

New HVOF Installation Technology for Super-Fine Powders –10µm and Internal Coatings

If HVOF technology is to become more widespread on the market, a major aspect of process development must be to reduce the costs for HVOF layers. HVOF technology has concentrated on powders with particle sizes from –53 +15µm to finer grains of –25 +5µm. Production costs can be significantly reduced by using super-fine powders with grain sizes of –10µm.

Until recently, the poor flow and measuring properties of super-fine powders made accurate measurement and low-pulsation feeding into the HVOF gun seem impossible. Moreover, HVOF guns which have been optimized for standard grain sizes tend to overheat the super-fine grain particles, thus limiting their use.

Thermico have developed an HVOF installation technology that allows the use of grain sizes of –10µm, at last broadening the range of possible applications of the HVOF process.

As part of the EU-funded GROWTH project, »NANO HVOF – The replacement of hard chromium coatings for mechanical components through high-pressure nanostructure HVOF coatings« (G5RD-CT-2000-00231), coatings consisting of super-fine WC-Co and CrC NiCr powders and uses for super-fine powder in the automotive industry, such as engine valves, piston rings and hydraulic bars, developed, using super-fine CrC NiCr powders were developed and characterized. The ultimate target is to develop cost-effective applications with contour-tracking, smooth, thin, high-performance HVOF layers, as well as cutting costs by reducing material requirements, and shortening not only spraying times but also the grinding and polishing procedures.

The project led to the development of an HVOF technology for the internal coating of pipes with internal diameters of up to 150mm. By using super-fine powders, the thermal strain on the components can be considerably reduced, allowing thermally uncritical internal HVOF layers.

EU GROWTH Project »NANO-HVOF«

April 2000 saw the launch of the EU-funded GROWTH Project, »NANO-HVOF«, aimed to develop chromium replacement layers based on CrC NiCr for applications in the automotive industry, such as

- engine valves,
- piston rings, and
- hydraulic components.

This project was inspired by increasing pressure from the automotive industry on their suppliers to develop alternatives for hard chromium. EU

Regulation 2000/53/EC prohibits the use of hexavalent chromium, lead, cadmium and mercury in automobiles and transport vehicles of up to 3.5 tons. The hard chromium layer itself does not contain hexavalent chromium, but large amounts are used during the production process, and concern that the hard chromium layer could become subject to similarly restrictive regulations has resulted in considerable efforts to develop alternatives to hard chromium.

If hard chromium layers are to be replaced, the CrC-NiCr and WC-CoCr systems have the potential to fulfill the tribological and corrosive requirements. Hard chromium will only be replaced if the alternatives are comparable in costs. HVOF layers featuring conventional powders are many times more cost-intensive than a conventional hard chromium layer. The target is to reduce material requirements by using super-fine powders, and minimize grinding costs through contour-tracking spraying results.

The work packages of the NANO HVOF project basically look at the following areas:

- development of a model for the HVOF process, using powders with grain sizes of below 10 μ m;
- development of CrC NiCr powders with grain sizes of below 10 μ m;
- development of an HVOF installation, powder feeder and gun for super-fine powders;
- development, coating and characterization of layers for test specimens, tribo-tests and engine components;
- examination of the coated components in field and engine tests;
- analysis of the technical, economic and environmental data in comparison to hard chromium.

Excerpts from the results produced by the project are outlined below.

Powder Development for Super-Fine Grain Sizes

Decisive in the selection of production methods for super-fine grain sizes $\leq 10\mu\text{m}$ was the requirement of the NANO HVOF industry partners to use powders which can be produced at reasonable cost in serial production. The following two methods were selected.

Method one consisted of precipitating standard powders by air separation, while method no. 2 was based on the crushing of standard powders through ball-milling and subsequent air separation. In cases of WC Co agglomerates, sintered raw materials were used, while sintered raw materials as well as agglomerated, sintered and subsequently plasma-remelted raw materials were used for CrC-NiCr agglomerates.

The grinding of raw powders with grain sizes of $\leq 10\mu\text{m}$ leads to broken, sharp-edged particles with very poor flow properties. In contrast, the fine fractions taken from agglomerated, sintered raw powders basically consist of ball-shaped particles with considerably superior processing properties.

The carbide size of the tungsten carbides in the agglomerated and sintered WC powders used were in the 1-3 μm range, while carbides in the 1-5 μm range were used for the CrC-NiCr powders. A partly nano-structured chromium carbide structure was created by plasma-remelting the

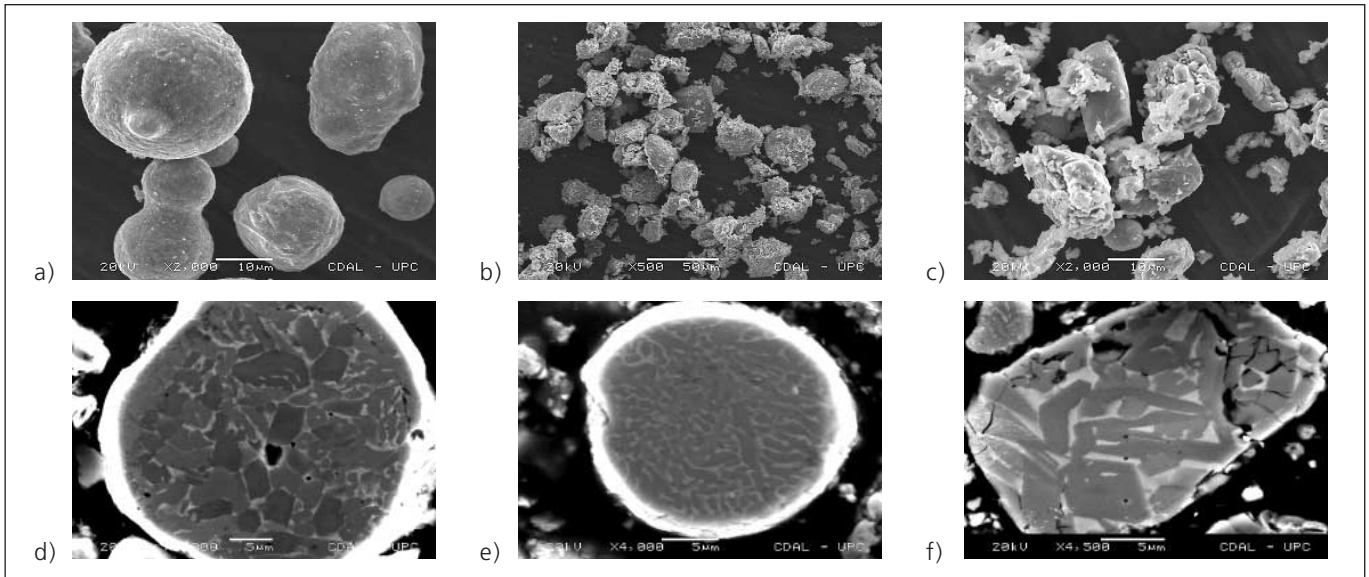


Fig. 1 a) + d) Powder CrC-NiCr20 75-25, agglomerated, sintered and plasma-remelted
 b) + e) Power CrC-NiCr20 60-40, agglomerated, sintered, plasma-remelted and ball-milled
 c) + f) Powder CrC-NiCr20 75-25, agglomerated, sintered and ball-milled

CrC-NiCr powders. The melting and subsequent congelation cause a predominantly submicron chromium carbide structure, marked mainly by Cr₇C₃ and Cr₂₃C₆-type chromium carbides with sizes of between 200 nm and 1000 nm and residual chromium carbides from the raw material.

NANO HVOF Powder Feeders for Super-Fine Powders

The NANO HVOF powder feeder is based on Thermico's MPF. To overcome the poor flow properties of super-fine powders of $\sim 10\mu\text{m}$, a vibration system to fluidize the powder was developed, creating a condition featuring flow properties similar to a fluid medium. A feeder wheel based on a volumetric feeding principle feeds the powder into a carrier gas stream, allowing accurate measurement.

As documented in the main sketch, an oscillatory powder container is activated by a vibration mechanism, fluidizing the powder inside the container. Amplitude, amplitude direction, and frequency depend on the control and design of the vibrator and container used, as well as on the powder and the position of the vibration activator. The flow direction is determined by amplitude and amplitude direction. The fluidized powder circulates in the container, flowing along the container base through a connecting channel into the feeder wheel, which feeds it into the carrier gas stream. Inside the feeder wheel, the fluidization of the powder is suspended to a large extent. The powder feed rate is proportional to the rotation velocity of the feeder wheel.

The combination of fluidization on the one hand and volumetric measurement through the feeder wheel on the other allows the accurate measurement of super-fine powders with grain sizes of $\sim 10\mu\text{m}$ and variations of up to $\pm 5\%$ of the mean, feeding them into the HVOF gun. The construction principle allows powder measurement independent of the carrier gas flow via the rotary frequency of the feeder wheel. The carrier gas flow is mass flow-controlled with an accuracy of $\pm 2\%$ from



Fig. 2 Thermico MPF powder feeder

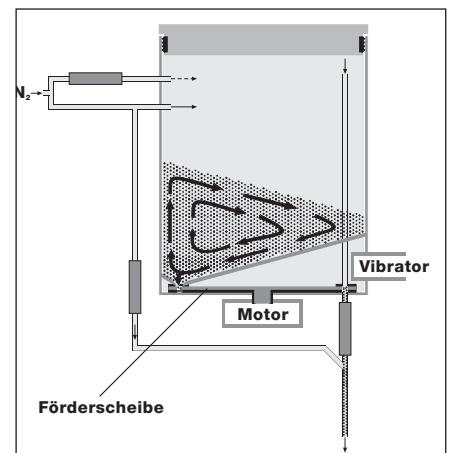


Fig. 3 Principle sketch MPF Powderfeeder

the chosen flow values. The diagram features the typical feeder curve of CrC NiCr20 75 25 powders with particle sizes of $-10\mu\text{m}$ and a fractured chromium oxide powder with particle sizes of $-12 +2\mu\text{m}$.

Carbide Jet System NANO HVOF Gun

The CJS HVOF gun is a fuel gas kerosene oxygen HVOF gun featuring a radial powder feeding system in the supersonic range of the process gas flow. Thermico's CJS gun technology makes use of the different dynamics caused by the combustion of the liquid fuel, kerosene, and a fuel gas, such as methane or hydrogen. This design makes it possible to control the flame temperature through the kerosene feed and the flame velocity through the fuel gas feed.

The advantage of the CJS gun system's construction lies in its modular design and the simple exchangeability of nozzle configurations, consisting of combustion chamber, powder feed and acceleration nozzle. Nozzle configuration K1 is used for difficult-to-melt powders, such as WC Co with grain sizes of $-125 +75\mu\text{m}$ or 75CrC 25 NiCr20 with grain sizes of $-63 +32\mu\text{m}$. K2 and K4.2 are used for standard grain sizes in the $-45 +15\mu\text{m}$ and $-25 +5\mu\text{m}$ range. The »cold-working« nozzle configuration K5.2 was developed specifically for the Nano HVOF project.

The design of the CJS combustion chamber is marked by a relatively small combustion chamber volume in the high pressure range, designed for the combustion of a hydrogen-oxygen flame. The gas velocity of the HVOF flame is basically controlled by the hydrogen combustion. The kerosene is burned in another section of the combustion chamber, where the flame reaches supersonic velocity. If more velocity is required, the hydrogen flow is increased. If the flame temperature is too high, the kerosene rate is reduced. This process allows the precise control of an ideal operating point. The characteristics of the parameter field of each nozzle configuration from hot / slow to cold / fast is defined by a variation in the combustion chamber in the high pressure component and the supersonic range section.

The development of a gun for super-fine powders inevitably led to a nozzle configuration which feeds the powder into the flame in a »cold« zone, where the combustion reaction is almost complete. The expansion of the high-pressure section and the supersonic range of the combustion chamber have produced simple operating points which do not overheat super-fine powders, allowing their application at a rate of 50 – 60%.

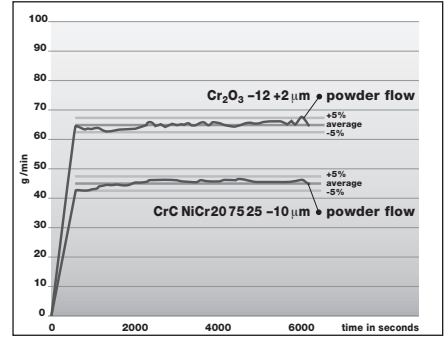


Fig. 4 Typical feeding curves with MPF



Fig. 5 CJS HVOF gun

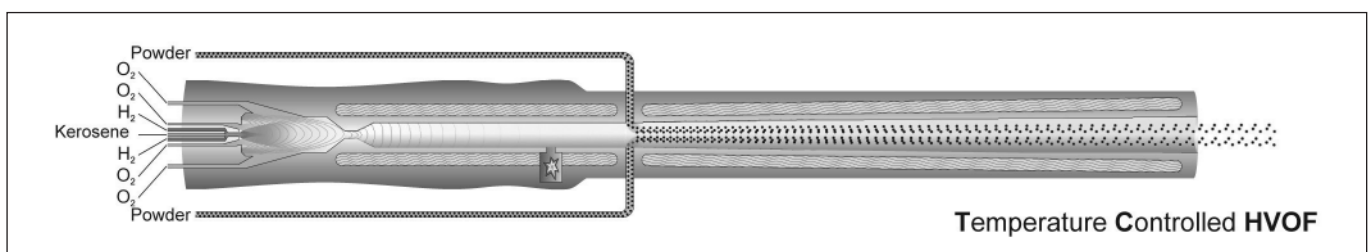


Fig. 6 Principle sketch of the CJS HVOF gun

Development of NANO HVOF Control Unit C-CJS

Used in the NANO HVOF project and enhanced further, the C-CJS (Computerized Carbide Jet System) unit concept combines the comfort of a computer-controlled unit and the precision of a precision class A installation, featuring mass flow-controlled gas and kerosene lines. Remote diagnosis and technical support can be provided by telephone.

This concept allows optimized functionality and mobility. For HVOF, the control unit is composed of four individual recase units. The extension to plasma control requires an additional fifth recase unit. Placed on top of each other, these components make up an ergonomic, mobile operating tower.

- The complete control unit consists of a maximum of five recase units
- Recase 0 electrical control unit
 - Recase 1 oxygen lines
 - Recase 2 fuel gas and inert gas lines
 - Recase 3 water and kerosene lines
 - Recase 4 plasma gas lines

Mobility

The recase design allows HVOF control and gas cabinets a high degree of mobility. After the tube packets have been released, the complete unit can be pushed to the next cabinet and started up there. The mass flow control, valves, filters, pressure sensors and gas back-flow prevention devices of a complete gas line have been fitted into the condensed space of a block. This space-saving solution makes it possible to fit the full gas control cabinet into a compact, modular and thus mobile system with clear advantages compared to a stationary installation which is linked firmly to one cabinet.

For field work, the recase units are easily disassembled and transported in an estate car.

Functionality

The multi-functional, mass flow-controlled HVOF control unit, C-CJS, may be operated in combination with all commercially available HVOF guns. A PLC controls the process in the background, while it is visualized on a computer screen. The following single menus simplify the operation and control of the parameter settings in the HVOF process:

- selection of HVOF gun
- control menu HVOF gun with parameter representation in bar charts
- selection of spraying formula and formula memory
- gas inflow pressure control
- water-cooling flow control, in- and outgoing temperature
- ignition parameters
- gas and kerosene trends
- cooling-water trends
- parameter history
- alarm journal history
- PLS status and service menu => Force individual control of all actuators and sensors
- parameter pressure protocol



Fig. 7 Recase design of the C-CJS



Fig. 8 Touchscreen operation of the C-CJS

**Comparison of HVOF CrC-NiCr and WC-Co Layers
Sprayed with Standard Powders and Super-Fine Powders – Layer
Properties and Tribology**

Layer optimization and production of the CrC NiCr and WC Co super-fine powder layers were accomplished with the HVOF gun, CJS K5.2. The CrC NiCr system is oxidation-sensitive, which also materialized in the layer optimization cycles of the powders. A high degree of adhesion and cohesion in the CrC NiCr layers applied with super-fine powders tended to be achieved through »hot parameters«, which led to a clearly higher oxidation rate than in standard powders. However, the oxide content had no negative effects on the tribo-tests.

Figures 9 a) and e) feature a CrC NiCr20 75-25 layer of agglomerated sintered powder with grain sizes of $-30 +10\mu\text{m}$ featuring a typical low-oxide structure, low porosity and a hardness of 960 HV0.3. Figures 9 b) and f) feature a layer of the same powder material with a grain size of $-10\mu\text{m}$. This layer has a finer structure and very low porosity. The hardness of the layer is 10–15% below that of the layer applied with the coarser powder.

In cases where the WC is overheated and dissolved in the Co matrix, WC Co has a tendency to produce unwelcome, partly amorphous mixed Co (W,C) crystals and brittle $\text{Co}_3\text{W}_3\text{C}$ and $\text{Co}_6\text{W}_6\text{C}$ phases. The layer optimization of the agglomerated sintered WC Co 83 17 power with grain sizes of $-15 +5\mu\text{m}$ proved that the spraying parameters may be adjusted in a relatively wide range without producing an unwelcome high dissolution of the WC. The WC Co 83 17 layer in figures 9 d) and h) has a very low porosity with a typical hardness of 1230 HV 0.3. The tungsten carbides are sharp-edged, hardly rounded and have, for the most part, a light W2C edge. In terms of WC Co, this structure is an indication of a successful bonding of carbide and matrix. This layer had the lowest wear rate in the pin-on-disk tribo-test.

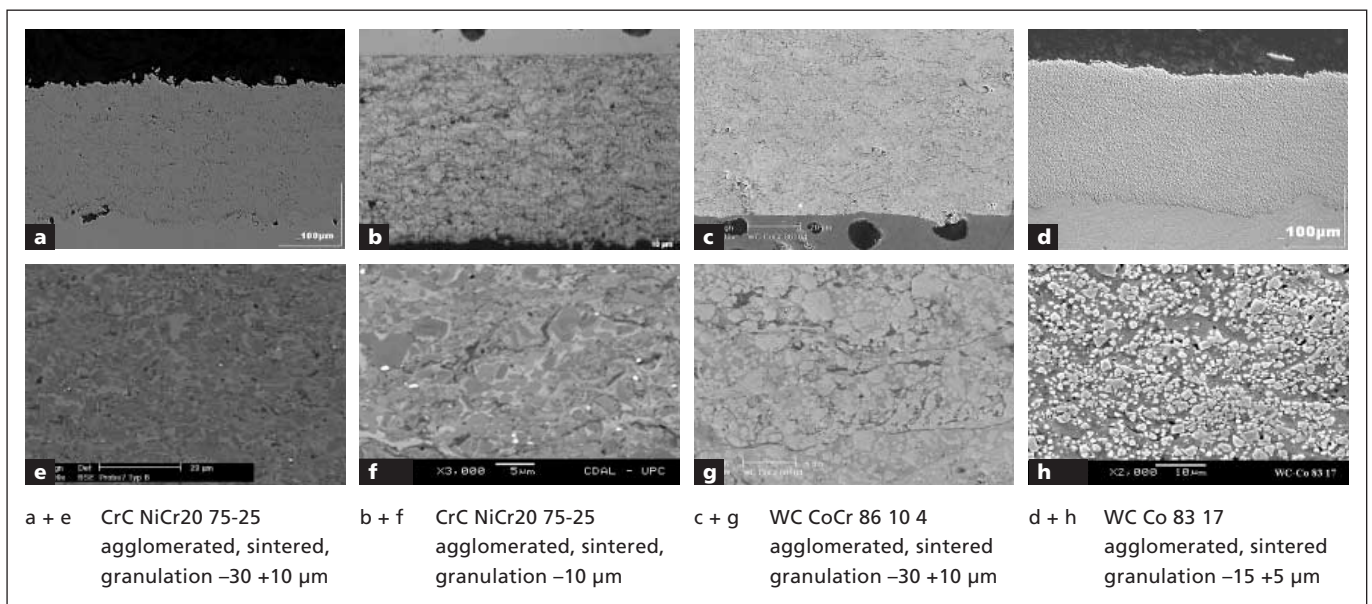


Fig. 9 CJS HVOF coatings

Tribological Tests

Tribological tests were carried out as part of the NANO HVOF project for the piston ring – cylinder bore, engine valve stem – shank guidance and hydraulic cylinder systems. The results of the pin-on-disk and block-on-ring tests in a 3.5% NaCl solution are outlined in the paragraph below.

Pin on Disk – Surface Disruption

The pin used consisted of hard WC-type metal with 6% Co. The test and the calculation of the abrasion were carried out according to ASTM G-99. A pin-on-disk test provides information about friction coefficient and abrasion, lubricated with 15W40 oil and in dry conditions. The wear mechanism is marked mostly by surface disruption and adhesive wear. In this case, a successful integration of the particles into the layer has a positive effect. The wear traces of the WC 6%Co pin on CrC NiCr layers in dry conditions clearly show the effects of surface disruption and tears in the surface of the layer.

There were no significant differences in the friction coefficients of the tested Co, WC CoCr and CrC NiCr layers, the friction coefficients of all layers being 0.2 in dry and 0.1 in lubricated conditions.

WC Co and CrC NiCr layers sprayed with super-fine powders produce better results than layers sprayed with coarser grain sizes. The finer structure shows a reduced tendency to produce tears and a higher surface disruption resistance.

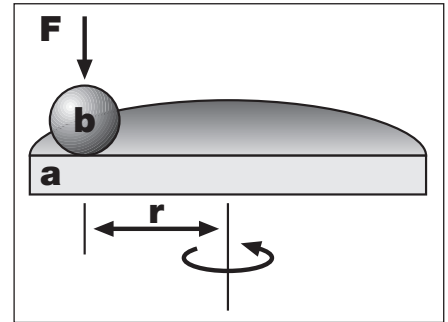


Fig. 10 Principle sketch Pin on Disk test

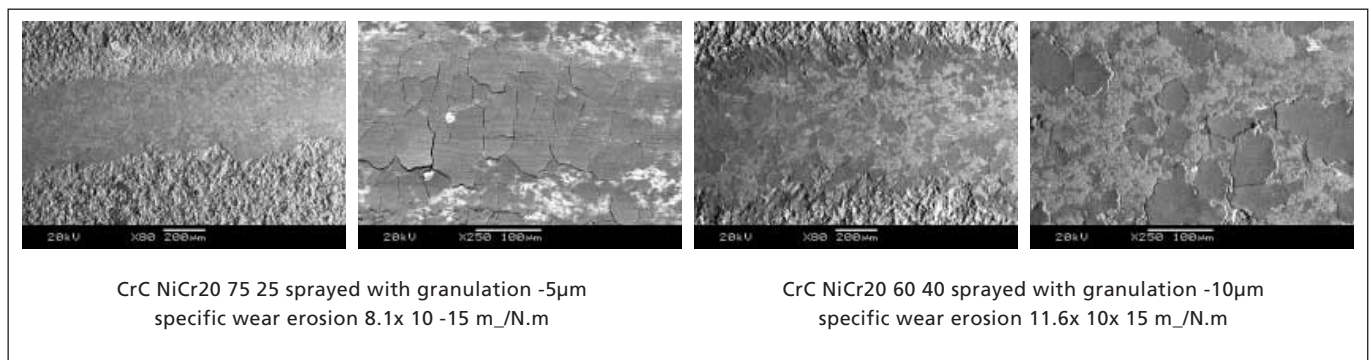


Fig. 11 Wear way of the Pin's on the layer under dry conditions (40N, 10,000 over runs)

Block-on-Ring Test – Abrasion with Overlying Corrosion

The block-on-ring test, a combined test for abrasion with overlying corrosion, was developed specifically for the NANO HVOF project. The test was developed with regard to a hydraulic rod coating in steel construction / hydraulic engineering in a marine environment.

A coated non-alloyed steel ring is pressed in rotation against an aluminum oxide block. Both the ring and the block are submerged in a 3.5% NaCl solution at a pH of 6.3. The ring is polarized cathodically or anodically for a precise analysis of its corrosion resistance.

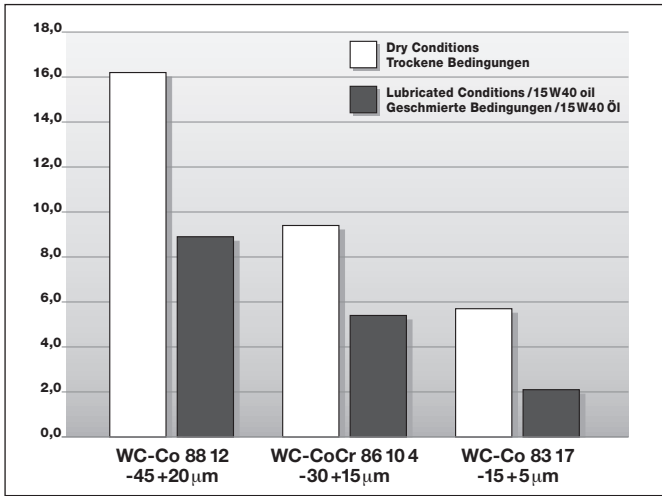


Fig. 12 Specific wear rate (m³/m.N x 10-15) of CJS HVOF coatings Pin on disc test according ASTM G-99 of WC Co and WC-CoCr

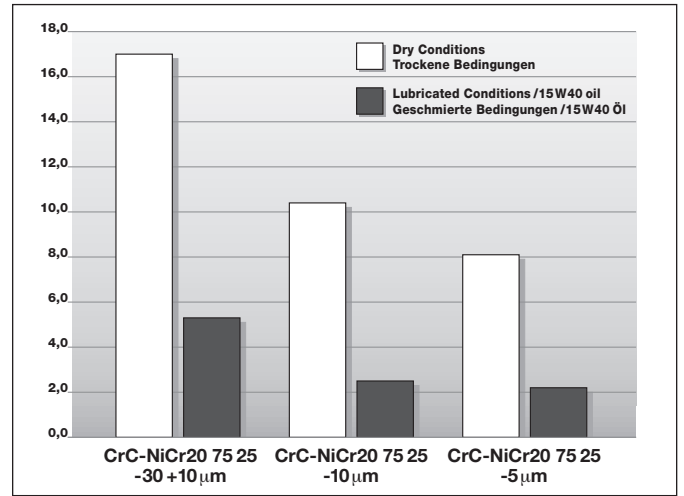


Fig. 13 Specific wear rate (m³/m.N x 10-15) of CJS HVOF coatings Pin on disc test according ASTM G-99 of CrC NiCr

The following tests were carried out:

- abrasive corrosion with free corrosion
- abrasive corrosion with cathodic polarization
- abrasive corrosion with anodic polarization

Figure 15 shows the volumetric loss in the WC CoCr86 10 4 and CrC NiCr20 75-25 layers sprayed with standard powders featuring grain sizes of -30 +10µm, and the layer sprayed with super-fine CRC NiCr20 75 25 (grain size -10µm). In this test, WC CoCr had the least volumetric loss. The CrC NiCr20 75 25 layer (sprayed with standard powder) featured an abrasion rate typical of abrasive wear tests, producing 4 to 5 times more abrasion than the WC CoCr layer. The CrC NiCr20 75-25 layer sprayed with super-fine powders has wear properties superior to the CrC NiCr20 75 25 layer sprayed with a grain size of -30 +10µm.

The metallographic test and the results of the tribo-tests proved that the systems sprayed with super-fine CrC NiCr20 and WC Co powders in the -10µm range produced superior results compared to layers sprayed with standard powders featuring grain sizes of -45 +20µm and -30 +10µm.

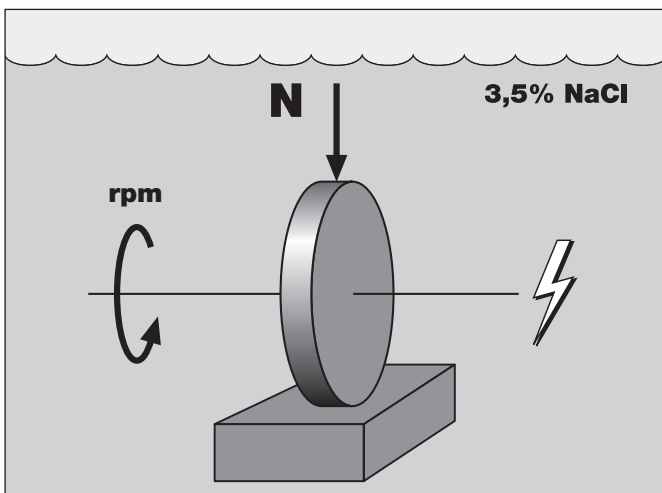


Fig. 14 Principle sketch Block on ring test

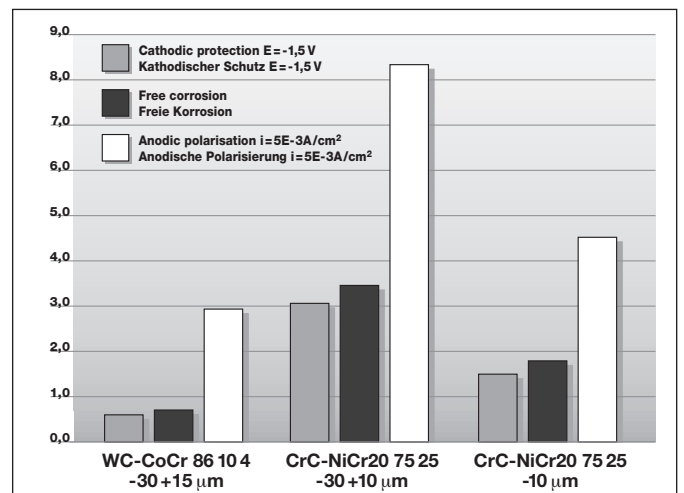


Fig. 15 Volume loss (mm³) of CJS HVOF coatings during Block on ring test

HVOF Internal Coatings with the Gun System, ID CoolFlow

There has been keen interest in HVOF internal spraying guns and small HVOF spraying guns designed for the internal spraying and coating at short distances of complex component part geometries without overheating them. Until recently, it has been impossible to satisfy the demand, because the technologies available, based on powders with grain sizes of for example $-45 +15\mu\text{m}$, failed as components overheated. One reason was the high energy level of the HVOF flame stream of around 80–120 kW, which is required to melt the powder. Additionally, the particles require a flame length of around 200–300 mm to build up the required temperature. Consequently, typical spraying distances lie – depending on the gun design – at around 250–400 mm, rendering impossible HVOF internal coatings with standard powders below a pipe diameter of 500mm.

Based on the positive results of the NANO HVOF project with superfine powders of $-10\mu\text{m}$, a small HVOF gun was developed, suitable for internal coatings of diameters from 150mm. This internal spraying gun is available under the name of ID CoolFlow.

The gun operates at a spraying distance of 70–120 mm and is available with two nozzle configurations, the first one operating at an energy level of 10–70 kW, the second one at an energy level of 5–30 kW.

The ID CoolFlow was inspired by a development project initiated by Cerma Shield in Boxburg / South Africa, who were also the first company to use the ID CoolFlow. Cerma Shield spray the cylinder liners of diesel railway engines with CrC-NiCr and WC-CoCr layers to extend their repair cycle and save fuel through reduced friction.



Fig. 16 ID CoolFlow Gun

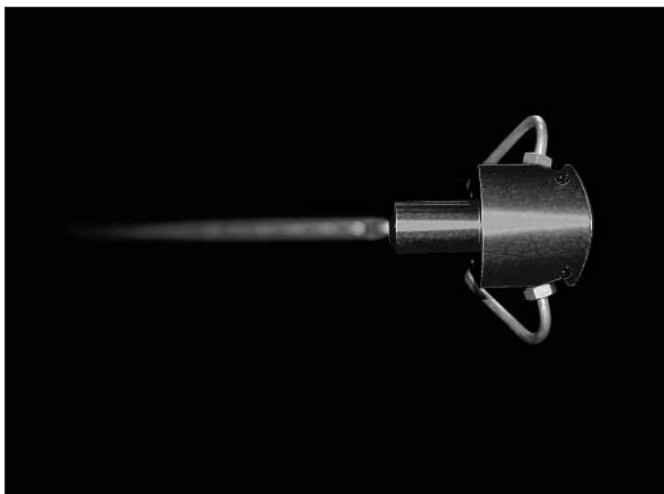


Fig. 17 ID CoolFlow HVOF jet



Fig. 18 Internal coating of a liner of a lokomotive diesel engine with ID CoolFlow

Summary

HVOF spraying of super-fine powders with grain sizes of $-10\mu\text{m}$ has a great potential to significantly influence the future distribution of HVOF applications. Its advantages lie in the quality of fine coatings and the reduced operating and manufacturing costs of smooth, contour-tracking layers.

A powder feeder and gun technology that allows the processing of super-fine powders has been developed. As part of the EU Growth NANO HVOF project, the layers were characterized. The tribo-tests in particular showed that fine layers had properties superior to layers applied with more coarsely grained standard powders.

Thanks to the use of super-fine powders, HVOF internal coating has become a realistic technology. The HVOF internal spraying gun, ID Cool-Flow, has been developed specifically for super-fine powders. This small HVOF gun subjects the components to only moderate strain, avoiding their overheating.

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