

Development of Ultra Thin Carbide Coatings for wear and Corrosion Resistance

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Abstract

The increasing demand of the industry for high quality coatings with a low cost aspect has led to the development of ultra thin, nearly finishing free carbide coatings. The R&D work performed for this publication was focused on the tailoring of carbide powders together with the development of a new generation of HVOF-Systems working on higher combustion chamber pressures. An as-sprayed surface roughness of less than 1,5 μm has to be envisaged for a thin nearly finishing free coating. Therefore, the starting powder has to have fine particles size with a homogenous distribution of carbides and matrix metals. To ensure the corrosion resistance, the matrix metals have to be completely alloyed and the coatings have to be dense.

The used HVOF-System must be able to feed and spray these fine powders without any blockage of the powder feeder or nozzle clogging.

The coating quality has to fulfil the requirements of hard-chrome plating as wear and corrosion resistance is concerned. The low cost level of thin hard-chrome coatings shall be matched. The suitability for using this coating on applications like hydraulic cylinders has been proven.

Generally, this technique of thermal spraying can be used as a hard-chrome alternative as well as for new applications where thermal spraying was not put into account due to cost and technical reasons. The aim was to fill the gap between thin film technologies as PVD or CVD techniques and conventional thermal spraying. The new technology enables the industry to coat large components with nearly no restrictions in size and for competitive prices.

Powder Manufacturing

The raw materials for the powder need to be in a fine, i.e. narrow distribution. To ensure the surface roughness and to minimize grinding costs, for the tungsten carbide mean grain size of 0,8 μm has been chosen. This is necessary to get a smoother surface during service life of the coated components. Also the carbide distribution will be more homogenous by using finer raw materials. As raw material extra fine cobalt was used to ensure a complete alloying of the matrix metals during the sintering. The alloying is depending on a diffusion process. The deepness of the diffusion is depending on the sintering time and the sintering temperature. To avoid any formation of η -carbide phases, the tungsten carbide was added to the process with a strictly controlled carbon content of 6,0–6,2 wt.-%.

In the first step, the raw materials were filled into an attritor together with a binder and a solvent. The solvent is necessary to prevent a crushing of the tungsten carbides and an oxidation of the metal binders. Due to the exact size control of the carbides and a homogenizing process

without milling action, the carbides size distribution is very tight.

After mixing, the suspension was spray-dried in a closed loop system under controlled atmosphere. The oxygen content of the atmosphere was held below 0,2 wt.-% to avoid any oxidation. The oxide content of the finished powder was between 100-300 ppm. Therefore it is comparable with gas atomised powders. Especially for the production of multi metal matrices such as Co-Cr or Ni-Cr this oxidation is dangerous. The oxide skin on the metallic particles acts as a diffusion barrier and prevents the alloying process during the sintering. The consequences of not completely alloyed powders are an inhomogeneous corrosion resistance of the coating or dark chromium oxide layers in a CrC-NiCr coating.

The produced micro pellets are very dense without any hollows or large pores (Fig.1). The distribution of carbides and the metal matrix is very homogenous.

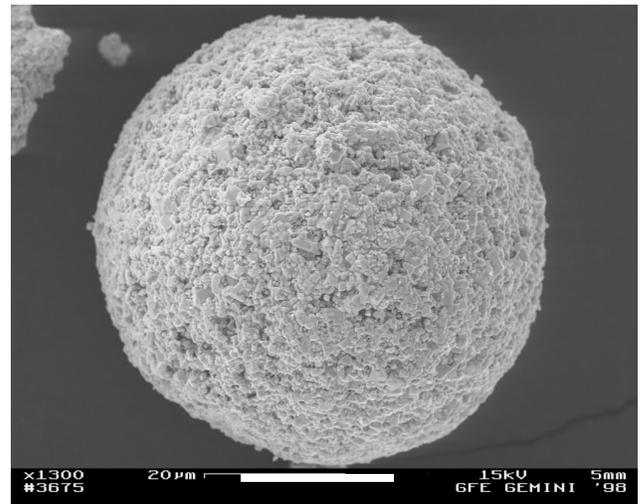


Fig.1: Tungsten Carbide-Cobalt-Chromium Pellet

The sintering was done in a combined Hydrogen-Vacuum furnace. The first sintering phase is the binder evaporation phase where the organic binder is removed. This phase is critical because the consequence of a too slow evaporation would be a deformation of the micro pellets. A too fast driven evaporation could crack the organic binder and contaminate the material with carbon or alkali metals.

For the sintering process different types of furnaces can be used. Generally temperatures are between 1100°C and 1400°C. The temperature and the sintering time influence the cohesion between the carbides and the metallic particles. Too low sintered powders tend to burst or crack when they are injected in the nozzle or the burning chamber, especially at high combustion chamber pressures. The result is nozzle clogging. Too high sintered powders can not be molten well during the spraying. Internal

porosity in the coating and a low deposition efficiency are the consequence.

In spray dried powders the sintering causes small sinter bridges between the micro pellets. The destroying of these sinter bridges can be done with less energy. The grain sizes of the pellets is a result of the spray drying process and not of the crushing process. Therefore the use of heavy crushing equipment is not necessary. The iron contamination can be neglected. This is very important for the corrosion resistance. In the used powders for this R&D work, the iron content was limited to 0.1 wt.-%.

A screening process follows the crushing. The ultra thin coatings require a special grain size distribution. This has to be done by air classifying to get exact cuts. A well screened powder can often absorb the higher powder costs by reducing finishing costs, machine down-times due to blockages, scrap production and increased deposition efficiencies.

HVOF Device

As still in 1995 demonstrated, existing HVOF systems don't reach the limits to produce coatings with increased properties [1]. At that time the idea of so called HVIF system was created. However, the problem with running HVOF systems in the HVIF mode causing an increase of fuel and oxygen consumption up to uneconomic values. Particle temperatures far below the melting point of the metallic matrix for hard-metal powders causes also an intolerable decrease of the spraying efficiency. A better way is on the one hand the controlled heating of the spraying particles near the melting point of the metallic matrix and on the other hand to realize maximum particle speed. This can be arranged with maximum thrust spraying devices, keeping the hot gas jet temperature at a controlled temperature level for proper heating of the particles and in parallel achieving an optimized particle acceleration in the barrel. High particle acceleration allows to realize maximum particle speed in a given acceleration zone as it is the barrel itself. When the kinetic energy of a particle reaches a special value larger than the bonding mechanism with the surface, the spray particle impacts following the rules of explosion plating [2, 3]. The assumption therefore is, a good bonding on a non prepared surface (not grid blasted) could be possible. The correct adjustment of thermal energy of the spray particles is needed to have a good spreading of the particles on the surface for getting minimum surface roughness of the resulting coating.

The combustion pressure as one possibility to increase the thrust of a system should be also controlled in that manner that existing safety standards for oxygen supplies should fulfilled world-wide. Kerosene/Oxygen combustion is still the most save and simple solution for the industrial design of the next generation of High Thrust HVOF systems (HT-HVOF). Due to the reason that the particle

acceleration is mainly determined by the particle size and the momentum flux of the jet [4] the system design has to be done hand in hand with the powder design.

Experiments and Results

To prove the previous mentioned assumptions several carbide coatings were sprayed in the HT-HVOF mode and for comparison one coating in the classical HVOF mode. The following table 1 gives the powders used for these experiments as well as the combustion pressure, energy level and relative thrust increase. The value 100 for the relative thrust increase corresponds to thrust of common HVOF systems running with supplier recommended parameters for a comparable spray consumable as for example the TJ 4000, JP 5000 of TAFE or the CJS of Thermico, former OSU. The spraying with the HT-HVOF was done on degreased, non grid-blasted surfaces. Spraying was done in hand-held operation doing 5 to 10 μm coating increase per path. Coating temperature was arranged below 200 °C. The standard HVOF coating was sprayed on a grid blasted surface.

Table 1: Powder properties and spraying parameter.
 λ = Kerosene-Oxygen combustion equivalence ratio.
 1 corresponds stoichiometric ratio

Sample	Powder	Cut [μm]	Power [kW]	Chamber Pressure [MPa]	λ	Rel. Thrust increase [%]
WCCr	WC-Co-Cr	15 - 45	110	0.64	0.86	100
HT-WCCr	WC-Co-Cr	5.6 - 22.5	80	1.17	1.21	210
HT-WCCo	WC-Co	5.6 - 22.5	62	0.94	1.66	180

The as-sprayed roughness of the coatings and the realized coating thickness are given in the table 2. The general aim is to go to a coating thickness below 50 μm , however for comparative wear tests and bond strength measurements higher coating thickness were chosen first. The surface roughness was measured using an AltiSurf 500 white light equipment following the standard test procedure according to DIN 4768. For the roughness range of $R_a = 0.1 \dots 2 \mu\text{m}$ the required measurement length was 5.6 mm. For all HT-HVOF coatings an average as-sprayed surface roughness below 1.9 R_a was determined, independently of the coating thickness. This low roughness value is for several industrial application absolutely sufficient and no further finishing steps are needed or if it is necessary, the finishing can be done much faster.

Table 2: Coating thickness, as-sprayed roughness and bond-strength of HVOF and HT-HVOF carbide coatings.

Sample	Thickness [μm]	Roughness [mm]		Bond strength [μm]
		Ra	σ	
WCCr	480	7.16	0.33	> 90 *
HT-WCCr	260	1.85	0.31	> 73 *
HT-WCCo	80	1.84	0.10	n.m.

* sample failed in the gluing zone

Beneath a reduced surface roughness the bond strength of a carbide coating is essential. Therefore, the bond-strength was measured for the WC-Co-Cr coatings according to the standard EN 582 (equivalent to ISO 14916). Remarkable is, that all coatings failed only in the gluing zone. The reduced bond-strength of the High Thrust HVOF coating was caused by the reduced surface roughness reducing the adhesion of the glue. Reference values for glued samples only (without coating) were measured to be 98.7 MPa.

The hardness and the standard deviation of the hardness measurements are given in table 3. HT-HVOF doesn't increase the coating hardness. Although, the coating homogeneity is increased as one can see from the decreased standard deviation of the hardness values for these coatings. Furthermore the hardness of the sprayed coatings corresponds to the hardness of sintered specimen of the same material composition [5].

Table 3: Hardness of HVOF and HT-HVOF carbide coatings

Sample	Hardness HV 0.3	
	\bar{X} $n=10$	σ $n=10$
WCCr	1299	161
HT-WCCr	1272	99
HT-WCCo	1048	68

Figure 2 shows the metallographic cross-section of the WC-Co 83-17 coating. The coating has no visible porosity and a very homogenous structure. Surprising is the high roughness in the intermediate zone between coating and substrate. This confirms the theory that the bonding mechanism is comparable to the explosion plating process as described in reference 3.

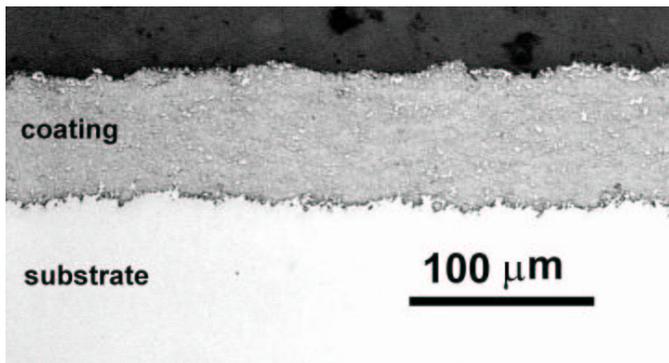


Figure 2: Light-microscopy of a metallographic cross-section of HT-HVOF WC-Co 83-17

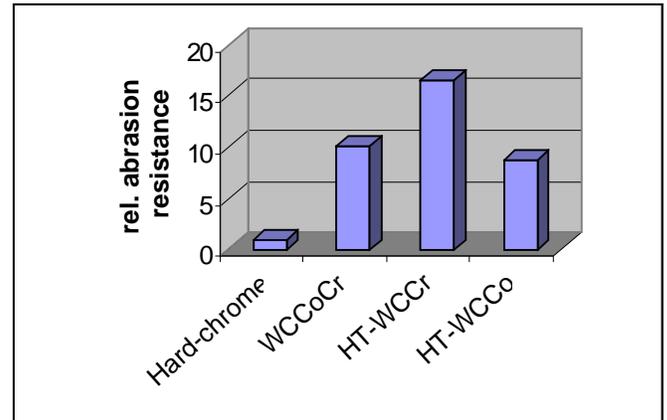


Figure 3: Relative abrasive wear resistance according to ASTM G-75 of HVOF and HT-HVOF sprayed WC-Co coatings compared to hard-chromium

The Miller wear test according to ASTM G-75 was used to characterize the coatings abrasive wear properties. For further comparison a hard-chromium coating was tested as well. The volume loss was calculated by using the theoretical density for hard-chromium ($d = 7.19 \text{ g/cm}^3$) and for WC-Co ($d = 14.7 \text{ g/cm}^3$). In Fig. 3 the relative wear resistance of the HVOF and HT-HVOF sprayed coatings related to hard-chromium are presented.

The abrasive wear resistance of the HVOF and HT-HVOF sprayed WC-Co layers is by the factor 8 to 16 times more resistant than hard-chromium. The value for the Kerosene HVOF sprayed WC-Co-Cr coating is in agreement with previous observations presented in reference [6]. For the same material the HT-HVOF process increased the abrasive wear resistance approximately by the factor 1.6. One explanation could be the more compact/dense structure of HT-HVOF sprayed coatings. However, the light-microscopic evaluation of metallographic cross-sections doesn't allow to determine a significant difference of the investigated layers. Other investigations methods as e.g. neutron scattering should give in future more detailed information [7].

Abrasion wear resistance is in a first magnitude of order a function of the hardness of a surface and the cohesion of the spray particles in the layer. The erosion resistance, specially in case of perpendicular impact, gives furthermore some information on the toughness of a layer. Therefore, the erosion resistance was determined using a liquid erosion test rig with solid abrasives developed by the EMPA [8]. This test rig was designed to simulate erosion conditions in hydro-power installations. The testing conditions were as follows:

Solid erosive:

Al_2O_3

Solid erosive particle grain size: 0.045-0.075mm
 Solid erosive contents: 0.03 wt-%
 Fluid velocity: $v \approx 160$ m/s
 Impact angles: 30°, 60°, 90°

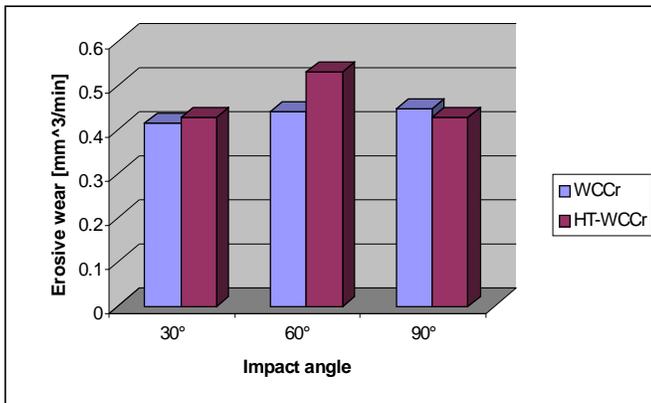


Figure 4: Erosive wear of HT-HVOF and HVOF sprayed WC-Co-Cr coatings as function of erosive impact angle

The absolute volume loss as function of impact angle for the HVOF and HT-HVOF coatings is given in fig. 4. In opposite to the results on abrasive wear resistance the difference between the HT-HVOF and HVOF coatings as well as between the WC-Co-Cr coating and the WC-Co 83-17 coating is not significant. Although, remarkable is the nearby constant wear behaviour of the sprayed carbide coatings over the whole range of impact angle. The WC-Co-Cr coating made out of a spray consumable with optimized chemical composition and carbide size is in the range of 15 % to 50 % more resistant compared to the coating made out of a standard WC-Co 83-17 carbide powders.

The results of all the measurements compared to hard-chromium are given in fig. 5 for an impact angle of 30°, 60° and 90°.

At small impact angles HT-HVOF and standard HVOF sprayed coatings showing a slightly better wear resistance compared to hard-chromium coatings. With increasing impact angle the hard-chromium coating tends to increased wear resistance up to nearly 50 % at 90°. The results for an impact angle of 90° for HVOF coatings fits also together with published measurements for conventional Kerosene HVOF sprayed carbide coatings in reference [9].

Summary and Conclusions

A new generation of HVOF systems so called High Thrust HVOF (HT-HVOF) systems allowing the efficient production of very dense carbide layers.

With this new technology it is possible to apply coatings directly on the non-grid blasted surface with a bond strength comparable to good standard HVOF sprayed carbide coatings.

The production of very smooth and thin coatings with an as-sprayed surface roughness better than $Ra 1.9 \mu m$ was realized without any problems, even in handheld operation.

In combination with in chemical composition and grain size optimized carbide powders the abrasive wear resistance of such coatings is up to a factor of 2 better than standard kerosene HVOF sprayed coatings of the latest generation and up to the factor 16 better than hard-chromium.

The erosion resistance of HT-HVOF carbide coatings is equal or even better to that of hard-chromium coatings at small impact angles and up to 50% less for an impact angle of 90°.

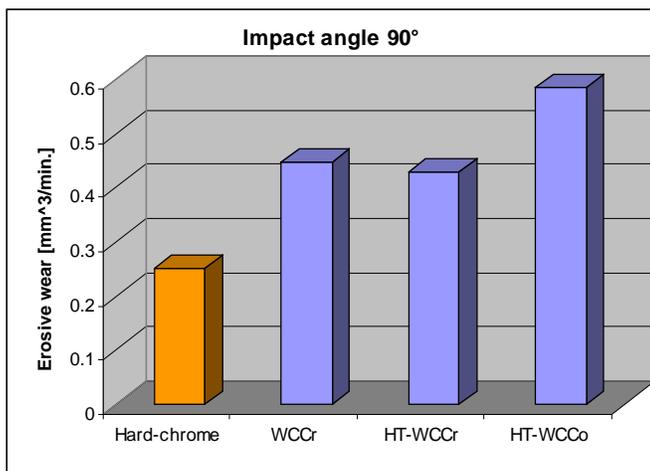
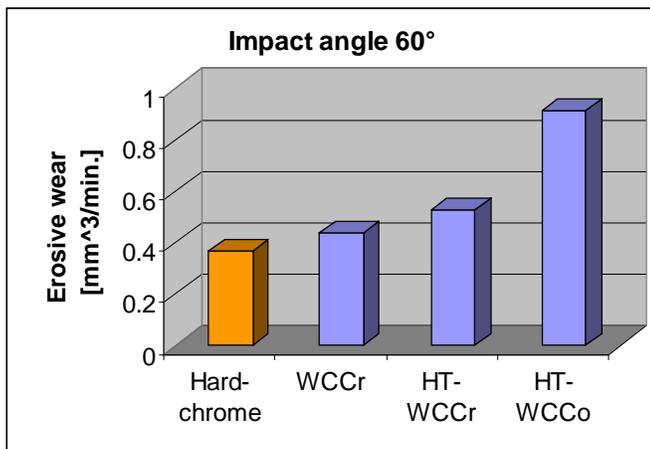
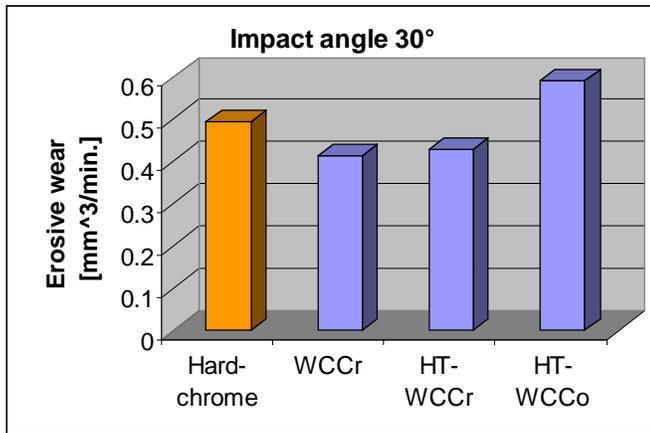


Figure 5: Erosive wear of HT-HVOF and HVOF sprayed WC-Co and WC-Co-Cr coatings compared to hard-chrome

Future Work

To complete the investigations corrosion tests and practical test will be done and presented at the conference. The final aim is the low cost production of highly resistant carbide coatings with a coating thickness < 30 μm and an as-sprayed surface roughness ≤ 1.2 μm.

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HVOF; Hard-chrome replacement; WC-Co-Cr; WC-Co 83-17; Erosion resistance; abrasive wear resistance; HT-HVOF; thin coatings; finishing poor coatings