

•Finishes using the example of tools

The cost/benefit ratio for the application of coated tools in shape cutting and non-cutting shaping is primarily influenced positively by

- the tool life quantity increase of new tools
- the tool life quantity increase by the application of reground tools
- shorter workpiece machining time
- reduced tool changing times.

Depending on the method and coating, the costs have an effect on the sales price of tools.

In Fig. 8.3, related to cold-forming tools, relative costs after /4.1/ are determined and compared for different coating techniques.

The absolute coating costs are dependent on the tool geometry. For a PVD coating of a 6 mm drill, for example, the share is approx. 20 % of total fabrication costs. The estimated sales prices for coated metal-cutting tools are approx. 50 % above non-coated variants.

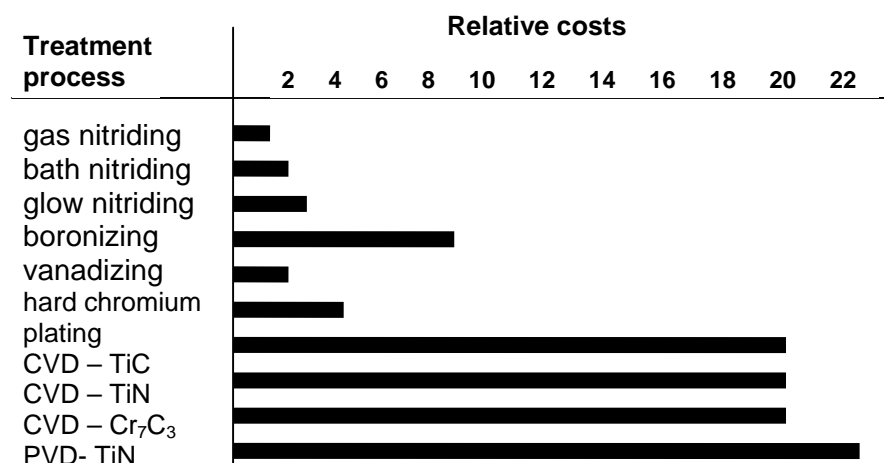


Fig. 8:3 Cost comparison of different coating techniques for tools for cold working /4.1/

In spite of the increased tool costs, savings can be achieved for the product costs. On example should be mentioned here.

The economic efficiency of TiN-coated milling cutters is shown by /4.10/ using a fabrication comparison for shape cutting.

1500 workpieces were to be fabricated from hot-work steel 40 CrMnMo₇. In comparison to a non-coated tool, it was possible to work with the coated roughing cutter, diameter 16 mm, with increased feed and elevated cutting speed. By the application of TiN-coated cutters, in comparison to uncoated tools, costs for machining and cutting tool of approx. 58 % have been saved. Regrinding of the milling tools was taken into account.

For metal working technology, in addition to CVD and PVD, the TD technique /2.32/ plays an important role in tool coating. The time and cost of the TD process are comparable to nitriding. In the Japanese sheet fabricating industry, carbide coating according to the TD process has largely been established. It is reported that these coatings have not only led to significant tool life increases, but that also

- costs for lubricants were saved,
- cost savings of up to 50 % occurred in reworking stainless-steel body parts,
- cost savings for tool steels were achieved by early recoating and
- testing and acceptance costs as well as reduced plant downtimes led to cost savings.

•Repair by surface finishes

The economic efficiency of fabrication shops is not least also dependent on how well their repair shop is working. Surface finishes by deposit welding, electroplating and thermal spraying can decisively contribute towards saving costs.

Components already "in operation", which have reached or exceeded a critical degree of wear and tear or suffered a sudden damage event, can in most cases still be regenerated with high quality on site. Costs for extensive dismantling, transports and stocking of spare parts can be reduced. Preventive maintenance by coating components exposed to corrosion and wear at defined intervals also leads to production flows with minimized disturbances or the avoidance of high follow-up costs. If the coat layers additionally increase component life, it may become economical to apply preventive layers onto new components.

In the following, some economical application examples will be given:

- Roller shells for table rollers of commercial tubes coated with self-fluxing alloy by flame spraying exhibit a 3-fold higher lifetime than the normally used chilled-iron rollers and entail 25 % cost savings /81./
- With deposit weldings on fly cutters exposed to abrasive and corrosive stress, lifetime increases and cost savings of up to 42 % compared to tool steels were achieved /4.27/

- Periodic spraying of Cr steel onto drawing disks involves about 5 % of the costs of new disks, so that the acquisition of new disks is avoided for a long period of time /8.2/
- Three-fold lifetime increases were achieved by applying self-fluxing alloys onto fans subject to abrasion /8.1/. Maintenance costs decreased by 100 % in spite of the spraying costs /8.2/.
- It was possible to electroplate a bearing seat on a 5 m long shaft on site to finished size without extensive dismantling, transport and reassembly. In comparison to a conventional repair involving removal of the shaft it was possible to reduce the loss of production by approx. 90 % /8.3/.
- Valve rods and valve seats used in the petrochemical industry were protected by thermal spraying with tungsten carbide. Costs for loss of production totalling approx. €5,000 per year and valve and material costs of €300 per valve were saved by layer application (using less expensive substrate materials) /8.4/.
- Components used in aeronautics are overhauled on a large scale by electroplating. If the overhaul expenditure for a component is less than 60 % of the price of a new component, overhaul is performed. If the component exhibits a better quality and thus prolonged operating times due to the coating or if a subsequent supply of a missing part is not possible, repair even takes place if the costs amount to 100 % of the price of a new component /4.35/.

•Finishes as substitutes and for functional reasons

Examples of economical applications:

- High-gloss metallic vapour deposition coatings on plastic caps can be produced at low cost by PVD high-vacuum vapour deposition. At present, no less expensive technique is available /8.5/.
- In comparing hard-chromium-plated surfaces with surfaces produced by QPQ-TENIFER (a salt-bath nitriding process), investment and energy cost savings of up to 37 % were obtained /2.11/.
- In tanks for the preparation of ferments, problems of particle and fibre contamination of the product were encountered. The particle and fibre problem was reduced below the measurement range limit by electrochemical polishing of the tanks. Due to undisturbed production, the expenditure for the surface treatment has paid back after 1 month /2.3/.
- By the application of existing know-how in the field of corrosion protection by surface finishes on components, according to estimates, approx. €3.5 billion, i.e. 25 % of the corrosion loss arising for Germany, can be saved /1.3/.
- High-temperature-resistant coatings on turbine blades of jet engines permit higher operating temperatures and have thus led to considerable fuel savings /4.31/.

- By a PVD coating of architectural glass 90 % of the arising infrared radiation can be reflected. This means that in hot regions less thermal energy must be removed by air conditioners and in our regions less heat from rooms is transmitted outside. About 18 litres of fuel oil can be saved per square metre of double-glazed window area and heating period. In contrast to electroplating, environmentally harmful process water can be dispensed with here owing to the PVD coating method /4.31/.

•Reduction of product costs and increase of product quality

The introduction and use of surface finishing measures for industrial applications has not yet been completely established despite various advantages such as:

- increasing the economic efficiency
- saving raw materials and energy
- reducing environmental burdens
- increasing component reliability
- developing new technical applications.

Surface techniques require a better knowledge of their possibilities /8.2/. In evaluating how well these techniques are known, an increasing application of this technology may be expected. Rising demands made on components and materials, however, also imply new property profiles and thus modern methods of surface technology. If it is possible to achieve special composite properties by the finishing of component surfaces, this may be the key to superior and high-quality products. Example: ion-implanted solid lubricants in highly stressed turbine bearings. From this aspect, surface finishing is a basic technology without which an economical marketing of products remains restricted.

By targeted further development of the surface technologies and finishing materials and by a reasonable application of the experience gathered, numerous applications can certainly be developed.

Approaches are here:

- steel-producing industry
 - steel-processing industry
 - automobile industry
 - mechanical engineering
 - chemical industry
 - apparatus and plant construction
- as well as the wide areas of
- electrical engineering, electronics, optics and medical engineering.

In these areas, we consider further and new developments worth pursuing, above all on the basis of

- physical vapour deposition
- thermal spraying
- surface layer hardening - laser technologies

- sol-gel method and
- ion implantation.

9. Summary

In this study, the activities in connection with the problems involved in "coating against friction and wear" of HTR components have been described.

The problem of "self-welding" in helium atmosphere and under HTR conditions has been illustrated.

On this basis, structural proposals have been evolved. Different coating materials and processes as well as their application in various branches of industry have been compiled.

Another chapter of this study gives a detailed survey of the test results on protective layers selected for components in PNP atmosphere.

Classifications of surface finishing variants for conventional applications and for use on PNP components were performed. Brief process descriptions, goals pursued, suitable materials and market areas have been compiled in tabular form.

Listings showing limitations and allocations characterize the processes under consideration.

Process allocations for corrosion protection or friction and wear protection measures have been corroborated by technical application examples. A classification of the process variants according to their technical application status was performed ranging from the stage of "research and development" up to "established processes used".

The technical development status reached is characterized by means of surface finishes from the areas of tool engineering, power plant engineering, the aeronautical industry and high-temperature technology as well as for friction and wear protection under PNP conditions.

The advantages and drawbacks of processes used are assessed and compared for apparatus construction, tool engineering, power plant engineering and others.

Process parameters that delimit surface treatments and coatings for PNP components have been examined with the aim of pointing out processes worth pursuing. For the friction and wear protection coating, in addition to the practised methods of plasma spraying, detonation spraying and CVD, the following processes have recently proved worth testing:

- surface layer remelting dispersion
- hypersonic flame spraying
- laser shock hardening and the
- sol-gel method.

The experience formerly made has shown that carbide coatings are suitable for HTR conditions and temperatures of up to 850 °C and zirconia/yttrium-stabilized coatings for temperatures of up to 950 °C.

For reliable component fabrication, however, further investigations would have to be performed. Here some recommendations:

- incorporation of chromium-carbide protective layers into the qualification programme
- long-term assurance of the layer systems
- increased friction travel load
- load superimposition during the testing of coat layers
 - friction processes with helium-loop-induced vibrations
 - creep-stressed substrate material with subsequent fretting tests
- determination of the abrasion quantity
- behaviour of unilaterally coated test specimens
- influence of the coating component geometry
- post-examinations on test specimens and on applied operational coatings, reflux of results, if necessary, correction of specified data
- development of quality assurance measures
 - geometry influence
 - tolerance definition of the coating parameters
 - development of acceptance testing procedures, especially nondestructive techniques for testing coatings on original components

Further investigation steps required

Deriving allocatable statements on abrasive wear processes of metallic material pairings under HTR conditions.

- Determination of adhesive strength values
- Determination of quantitative wear, wear effects
- Determination of admissible load limits
- Influence of helium impurities

Impacts of surface coatings on the structural design and heat transfer capability were determined on heat-exchanging components for PNP plants. A reduction of the heat transfer coefficient of chromium-carbide coatings is negligible. Zirconium-oxide duplex layers, which are also used as thermal insulation coatings, make it necessary to take up to approx. 3 % more heat-exchange area into account.

Costs that arise due to the coating itself can amount up to approx. 30 % of the total construction costs of a PNP component. Cost savings can be primarily realized by minimizing necessary coating locations.

Tentative tests performed with nickel-gold-rhodium coatings produced by electroplating under helium and air atmosphere have not led to approaches worth pursuing for use as friction and wear protection.

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TSP-BD 001

Technical Specification for
Surface Finishing Processes
as Friction and Wear Protection
for PNP Components

Nominal Temperature 950 °C

Zirconia Duplex Layer

0.1 Test Certificate and Changes

Object: Specification "Surface Finishing Processes as Friction and Wear Protection for PNP Components"

Y₂O₃ stab. ZrO₂,
NiCrAlY layer

Prepared by: Dept. Ata-E, Schulz, on the basis of /1/
Date: 3/86
Verified:
Changes:

Type of change	Index	Date	Section page	Name	
				changed	verified
Adaptation to progress status /2/	-	7/86	1; 2 and 4		

0.2 Introduction

Statically and dynamically stressed metallic construction materials in contact with each other without surface protection tend to self-welding due to diffusion processes in vacuum and in reducing atmospheres at high temperatures.

If the separation forces acting on the individual components are sufficiently high, the contact points will crack. Seizure phenomena arise leading up to the destruction of the surface.

If welding causes an inseparable connection, operational "sliding" and "separating" of the components cannot take place.

PNP components that must operate with contaminated helium in the temperature range up to 1000 °C are subjected to the above conditions.

0.3 Annexes

- Preparation of Polished Sections – Test Specimens

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References

1. Scope of Application

This specification applies to:

- surface coating on PNP components, tubes, sheets and internal coatings of bores
- depth of internal coating $t = 0.5 - d$

The coated components are subject to the following requirements:

- o operating medium: HTR helium primary/secondary helium with impurities

- primary helium
helium

500	H ₂
15	CO
1.5	H ₂ O
20	CH ₄
5	N ₂
$\times 10^{-6}$	bar

- secondary

1600	CO
500	H ₂ O
1600	N ₂
400	O ₂
$\times 10^{-6}$	bar

- o nominal temperatures

T _{prim}	=	950 °C
T _{sec}	=	900 °C
- o maximum temperatures

T _{prim}	=	1002 °C
T _{sec}	=	918 °C
- o operating life

16 full power years 140,000 hours of operation
(heat-exchanging components)

- o maximum surface pressure

nominal temperature	$p < 5 \text{ N/mm}^2$
up to 850 °C	$p < 10 \text{ N/mm}^2$

Section 1
Technical Specification

- o admissible total elongation of the layer in parallel to the layer surface $< 0.6 \%$

- o maximum accumulated friction travel
 $s < 9 \text{ } 100 \text{ m}$

2. Materials Used

2.1 Base Material

- o design of the material to be coated:
with due regard to the "Rules for designing components and workpieces
suitable for spraying", Instruction Sheet DVS 2308
- o materials:
 - o Inconel 617, Inconel 625, Hastelloy X
- o surface roughness
all areas to be coated with roughness 10 µm; roughness 50 µm
- o surfaces free from oils, grease, chips and impurities

2.2 Blasting Abrasive

Admissible blasting abrasive:

fused alumina corundum (Al_2O_3) according to DIN 8201

Part 6

MKE 0.125 - 0.25

MKE 0,25 - 0.5

MKE 0.5 - 1 for tube wall thicknesses of 4 mm

Type of abrasive: noble corundum

Blasting pressure: 4 bar

Distance: 40 - 80 mm

Blasting angle: 30 - 50 °

2.3 Coating Material

2.3.1 Base coat

Ni Cr Al Y			tolerance	
Ni	balance	%		
Cr	16	%	+ 0.4	%
Al	6	%	+ 0.25	%
Y	0.7	%	+ 0.15	%

- o powder preparation
vacuum-smelted, shielding-gas-atomized
- o powder granulation according to DIN 32529
45 to 22.4 μm or
45 to 5.6 μm
- o layer thickness
 $S > 80 \mu\text{m}$

top coat and base coat
 $S_{\text{tot}} - 210 \mu\text{m} \pm 50 \mu\text{m}$
- o powder drying before spraying $= 100 \text{ }^{\circ}\text{C}$
- o porosity after coating max. 5 % (transverse section)
- o foreign inclusions max. %
- o grain size max. %
- o oxidation rate max. %

2.3.2 Top coat

ZrO₂ + 13 to 16 % Y₂O₃ stabilized DIN 32529

Standard analysis

ZrO ₂	5.3	%
Y ₂ O ₃	2.1	%
HfO ₂	2.2	%
Fe ₂ O ₃	.16	%
SiO ₂	.10	%
TiO ₂	.06	%
MgO	0.04	%
Al ₂ O ₃	0.03	%
CaO	0.01	%

- o preparation
smelted, broken
- o powder granulation according to DIN 32529
63 - 16 µm as a rule
75 - 15 µm exception

The coating producer has to adapt the grain size to the spraying facility, type of powder feeding and spraying capacity. If grain sizes other than those specified above must be used for reasons of plant configuration, this requires prior consultation with the customer.

- o layer thickness
S > 80 µm
- o top coat and base coat
S_{tot} = 210 µm ± 50 µm
- o powder drying before spraying > 100 °C
- o > porosity after spraying
15 > porosity > 10 %
evaluation on longitudinal specimen section
- o foreign inclusions max. %
- o grain size max. %

3. Process Constraints

3.1. Cleanliness of Surfaces and Tools

All devices and machine parts that come into contact with the specified components are designed according to DIN 25410 "Surface cleanliness of components of nuclear installations" Stage 2.

Cleaning of the surfaces to be coated is exclusively performed with chloride-free detergents.

Tools and auxiliaries are subject to the restriction that

- no ferritic materials
 - Cl-free plastics
- must be used.

Component contact with grease, oils, wax, dusts and chloride-containing substances must be excluded.

Gloves must be used for handling the components.

3.2 Blasting

The metal components are to be blasted prior to coating. New noble corundum is to be exclusively used.

The max. blasting time is 60 min. After blasting the components must be freed from residues (brushing, blowing with N₂).

The maximum allowable downtime between blasting (activating the surface area) and spraying is 30 minutes. Blasting and coating should follow each other at short intervals.

3.3 Process

The layers are applied according to the APS process.
Spraying must be automated.

Cooling of the surface to be coated during the coating process so that the temperature does not exceed 220 °C immediately after application of the ZrO₂ top coat.

Cooling is effected by:

- air cooling next to the plasma jet
- rear component cooling by air
- for external tube coating air cooling through the tubes.

It must be ensured that air cooling cannot mix with the argon plasma jet.

(Determination of the oxidation content of the NiCrAlY layer by micrograph evaluation).

3.4 Process Parameters

The data (component-specifically) defined for the qualification of the coating
such as

- production sequence and run
- speed of the device
- feed
- distance from torch
- component process gas
- cooling etc.

must be entered in a production instruction and must not be changed during the entire production sequence. The adjustment data are supervised by the internal quality assurance unit.

4. Production Constraints

4.1 Delivery

The components are delivered finish-machined and numbered. An allocation is to be found in the delivery papers. The delivery lot is defined in the order documents.

4.2 Receiving Inspection

The components to be coated are to be inspected for execution according to specifications. Compliance with contract drawings and documents is to be confirmed in a reception record.

In case of deviations the parts are to be discarded and presented to the customer's experts.

4.3 Plant Monitoring

In order to ensure an unchanged quality,

- the adjustment data of the facility are to be constantly supervised by the quality assurance unit
- work samples are to be produced at the beginning and end of daily production
- before and after each adjustment at the spraying facility
- before and after replacing a powder batch
- always after the 300th coating location or 20 m running coating length. The samples are destructively tested by the contractor.

If the adjustment data or the work samples do not correspond to the specified requirements, new samples are to be produced after a correction of the facility.

If a work sample fails, all the components fabricated after the last valid sample are blocked until further testing.

All checks and samples are to be recorded in an allocated form in a test plan.

4.4 Application of the Surface Layer

The application of the layers takes place according to the data specified by the contractor and the contract drawings.

The surface temperature of the ZrO_2 layer is to be measured by sampling directly after spraying. The temperatures are to be recorded.

If the trailing edge of the layer is not specifically defined in the component drawing, the transition to the base material must be uniformly decreasing (continuous transition to the base material).

Subsequent treatment may be performed by grinding the top coat according to DVS Guideline 2305.

The layer thickness must be 100 % checked. The results (maxima/minima measurement) are to be recorded.

The elimination of defects by overspraying is not allowed.

Repair is only possible after complete layer removal and recoating.

4.5 Accompanying Retained Samples

For each delivery lot 1 sample pair (large and small friction body corresponding to the facility) has to be coated at the beginning and end of production with the adjustment parameters of production.

4.6 Outbound Inspection

The completeness of the components coated according to specifications is to be confirmed in an outbound record.

5. Testing Procedure

5.1 Destructive and Nondestructive Testing

5.1.1 Layer thickness measurements

The layer thickness can be determined in a nondestructive manner by gauges or micrometer measurements or electronically. The thickness of the layer on the work samples is to be taken from the micrographs.

5.1.2 Visual inspection

Visual inspection of the layer surface with respect to

- irregularities
- bulging
- macrocracks

5.1.3 Metallographic inspections on work samples

The following determinations are to be performed on the microsections of the work samples:

- layer thickness measurement
- microcrack determination on longitudinal and transverse section 200-fold magnification
- microcracks and material erosions in the NiCrAlY layer and detachment zones between bond and top coat are not allowed
- determination of porosity
- determination of inclusions

5.1.4 Adhesive strength test

The adhesive strength test which belongs to process testing is performed by:

- indirect testing by thermal shock loading
- sample size: flat specimen 20 x 20 x 15

= 3 min	Test:	
	atmosphere:	helium
= 5 min	heating:	200 °C to 950 °C in t
	residence time:	5 min
	cooling:	950 °C to 200 °C in t
	residence time:	5 min
	number of cycles:	300

After this loading of the sample, no spalling or bulging must be macroscopically visible in the layer.

5.1.5 Temperature measurement

Temperature measurements of the ZrO₂ layer

The measurement on the surface of the top coat is to be performed with a digital indicator instrument (operational inspection device) approx. 5 sec. after spraying.

5.2 Process Testing

(qualification of the coating)

A process test (PT) is to be performed before starting component coating.

The PT comprises:

5.2.1 Spraying of test specimens for the PT

ZrO₂ duplex layer according to the APS process

5.2.2 Micrograph evaluation

- microstructure macrographs M 8 : 1
- microstructure micrographs M 200 : 1
- determination of porosity
- determination of inclusions
- layer thickness determination and edge trailing

5.2.3 Acceptance testing

These tests comprise:

- Rubbing 20 x 20 x 15 mm flat specimens against 50 x 50 x 15 mm flat specimens under 950 °C helium with a surface pressure of 5 N/mm² and a friction travel of 20 m.

The friction coefficient obtained must not exceed $\mu = 0.8$.

- Thermal shock on flat specimens

The adhesive strength must be demonstrated on the thermal shock test specimens (flat specimens 20 x 20 x 15 in thickness) with 300 cycles in air (200 °C to 950 °C and 950 °C to 200 °C; heating within 3 min., cooling within 5 min., 5 min. residence time in each case).

After this loading neither spalling nor bulging of the duplex layer should be observable.

5.3 Testing Instructions

The contractor draws up a chronologically ordered production and test sequence plan (PTP). This plan contains all production and testing steps necessary for executing the order. The PTP must be presented to the customer for verification prior to the start of production.

5.3.1 Producer tests

The coating producer must provide evidence of the necessary apparatus and staff prerequisites.

This evidence should comprise:

- sufficient and suitable storage possibilities for the components
- clean-condition production possible; DIN 25410, Stage 2
- suitable blasting, coating equipment
- the "Acceptance conditions and quality checks for thermal spraying

facilities" according to DIN 32521 must be fulfilled.

5.3.2 Production-accompanying tests, inspections and acceptance

The customer and the appointed testing bodies appointed reserve the right to supervise the coating process. The customer must be constantly allowed access during the production time to all production and test facilities in which parts of the order are treated.

5.3.2.1 Inspections, acceptance and proofs

The following tests are carried out and/or initiated by the contractor.

In the following steps subject to testing

W	means	company expert of the contractor
S	means	expert of the customer
()	means	at the expert's discretion

The customer may also entrust other experts with testing on his behalf.

Tests to be carried out by the expert must be announced to the customer 8 working days prior to the acceptance date.

The listed proofs are to be presented to the customer in triplicate at the latest 3 calendar weeks after completion of the delivery lot.

Section 5
Technical Specification

Type	Acceptance by:	Testing scope	Proof
1. <u>Producer evaluation</u>	S	1.1 - 1.4	record
1.1 Clean condition - Cl-free parts	S	DIN 25410, Stage 2	
1.2 Storage	S	compliance with DIN 25410, Stage 2	
1.3 Acceptance conditions and quality checks for thermal spraying facilities	W	DIN 32521	record
1.4 Checking the process test	S	pts. 2.1 - 2.4	record
2. <u>Process test</u>			
2.1 Test specimen fabrication	W (S)		
2.2 Micrograph evaluation -macrograph M 8 : 1 -micrograph M 200 : 1	W (S)	longitudinal and transverse section of 2 specimens	
2.3 Determination of - porosity - foreign inclusions - grain size - oxidation rate of bottom layer	W (S)	4 x per section	record
2.4 Acceptance testing - rubbing tests - thermal shock tests	W (S) W (S)	2 flat specimen pairs 2 flat specimens	record record
3. <u>Production and test sequence plan</u>	S	execution according to specifications	plan to be submitted before the start of production
4. <u>Visual component inspections</u>			
4.1 Receiving inspection	W	sampling 10 %	record
4.2 Outbound inspection	W (S)	sampling 10 %	record

5. <u>Dimensional inspection</u>				
5.1	Component	W	sampling	record
5.2	Production	W	100 %	record
	- layer thickness		and	
	- irregularities	(S)	sampling	
5.3	Final	W (S)	sampling	record
	inspection		10 %	
	- layer length			
	- irregularities			
	- edge trailing			
	- bulging			
	- macrocracks			
6. <u>Coating materials</u>				
6.1	Detergents	W	chemism	DIN 50049 2.2
6.2	Blasting	W	abrasive replacement	DIN 50049
	abrasives		after 60 min of operation,	2.2
			chemism, granulation	
6.3	Layer	W	chemism, granulation	DIN 50049
	material			2.2
7. <u>Production checks</u>				
7.1	Checking the	W (S)	continual checks	record
	parameters specified in		sampling	
	the production instruction			
7.2	Metallographic tests	W	per sample according to	DIN 50049
	of the work samples		Section 4, point 3	2.2
	- microcracks V 200 : 1		on longitudinal and	
	- material erosion		transverse section	
	- porosity			
	- inclusions	(S)	sampling	
8.	<u>Shop acceptance</u>	W (S)	successful completion of	record
			testing, samples, handing	
			over of proofs and	
			component delivery	

5. Packaging, Storage and Transport

Packing is intended to provide protection against damage and contamination during storage and transport. The parts are to be covered by PE foil after component coating.

Storage must be dry in closed rooms. The coated parts have to be protected against shock loads during transport.

All the information of importance concerning contents, storage and transport must be visibly applied on the packing or the components.

7. References

- /1/ Demus, "Technische Spezifikation - Luftplasmagespritztes Schichtsystem $\text{ZrO}_2(\text{Y}_2\text{O}_3)\text{-NiCrAlY}$ ", PNP-5179-CB-GHRA 000177, dated 18.05.1983
- /2/ Demus, "Technische Spezifikation - Luftplasmagespritztes Schichtsystem $\text{ZrO}_2(\text{Y}_2\text{O}_3)\text{-NiCrAlY}$ " received from HRB on 20.06.1986 at the UG 1, AK 8 meeting

Preparation of Polished Sections

Embedding: warm in suitable plastic compound (e.g. resin 5),
load 1000 kg, diameter 30 m

Grinding: a)

- 1) suitable grinding devices (e.g. Planpol, Pedemax)
- 2) 64 µm diamond-bonded grinding wheel
- 3) load 60 N (on 3 sections)
- 4) grinding time 30 minutes
- 5) wheel speed 150 rpm
(same direction of rotation)

b) as above, except:

- 2) Petrodisc M: 6 µm diamond spray
- 4) 15 minutes

Polishing:

a)

- 1), 3) and 5) as under grinding a)
- 2) 3 µm diamond fabric, e.g. PAN-W
- 4) 15 minutes

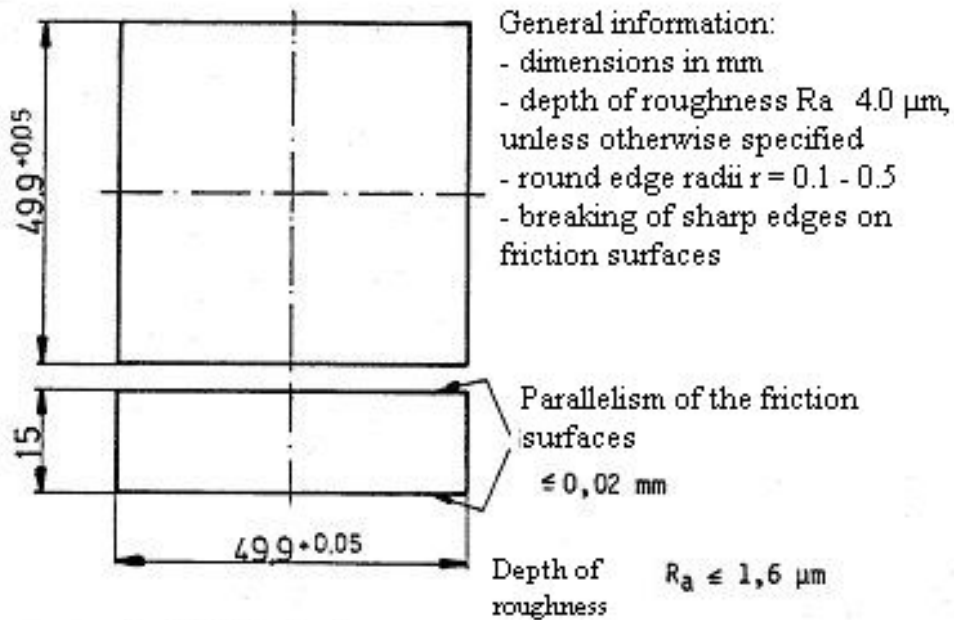
b)

- 2) 1 µm diamond fabric, e.g. NAP fabric
- 4) 10 minutes

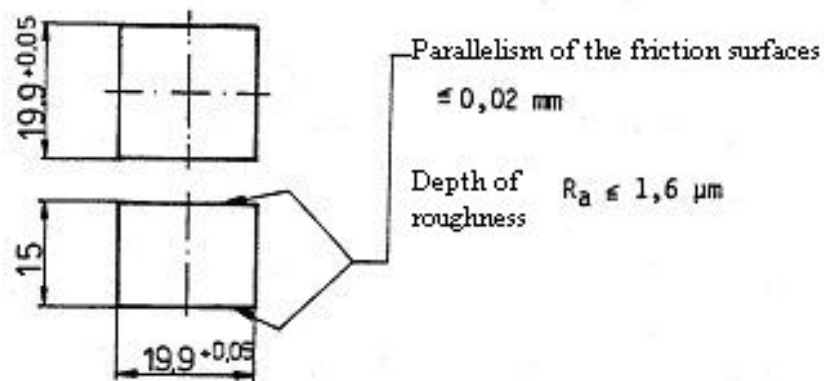
Intermediate steps: rinsing with H₂ and ethanol

Test specimen (material as used for the component)

Large friction body



Small friction body



TSP-BD 002

Technical Specification for Surface Finishing Processes as Friction and Wear Protection for PNP Components

- A - UCAR LC 1 C chromium-carbide cermet
application range < 700 °C
- B - UCAR LC 24/22 chromium-carbide duplex
application range < 850 °C

0.1 Test Certificate and Changes

Object: Specification "Surface Finishing Processes as Friction and Wear Protection for PNP Components"

chromium carbide cermet A – UCAR LC 1 C

chromium carbide duplex

B – UCAR LC 24/22

Prepared by: Dept. Ata-E, Schulz

Date: 3/86

Verified:

Changes:

Type of change	Index	Date	Section page	Name	
				changed	verified
	-				

0.2

Introduction

Statically and dynamically stressed metallic construction materials in contact with each other without surface protection tend to self-welding due to diffusion processes in vacuum and in reducing atmospheres at high temperatures.

If the separation forces acting on the individual components are sufficiently high, the contact points will crack. Seizure phenomena arise leading up to the destruction of the surface.

If welding causes an inseparable connection, operational "sliding" or "separating" of the components cannot take place.

For PNP components that must operate with contaminated helium at high temperature level, the above conditions cannot be excluded.

0.3

Annexes

1.

Test Specimens

04.	Contents	Page
0.1	Test Certificate and Changes	
0.2	Introduction	
0.3	Annexes	
0.4	Contents	
1.	Scope of Application	
2.	Materials Used	
3.	Process Constraints	
4.	Production Constraints	
5.	Testing Procedure and Test Specifications	
6.	Packaging, Storage and Transport	

1. Scope of Application

This specification applies to:

- surface coating of tubes, sheets and internal coatings of bores
- depth of internal coating $t = 0.5 - d$

The coated components are subject to the following requirements:

- o operating medium: HTR helium primary/secondary

- primary helium

500 H₂
15 CO
1.5 H₂O
20 CH₄
5 N₂
x 10⁻⁶ bar

secondary helium

1600 CO
> 500 H₂O
1600 N₂
400 O₂
x 10⁻⁶ bar

	A	B
o nominal temperatures	T _{prim} = 700 °C T _{sec} = 700 °C	850 °C 850 °C
o maximum temperatures	= nominal temperatures	

- o operating life
16 full power years = 140,000 hours of operation
(heat-exchanging components)
- o maximum surface pressure at
nominal temperature $p = 20 \text{ N/mm}^2$
- o accumulated friction travel $S = 20 \text{ m}$

2. Materials Used

2.1. Base Material

- o design of the material to be coated:
with due regard to the "Rules for designing components and workpieces suitable for spraying", Instruction Sheet DVS 2308
- o materials:
nickel-base alloys such as Inconel 617, high-alloyed austenitic steels
- o surface roughness
all areas to be coated with
Ra = 10 µm; Rt = 50 µm
- o surfaces free from oils, grease, chips and impurities

2.2 Blasting Abrasive

Admissible blasting abrasive:

fused alumina corundum	(Al ₂ O ₃)
MKE 0.125 - 0.25	DIN 8201
MKE 0,25 - 0.5	DIN 8201
Type of abrasive:	noble corundum
Blasting pressure:	5 bar

2.3 Coating Material

A ... $\text{Cr}_3\text{C}_2/\text{NiCr}$, cermet layer LC 1C

B ... $\text{Cr}_{23}\text{C}_6 - \text{Cr}_{23}\text{C}_6/\text{NiCr} - \text{Ni Cr}$; duplex layer LC 24/22

o Standard analyses

A ... cermet layer

type	wt %
Cr_3C_2	88 - 90
Ni Cr binder with Ni	74 - 82
Cr	18 - 22.5
C	0.2
Co fraction	0.1

After coating:

- | | | |
|---|-------------------------------------|-----------------------------------|
| o | oxide inclusions | max. 3.0 % |
| o | nonmetallic and metallic inclusions | max. 0.5 % |
| o | grit inclusions | max. 22.0 % |
| o | porosity | max. 1.0 % (reference chart) |
| o | grain size | max. 50 μm |
| o | hardness | DIN 50133 HV 0.3 = 650 - 900 |

B ...duplex layer

- o bottom layer Cr 23 + 80 Ni/20 Cr; LC 24

type	wt %
Cr	71 - 81
Ni	10 - 20
C	2.4 - 3.6
O ₂	max. 3.5
N ₂	max. 1.0
H ₂	max. 0.05
Co	max. 0.5
Fe	max. 1.0
Mg	max. 1.0
Si	max. 0.5
others	max. 0.2

After coating:

o	oxide fraction		max. 4 %
o	nonmetallic inclusions		max. 1 %
o	globular fraction		max. 1 %
o	porosity	max. 1 %	
o	grain size	30 - 50 µm	
o	hardness	DIN 50133	HV 0.3 = 600 - 800

- top coat – Cr23 C6; LC 22
-

type	wt %
Cr 23 C6	100

After coating:

o	oxide fraction	max. 1.5 %	
o	impurities	not allowed	
o	globular fraction	not allowed	
o	porosity	max. 1.5 % (reference chart)	
o	grain size	30 - 50 μm	
o	hardness	DIN 50133	HV 0.3 = 700 - 900
o	grit inclusions	max. 22 % with 200-fold magnification	

Layer thicknesses

A	cermet layer	$s = 0.08 + 20 \mu\text{m}$
B	duplex layer	
	LC 24	$s = 0.05 + 10 \mu\text{m}$
	LC 22	$s = 0.03 + 10 \mu\text{m}$
total coating thickness		$s = 0.08 + 20 \mu\text{m}$

Coating producer: Union Carbide

3. Process Constraints

3.1 Cleanliness of Surfaces and Tools

All devices and machine parts that come into contact with the specified components are designed according to DIN 25410 "Surface cleanliness of components of nuclear installations" Stage 2.

Cleaning of the surfaces to be coated is exclusively performed with chloride-free detergents.

Tools and auxiliaries are subject to the restriction that

- no ferritic materials
 - Cl-free plastics
- must be used.

Component contact with grease, oils, wax, dusts and chloride-containing substances is to be excluded.

Gloves must be used for handling the components.

3.1 Blasting

The metal components are to be blasted prior to coating. New noble corundum is to be exclusively used.

The max. blasting time is 60 min. After blasting the components must be freed from residues (brushing, blowing with N₂).

The maximum allowable downtime between blasting (activating the surface area) and D-gun spraying is 30 minutes. Blasting and coating should follow each other at short intervals.

3.3 Process

The layers are applied according to the UCAR D-gun process. Spraying must be automated.

Cooling is to be such that a component temperature of 150 °C is not exceeded.

The parameter adjustment of the coating facility is effected according to SPI (Standard Practice Instructions) and production is subject to QCI (Quality Control Instructions).

A	LC 1C	no. 12 11
B	LC 24	no. 12 23
	LC 22	no. 12 24

The data (component-specifically) defined in qualifying the layers LC 1C; LC 24/22 for the coating process such as

- feed
- detonation sequence
- speed of the device
- component-gun distance
- process gas
- cooling etc.

are to be entered in a production instruction and must not be changed during the entire production sequence.

The adjustment data are constantly supervised by the quality control unit of UC.

4. Production Constraints

4.1 Delivery

The components are delivered finished-machined and numbered. An allocation is to be found from the delivery papers. The delivery lot is defined in the order documents.

4.2 Receiving Inspection

The components to be coated are to be inspected for execution according to specifications. Compliance with the contract drawings and documents is to be confirmed in a reception record.

In case of deviations the parts are to be discarded and presented to the customer's experts.

4.3 Plant Monitoring

In order to ensure an unchanged quality:

adjustment data of the facility must be constantly supervised by the quality control unit

work samples are to be produced according to UC standard at the beginning and end of daily production

-before and after each adjustment at the spraying facility

before and after replacing a powder batch

- always after the 300th coating location or 20 m running coating length.

The samples are destructively tested by UC.

If the adjustment data or the work samples do not correspond to specified requirements, new samples are to be produced after a correction of the facility.

If a work sample fails, all the components fabricated after the last valid sample are to be blocked until further testing.

All checks and samples are to be recorded on an allocated form in a test plan.

Section 4 Technical Specification

Application of the Surface Layer

The application of the layers takes place according to Union Carbide standard practice instructions, specified data and associated drawings.

If the trailing edge of the layer is not specifically defined in the component drawing, the transition to the base material must be uniformly decreasing.

Subsequent treatment may be performed by grinding the top coat according to DVS Guideline 2305.

The layer thickness must be 100 % checked. The results (maxima/minima measurement) are to be recorded.

The elimination of defects by overspraying is not allowed.

Repair is only possible after complete layer removal and recoating.

4.5 Accompanying Retained Samples

For each delivery lot 1 sample pair (large and small friction body corresponding to the facility) has to be coated at the beginning and end of production with the adjustment parameters of production.

Outbound Inspection

The completeness of the components coated according to specifications is to be confirmed in an outbound record.

5. Test Procedure

5.1 Destructive and Nondestructive Testing

5.1.1 Layer thickness measurements

The layer thickness can be determined in a nondestructive manner by gauges or micrometer measurements or electronically. The thickness of the layer on the work samples is to be taken from the micrographs.

5.1.2 Visual inspection

Visual inspection of the layer surface with respect to

- irregularities
- bulging
- macrocracks

5.1.3 Metallographic inspections on work samples

The following determinations are to be performed on the microsections of the work samples:

- layer thickness measurement
- microcrack determination on longitudinal and transverse section – 200-fold magnification – microcracks and material erosions are not allowed
- determination of porosity (QCI reference chart)
- determination of inclusions (QCI reference chart)
- hardness test according to DIN 50133 Sheet 2 is to be performed on the layer in the section plane. 10 single measurements.

The average hardness is in the range of

A	LC 1C	HV 0.3	650 - 900
B	LC 24, 22	HV 0.3	600 - 900

5.1.4 Adhesive strength test

The adhesive strength test which belongs to process testing is performed by:

- indirect testing by thermal shock load
sample size: flat specimen 20 x 20 x 15

Test:

atmosphere:	helium
heating:	200 °C to 950 °C in t = 3 min
residence time:	5 min
cooling:	950 °C to 200 °C in t = 5 min
residence time:	5 min
number of cycles:	300

After this loading of the sample, no spalling or bulging of the cermet or duplex layer must be present.

5.2 Process Testing

(qualification of the coating)

A process test (PT) is to be performed before starting component coating.

The PT comprises:

5.2.1 Spraying of test specimens for the PT

A ... LC 1 C	SPI and QCI	no. 1211
B ... LC 24/22	SPI and QCI	no. 1223/24

5.2.2 Micrograph evaluation

- microstructure macrographs M 8 : 1
- microstructures micrographs M 200 : 1
- hardness test DIN 50133 HV 0.3
- determination of porosity
- determination of inclusions
- layer thickness determination and edge trailing

5.2.3 Acceptance testing

These tests comprise:

Rubbing 20 x 20 x 15 mm flat specimens against 50 x 50 x 15 mm flat specimens under 850 °C helium with a surface pressure of 5 N/mm² and a friction travel of 20 m.

The friction coefficient obtained must not exceed $\mu = 0.8$.

Thermal shock on flat specimens

The adhesive strength must be demonstrated on the thermal shock test specimens (flat specimens 20 x 20 x 15 in thickness) with 300 cycles in air (200 °C to 950 °C and 950 °C to 200 °C; heating within 3 min., cooling within 5 min., 5 min. residence time in each case).

After this loading neither spalling nor bulging of the chromium-carbide layer should be observable.

5.3 Testing Instructions

The contractor draws up a chronologically ordered production and test sequence plan (PTP). This plan contains all production and testing steps necessary for executing the order. The PTP must be presented to the customer for verification prior to the start of production.

5.3.1 Producer evaluation

The coating producer must provide evidence of the necessary apparatus and staff prerequisites.

This evidence should comprise:

- sufficient and suitable storage possibilities for the components
- clean-condition production possible; DIN 25410, Stage 2
- suitable blasting, coating facilities
- the "Acceptance conditions and quality checks for thermal spraying facilities" according to DIN 32521 must be fulfilled.

5.3.2 Production-accompanying tests, inspections and acceptance

The customer and the appointed testing bodies reserve the right to supervise the coating process. The customer must be constantly allowed access during the production time to all production and test facilities in which parts of the order are treated.

5.3.2.1 Inspections, acceptance and proofs

The following tests are carried out and/or initiated by the contractor.

In the following steps subject to testing

W	means	company expert of the contractor
S	means	expert of the customer
()	means	at the expert's discretion.

The customer may also entrust other experts with testing on his behalf.

Tests to be carried out by the expert must be announced to the customer 8 working days before the acceptance date.

The listed proofs are to be presented to the customer in triplicate at the latest 3 calendar weeks after completion of the delivery lot.

Type	Acceptance by:	Testing scope	Proof
1. <u>Producer evaluation</u>	S	1.1 - 1.4	record
1.1 Clean condition - Cl-free parts	S	DIN 25410, Stage 2	
1.2 Storage	S	compliance with DIN 25410, Stage 2	
1.3 Acceptance conditions and quality checks for thermal spraying facilities	W	DIN 32521	record
1.4 Checking the process test	S	pts. 2.1 - 2.4	record
2. <u>Process test</u>			
2.1 Test specimen fabrication	W (S)	SPI, QCI	record
2.2 Micrograph evaluation - macrograph M 8 : 1 - micrograph M 200 : 1	W (S)	longitudinal and transverse section of 2 specimens	record
2.3 Determination of - porosity - nonmetallic and metallic inclusions - oxide inclusions - hardness according to DIN 50133 HV 0.3	W (S)	4 x per section	record
2.4 Acceptance testing - rubbing tests - thermal shock tests	W (S) W (S)	2 flat specimen pairs 2 flat specimens	record record

3. <u>Production and test sequence plan</u>	S	execution according to specifications	plan to be submitted before the start of production
4. <u>Visual component inspections</u>			
4.1 Receiving inspection	W	sampling 10 %	record
4.2 Outbound inspection	W (S)	sampling 10 %	record
5. <u>Dimensional inspection</u>			
5.1 Component receipt	W	sampling	record
5.2 Production	W	100 %	record
- layer thickness	(S)	and sampling	
- irregularities	W (S)	sampling 10 %	record
5.3 Final inspection			
- coating length			
- irregularities			
- edge trailing			
- bulging			
- macrocracks			
6. <u>Coating materials</u>			
6.1 Detergents	W	chemism	DIN 50049 2.2
6.2 Blasting abrasives	W	abrasive replacement after 60 min. of operation, chemism, granulation	DIN 50049 2.2
8. <u>Shop acceptance</u>	W (S)	successful completion of testing, samples, handing over of proofs and component delivery	record

6. Packaging, Storage and Transport

Packing is intended to provide protection against damage and contamination during storage and transport. The parts are to be covered by PE foil after component coating.

Storage must be dry in closed rooms. The coated parts have to be protected against shock loads during transport.

All the information of importance concerning contents, storage and transport must be visibly applied on the packing or the components.

Test specimens

Large friction body

General information:

- dimensions in mm
- depth of roughness $R_a \leq 4.0 \mu\text{m}$, unless otherwise specified
- edge rounding radii $r = 0.1 - 0.5$
- breaking of sharp edges on friction surfaces
- parallelism of the friction surfaces $\leq 0.02 \text{ mm}$
- depth of roughness $R_a \leq 1.6 \mu\text{m}$

Small friction body

- parallelism of the friction surfaces $\leq 0.02 \text{ mm}$
- depth of roughness $R_a \leq 1.6 \mu\text{m}$