15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

PERFORMANCES AND RELIABILITY OF WC BASED THERMAL SPRAY COATINGS

A. Scrivani[1,2], M. Rosso[3], L. Salvarani[4]

1. Turbocoating S.p.A., Via Volta 3, 43040 Rubbiano, Parma, Italy
2. Università di Parma, Dipartimento di Ingegneria Industriale, Viale delle Scienze, Parma, Italy
3. Politecnico di Torino, Dipartimento di Scienze dei Materiali e Ingegneria Chimica, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
4. Flametal S.p.A., Via G. Di Vittorio 51, 43045, Fornovo Taro, Parma, Italy

Summary

Thermal spray processes are used for a lot of traditional and innovative applications and their importance is becoming higher and higher. WC/CoCr based thermal spray coatings represent one of the most important class of coatings that find application in a wide range of industrial sectors.
This paper will address a review of current applications and characteristics of this kind of coating.
The most important spraying processes, namely HVOF (High Velocity Oxygen Fuel) are examined, the characterization of the coatings from the point of view of corrosion and wear resistance is considered.

Keywords

Tungsten Carbide, HVOF, Thermal Spray, Corrosion, Wear

1. Introduction

Surface engineering studies the drawing of composite systems constituted by a substrate and a coating, or more generally a surface treatment, in order to obtain functional performances not possible with only substrate materials or

15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

coatings materials (1). Typical is the case of structural materials with good mechanical strength but bad behaviour in aggressive environments or when sliding or friction are present. In this cases a surface treatment is applied to the component in order to keep the good mechanical characteristics adding good anticorrosion or antiwear properties trough the application of hard materials like oxides or carbides.
An example could be found in petrochemical industry where the used devices are under conditions of simultaneous mechanical stress and chemical corrosion due to the presence of suspended particles in the fluid. Therefore in pipeline engineering it is important to consider the wear and erosion problems and to guarantee the long life of the equipments (pipes and valves) as well as the safety.
The Ni based alloys are good anticorrosion materials, but they have not good antiwear characteristics and can not be utilised in the seal parts of the line.
From the point of view of the tribological properties the use of hard materials as thermal sprayed coatings allows to improve drastically the in-service behaviour of the component. Quite all these coatings are produced by HVOF (High Velocity Oxygen Fuel) to obtain very hard coating with excellent cohesion and adhesion. This technology also allows to obtain very dense coatings that show good behaviour in aggressive environments. Namely tungsten carbide cobalt-chromium based is standard material for application in petrochemical field and finds place in the specification of the main companies.
Therefore the testing of this coating produced by HVOF is an important contribution to the understanding of its capability for petrochemical purpose.
This paper addresses the study and characterization of tungsten carbide thermal spray coatings.
WC based thermal sprayed coatings have been submitted to several corrosion and wear tests in order to determine the performance as anticorrosion (H_2S+CO_2 test, $FeCl_3$ test according to standard ASTM G48-92 and Co release in aqueous environments), antiwear (pin on disc test) and antiabrasion material (test ASTM G98-75).

2 Metallurgy

The carbides object of this study could be considered as interstitial compounds: the small carbon atom is located in the octahedral interstitial site as well as at the centre of a trigonal prism with the close-packed transition metal atoms (2).

15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

The crystal structures of the carbides of a transition metal are determined by the radius ratio:

$$r = r_C/r_T$$

where: C = carbon
T = transition metal.

If $r < 0.59$, the metal atoms form very simple structures with close-packed cubic or hexagonal arrangement with carbon atoms located at interstitial sites that are smaller than the carbon atom because otherwise there will be insufficient bonding resulting in an essentially unstable structure. Namely in the case of tungsten carbides the most common phases are WC and W_2C both crystallising in the cubic (NaCl) structure.

Tungsten carbide is stable at room temperature as cubic α-WC that melts at 2867 °C. The hexagonal W_2C-phase melts at a slightly lower temperature of 2750 °C. WC loses carbon at appreciable rate above 2200 °C and will form a surface layer of W_2C (2).

Cemented carbides are composite materials of pure carbides with a binder metal of low melting point and high ductility. The term refers usually to a carbide of group 4b-6b elements of the periodic table together in a metal matrix such as cobalt or nickel. Mixtures of these metals, also together with chromium are often utilised. The selection of the binder metal depends to a large extent on its ability to wet the surface of the carbide particles to ensure secure coating cohesion. Namely the addition of Cr to WC/Co-cemented carbide causes important property changes in terms of surface behaviour.

The corrosion resistance of cemented carbide coatings is determined by both the corrosion resistance of the carbide(s) and the binder metals.

3. Coating technologies

Thermal spray technologies find a lot of use in all industrial sectors due to the wide range of materials that can be sprayed by means of these technologies and the large range of thickness that can be obtained (3).

The principle of these technologies is melting the coating materials by means of heating in gaseous environment and its projecting with high velocity on the surface that shall be coated. The coating materials is generally in form of powder or (less frequently) wire.

Thermal spray technologies can be classified according to the energy source used to melt the coating material: flame spray and HVOF (High Velocity Oxygen Fuel) technologies use the energy deriving from a combustion, electric arc spray technology uses an electric arc to melt the coating materials while plasma spray technology uses a plasma generated by an electric arc.

15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

The best results in order to get dense and hard WC based coatings have been achieved by HVOF (High Velocity Oxygen Fuel) technologies.

3.1 HVOF Technologies

These systems use the energy obtained by a combustion. Figure 1 shows a commercial HVOF gun: the powder is injected in the flame by suitable carrier gas (usually nitrogen), it is molten and projected to the substrate surface. High velocity results in very dense coatings due to the ideal condition of splat on to the surface being coated.

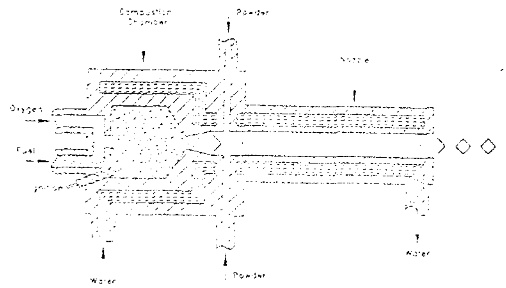

Fig. 1: commercial HVOF gun

It is possible to identify different systems that can be classified according to:

- the powder feeding that can be radial or axial
- the fuel/oxygen feeding: fuel and comburent can be feeded premixed or separated.

HVOF begins its development in the years 50s when Detonation Gun has been introduced on the market: the fuel mixture explosion was achieved by spark (4-8 cycles/s), the combustion chamber pressure was high. Further development brought the detonation to become continuous. In these way new system are developed with axial powder feeding.

A third HVOF generation brings systems with radial injection, with liquid fuel and with improved chamber/nozzle design to get always higher speed.

Due to the high flame speed it is possible to obtain very dense and very hard coatings: namely with carbides HVOF technology obtained its best results.

15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

4 Experimental results

In order to give an overview of the WC based coatings characteristics, the results of mechanical and chemical characterization of different kinds of WC based coatings will be presented.

4.1 Corrosion Resistance Data

4.1.1 Ferric Chloride Test

The WC/CoCr sprayed samples have been submitted to corrosion test according to ASTM G 48-92 standard (4), Method A and compared with the behaviour of other materials from the point of view of the pitting corrosion resistance (5).
The samples under analysis have been submitted to ferric chloride test (about 6% $FeCl_3$ by weight) for 24 hours at temperature of 35 ± 1°C, according to table 1 that show also the achieved results in g/m^2. Mass loss has been measured and visual inspection have been carried out in order to detect pitting on the samples surface.

Sample submitted to ferric chloride testing (ASTM G-48)		
Materials	Weight loss (g/m^2)	Visual inspection
NiCrBSi alloy	225,0	no visible pitting after test
Inconel 718	142,4	no visible pitting after test
Cr_3C/NiCr	54,2	no visible pitting after test
WC/CoCr	18,9	no visible pitting after test

Table 1 Sample submitted to ferric chloride testing (ASTM G-48)

Although several coating show good corrosion resistance in Ferric chloride environment, WC/CoCr shows the minimum mass loss.

15[th] International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

4.1.2 Co release in acqueous environments

Three different WC/Co based coatings have been submitted to test to determinate cobalt release in water as follows:
WC83 Co17
WC86 Co10 Cr4 sprayed with high level of energy
WC86 Co10 Cr4 sprayed with low level of energy (5).

The samples have been immersed in water. At 24 h, 48h, 72h, 96h the cobalt release of the coatings to the water has been recorded.
Figure 2 shows how the coating where chromium is present show better behaviour in aqueous environment.

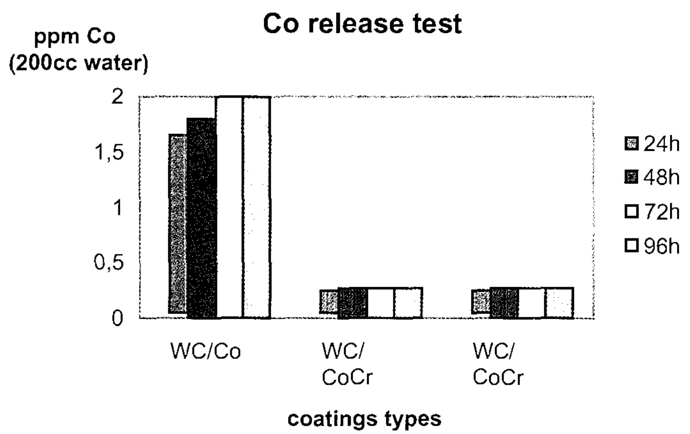

Fig. 2 Corrosion test in aqueous environment

4.1.3 Corrosion test in H_2S/CO_2 environment

WC/CoCr based coatings find a wide range of application in the petrochemical field where an important problem is the behaviour of materials in aggressive environments, when hydrogen sulphide, carbon dioxide and sand, which contribute to corrosion-erosion of the surface, are present.
A procedure has been set up (6,7) in order to test the resistance of WC/CoCr HVOF sprayed coatings to an atmosphere of H_2S and CO_2 by determining weight loss and surface damage of the sample. This procedure is based on NACE standards (8,9) but the tensile stress is not considered.

15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

Substrate material is stainless steel and the uncoated areas are nickel plated by an electroless procedure to avoid corrosion. The samples are immersed in acidified sodium chloride solution saturated with hydrogen sulphide at ambient pressure and temperature for 720 hour.

The behaviour of tungsten carbide cobalt-chromium based has been compared with other materials that usually find application in the petrochemical field: chromium carbide nickel-chromium based and Inconel 625. All these coating have been produced by HVOF (High Velocity Oxygen Fuel) on stainless steel AISI 304 substrate. The average thickens has been 200 μm ± 50 μm.

The materials have been characterised before and after corrosion test considering the following characteristics: surface roughness, Vickers hardness, crack analysis by penetrant liquid test, morphology and structure analysis by optical microscopy and scanning electron microscopy.

Hardness test was conducted on the polished surface of the samples in the two cases, before and after corrosion attack. A test load of 100 g and dwell time of 15 s were used.

Penetrant Liquid Test has the scope to reveal discontinuities that are open to the surface of the solid for these non porous materials. The test has been carried out with visible liquid according to the procedure ASME Sez V, Art. 6 and Art. 24 - SE 165 (10).

Mass loss of the coatings permits have been determined according to suitable laboratories procedure based on international standards.

Before the corrosion test the penetrant inspection did not show any defects on the samples examined, except for the area were electroless Ni overlaps the thermal spray coating. This area is, however, not important for the purposes of the present test.

Surface finishing of samples has been measured and is 0.1 ÷ 0.15 μm (Ra).

The metallographic analysis helps to state that the coatings show not-porous structure (1-3% porosity).

After corrosion test at visual inspection, the tungsten carbide cobalt chromium based (WC 10Co 4Cr) seems to have acquired a darker colour after the corrosion test. On the contrary, the chromium carbide nickel chromium based and Inconel 625 samples do not show any difference before and after corrosion test.

Penetrant inspection did not show any difference with respect to samples before corrosion test.

The acid attack does not affect the roughness that remains in the range as before the test.

15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

Metallographic analysis allows to exclude any changing of structure and modification of thickness (Fig. 3). No intergranular corrosion has been noted. Only it is possible to observe some stainless steel corrosion points under electroless nickel layer.
Hardness measurements according to the Vickers method scale, load 100 g, confirm that the hardness remains unmodified before and after corrosion test as shown in the table 2.

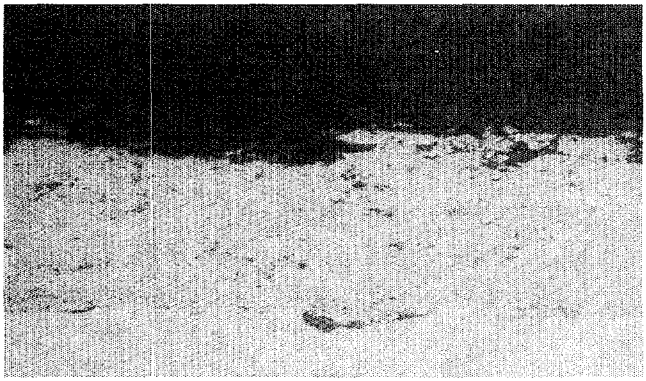

Fig. 3 WC-CoCr coating micrograph after corrosion test.

Material	**Hardness average before test ($HV_{0.1}$)**	**Hardness average after test ($HV_{0.1}$)**
WC-CoCr	1210	1381
Cr_3C_2-NiCr	917	1070
IN625	458	462

Table 2 Hardness Vickers value, before and after corrosion test.

Mass loss values are shown in table 3. WC/CoCr based coatings show the best behaviour but the values are of the same order of magnitude. It is interesting to note how the Cr_3C_2/NiCr based coatings show an increasing of the weight after corrosion test probably due to the formation of corrosion products under the Ni electroless plated layer.

15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

Material	Average mass loss [g]
WC-CoCr	0,364306
Cr_3C_2-NiCr	-0,01242
IN625	0,4575

Table 3 Weight before and after corrosion test, weight difference

Summarizing no important decreasing of structural and mechanical properties of the coatings has been noted. The only important effects are observed at the interface between electroless Nickel and thermal sprayed coating. This result could be, however, expected as deriving from the general weakness of the interface between two different materials. Some points of corrosion have been noted under Nickel plating in the samples coated with chromium carbide. The formation of corrosion products can explain the increasing of the samples weight after the corrosion test.

4.2 Wear Resistance Data

In order to determine the wear resistance of the WC/CoCr based coatings, their behaviour in sliding conditions against CrC/NiCr coated steel and in abrasive environment has been tested (5, 11,12)

4.2.1 Pin on disc test

WC/CoCr coated samples have been submitted to pin on disk test in order to evaluate the wear resistance and the coefficient of friction.
The test has been carries out according to the following parameters:
- load: 100 N
- pin: CrC/NiCr HVOF sprayed coating
- disc: WC/CoCr HVOF sprayed coating
- lubricant: MoS_2

Figure 4 shows the test results carried out for a distance of 30 km: the average coefficient of friction is 0,172 that remains constant for more than 10 km (distance considered in the Fig. 4). The WC/CoCr coating shows a mass loss of 0,4 mg after 30 km.

15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

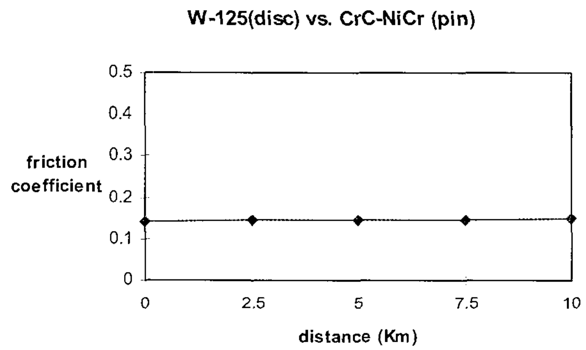

Fig. 4 Friction coefficient value in the first 10 km test

4.2.2 Slurry test

The slurry test has been carried out according to ASTM G75-95 (13) using a mixture of sand and aggressive solution. The design of the abrasion apparatus was based upon the conditions experienced by reciprocating equipment in contact with sand. This phenomenon is liable for the progressive loss of original material from a solid surface, due to mechanical interaction among that surface and solid particles. The test method is based on the mass loss recording and consequent determination of Miller Number and SAR (Slurry Abrasion Response) Number.
Miller Number expresses the abrasivity of the slurry while SAR Number is related to the behaviour of different materials to the abrasivity of the considered slurry.
The test procedure according to ASTM G75-95 is planned in the following phases:
- test block placed in the tray with the coated surface turned down;
- 2 h uninterrupted run of test block;
- stop and specimen disassembly, cleaning in a suitable solution, rinse and drying for 15 min;
- weight loss measuring and recording;
- repetition of the previous phases (three times).

The results of the test carried out on WC/CoCr thermal sprayed coatings, have been compared with those obtained by CrC/NiCr and Inconel625

15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

coatings that find application as alternative or complementary materials of the WC in the petrochemical field (14).
Slurry test has been carried out using the standard wear block material and the considered slurry (mixture of 150 g quartz sand and 150 g mineral oil). Miller Number of this slurry is 22.
Therefore the examined slurry represents well the petrochemical environment where the treated products generally have Miller Number in a range of 10 – 30.
The test is constituted by thee 2-hours runs. At the end of each run the sample weight loss is recorded and shown in table 4.

Cumulative Loss [mg]	**WC/CoCr**	**Cr_3C_2-NiCr**	**Inconel 625**
After 2 h	0.00	0.00	55.70
After 4 h	0.00	0.26	108,95
After 6 h	0.00	0.15	160,25

Table 4 Average cumulative weight loss during the Slurry Test.

Using the least square method, the value of coefficient A and B (needed for calculation of Miller Number) for each coating, are calculated for the curve closely matching the test data curve (Fig. 5-6).
Note that the tungsten carbide cobalt-chromium based coating, during the Slurry Test, did not exhibit a significant weight loss, therefore the graphic is senseless.
Accordingly to the standards the rate of mass loss, the Miller Number and SAR number are calculated and shown in the table 5.

Material	**Miller Number**	**SAR Number**
WC-CoCr	0	0
Cr_3C_2-NiCr	1	1
IN625	487	428

Table 5 Miller Number and SAR Number values for examined coatings.

15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

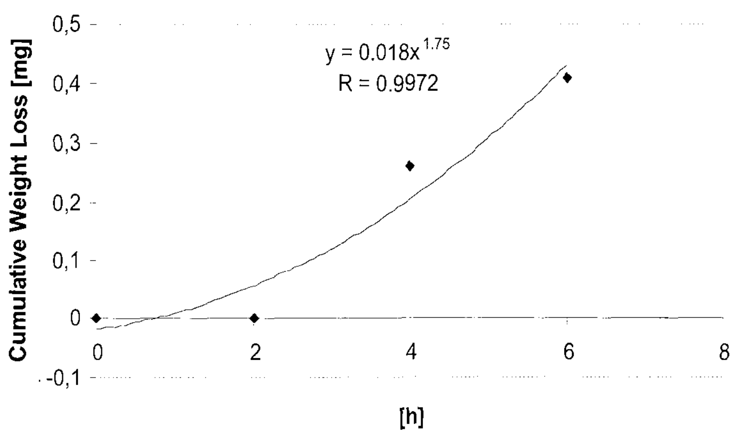

Fig.5 Curve closely matching the Slurry Test data for the chromium carbide nickel-chromium based, with correlation index R= 0.9972.(A=0.0018 and B=1.75)

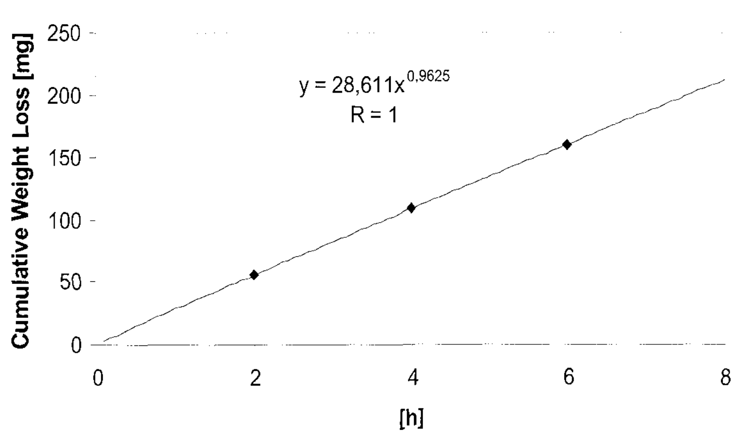

Fig.6 Curve closely matching the Slurry Test data for the Inconel 625, with correlation index R= 1.(A=28.611 and B=0.962)

15th International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 2

5 Discussion and conclusion

The WC/CoCr HVOF sprayed coatings submitted to corrosion test according to ASTM G 48-92 standard, Method A and compared with the behaviour of other materials from the point of view of the pitting corrosion resistance, show the minimum mass loss and therefore the best behaviour in ferric chloride environment.
From the point of view of the corrosion in water, the coating where chromium is present show better behaviour.
Corrosion attack due to H_2S/CO_2 environment does not produce important decreasing of structural and mechanical properties of the examined coatings.
From the point of view of wear data it is possible to note how the WC/CoCr HVOF sprayed coatings show low friction coefficient when in contact with other metal alloys.
The Slurry Test allow us to clear discrimination among the performances of examined materials. The cemented carbide coatings under examination, namely the WC/CoCr, have higher erosion resistance than Inconel 625. This confirms a link between mechanical properties and abrasion resistance due to the microhardness of Inconel 625 smaller than that of cemented carbides.
According to the presented characterization WC/CoCr based coatings confirm to be very versatile and useful for a wide range of industrial application.

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