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Alternatives to hard chromium plating on piston rods

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Abstract

As a main part of hydraulic cylinder, the piston rod is used in tough surrounding and corrosive condition; consequently a high quality protecting layer is essential. Currently EHC, electroplating hard chromium (hard chrome) is a widespread method for piston rod due to powerful performance and low cost. Unfortunately the plating process contains hexavalent chromium (Cr^{6+}) which is toxic and carcinogenic; perhaps it will be prohibited in the nearing future. Therefore it is crucial to seeking alternatives to hard chrome for piston rod manufacturer.

Through extensive searching for alternatives to hard chrome, the competitors like HVOF, electroplating tungsten plating and stainless steel linear were studied in the present work. Since microhardness and corrosion resistance are top priorities, after comparison perhaps Cr_3C_2-NiCr20% HVOF is the most promising technique.

Distinct pretreatments Cr_3C_2-NiCr coatings were compared with hard chrome in pendulum impact test, hardness test and acetic acid salt spray (AASS) test. The results indicate that hard chrome show higher toughness more than 40% compare with HVOF, the microhardness of HVOF is higher than hard chrome, mean value 1784 Vs. 1244 HV and both coatings have excellent bonding strength. After 40 hours in AASS test, the hard chrome was rated No. 10, however the HVOF just No. 6.

Contents

1. Introduction

Hard chrome coatings are widely used for the manufacture of the piston rods in hydraulic cylinders at present due to excellent characteristics. However, the plating process is toxic and carcinogenic; it probably will be prohibited in the near future. Therefore, to keep an advantageous position among competitors, it is essential for piston rod manufacturers to find out alternatives to the hard chrome.

1.1 Hydraulic cylinders and work conditions

Hydraulic cylinder is a mechanical component that uses liquid under pressure to apply a linear force. Typically, a hydraulic cylinder consists of pressurized liquid, cylinder barrel, piston and piston rod. Piston rod is a main part of hydraulic cylinder, piston rod is stiffly connected to the piston, which moves forth and back in cylinder barrel and slide against sealing part frequently, shown in figure 1.

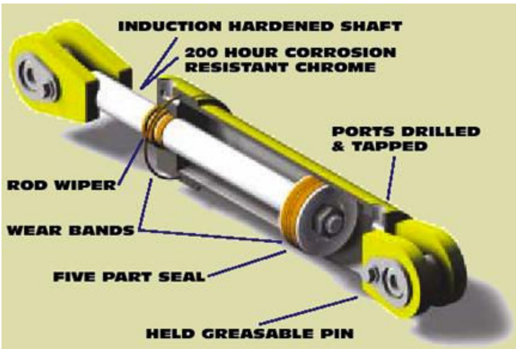


Figure 1.Schematic of hydraulic cylinder **Figure 2.Typical application of hydraulic cylinders**

As a transmission technology, hydraulic cylinder could continuously produce a wide range of great power; the output value can be controlled accurately and easily. Nowadays hydraulic cylinder has been applied in various power units of machinery like heavy excavators and diggers industry as shown in figure 2. In tough work conditions like mining, marine, metallurgy and papermaking industry, the piston rods are usually exposed extreme environments like sea water, high temperature and among angular hard stone surroundings. Consequently a thin high quality protecting layer on rod with good toughness, corrosion resistance, wear resistance and adhesion bonding strength is crucial for hydraulic cylinder performance.

1.2 Criteria of piston rod coating

a) Toughness

Toughness is an essential characteristic for piston rod coatings. Coatings demonstrating poor toughness or being not tough enough could not absorb much energy during the angular stone or hard grit strike the piston rod, surface damage then happens easily, the hydraulic cylinder will in turn fail to work immediately due to coating delamination or flaking.

Impact test is a dynamic test in which a selected specimen is usually struck and broken by a swing pendulum. The most common tests of this type are Charpy V-notch test and Izod test which are described in ASTM E23. The principle difference between two tests is the manner of the specimen is fixed. A typical pendulum machine is shown in figure 3.

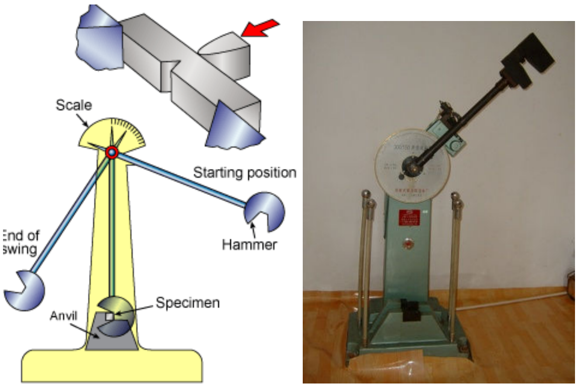


Figure 3.impact test and pendulum machine

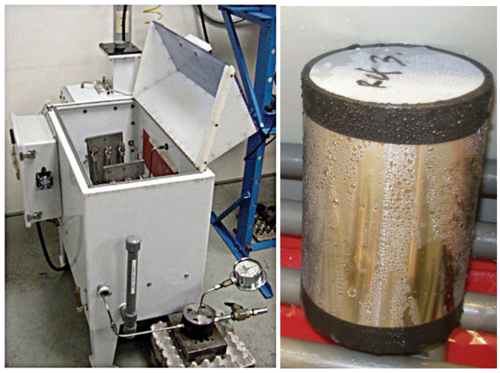


Figure 4.a salt spray cabinet and rod sample

b) Corrosion resistance

Due to poor working environment, the corrosion resistance is very important for hydraulic cylinder piston rod coating. Salt spray test is a conventional standardized test method used to check corrosion resistance of hydraulic cylinder piston rod coating; it is an accelerated corrosion resistance test and the appearance of corrosion products is evaluated after a period of time.

The apparatus for testing as shown in figure 4 consist of a closed testing chamber, where a salted solution, mainly a solution of sodium chloride, is sprayed by means of a nozzle. This produces a corrosive environment in the chamber and thus, parts in it are attacked under this severe corroding atmosphere.

Table 1.Protection rating vs. area of defect from ASTM B 537-70

Area of defect (%)	0	0-0.1	0.1-0.25	0.25-0.5	0.5-1.0
Rating	10	9	8	7	6
Area of defect (%)	1.0-2.5	2.5-5	5-10	10-25	25-50
Rating	5	4	3	2	1

Tests performed with a solution of NaCl are known as NSS (neutral salt spray). Results are generally evaluated as testing hours in NSS without appearance of corrosion products. Other solutions are ASS (acetic acid test) and CASS (acetic acid with copper chloride test). Chamber construction, testing procedure and testing parameters are standardized under national and international standards, such as ASTM B117, DIN 50021, and ISO 9227. After test duration, sample could be rated according to rusted surface area using reference standard as shown in table 1. [1]

c) Wear resistance

As a power transmission unit, piston rod needs to move forth and back frequently, at the same time wear happens during coating surface slide against the cylinder sealing. Hence wear resistance is also an important requirement for piston rod lifetime. Surface hardness is the key parameter for wear resistance. Besides toughness, corrosion resistance and wear resistance, according to various industry standards and customers' requirements, other criterion of piston rod coatings are listed in the table2.

Table 2.Typical values for piston rod coating

Characteristics	Typical values of piston rod coatings
Hardness	> 900 HV 0.1, > 789 HV 0.5
Corrosion resistance	AASS 40 hours rating number 10 NSS 96 hours rating number 10
Surface roughness	R a 0.2; R max 1.6
Adhesion	> 10,000 psi (ASTM C633), no flaking after test
Crack tightness	< 800/cm
Surface finish	Defects are not permitted, must be glossy

1.3 Hard chrome coating

At present time, the most common process has been used for piston rod coating is hard chromium plating, also referred simply as hard chrome or engineered chrome. Hard chrome has been used for piston rod coating since 1940, involves the reduction of metallic ions at the surface of the substrate, which is made the cathode in an electrolytic cell.

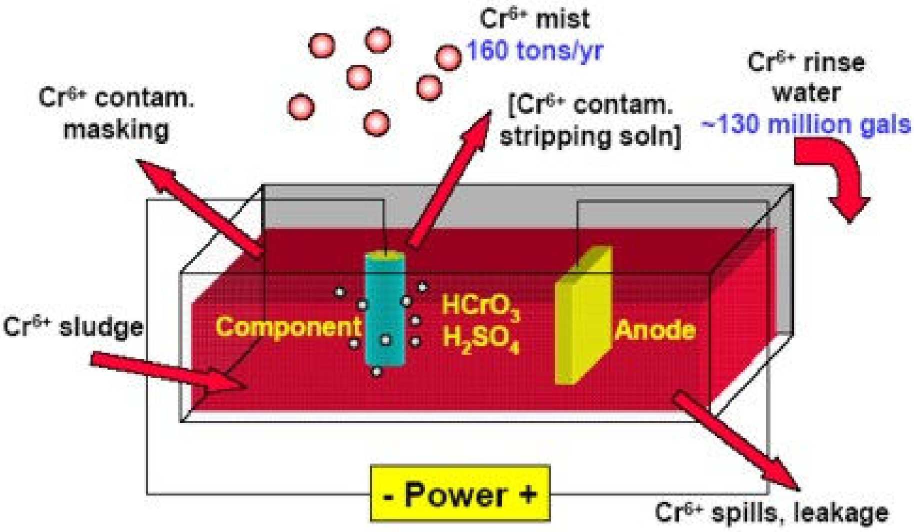


Figure 5.Schematic of hard chromium plating process [3]

The traditional solution used for industrial hard chrome plating is made up of about 250 g/l of CrO_3 and about 2.5 g/l of SO_4^-. In solution, the chrome exists as chromic acid, known as hexavalent chromium. A high current is used, in part to stabilize a thin layer of chromium (+2) at the surface of the plated work [2]. Hard chrome process for piston rod includes degreasing, masking, and cleaning prior to plating. Following the plating step, the piston rods are removed from the bath, masking is released from the rods, the piston rods are baked for brittle relief, finishing such as grinding, lapping, and polishing is completed. The process is illustrated schematically in figure 5. [3]

a) Hard chrome coating properties

Compare to conventional coating methods, hard chrome coating is powerful, inexpensive, well understood and easily performed. Typically the thickness of hard chrome coating is about 10~500µm, and the microstructure is extremely fine, containing a very small amount of oxide incursions and microcracks.

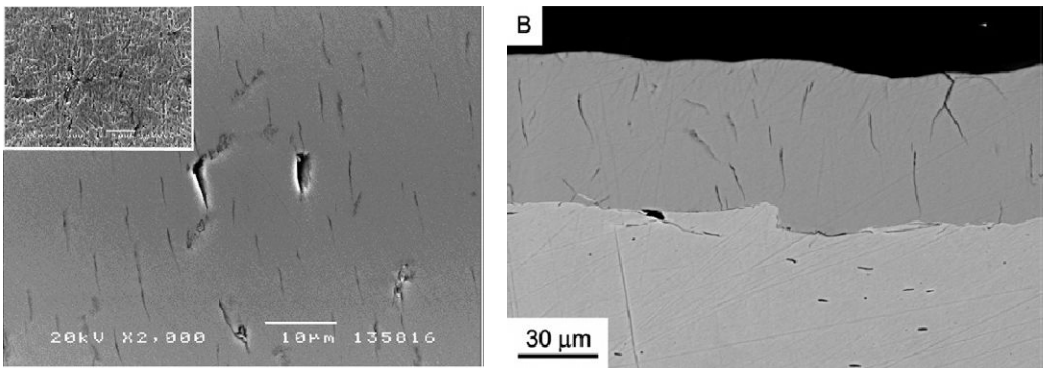


Figure 6.SEM micrographs of hard chrome coating cross-sections:

A. small vertical microcracks **B. excellent interface with grit blasted substrate [4]**

From previous study, the coatings are characterized by numerous small vertical microcracks as shown in figure 6A; All of the hard chrome coatings possess an excellent interface with substrate almost complete free from defects as shown in figure 6B [4].

b) Why replace hard chrome

Chrome plating has been used as a fundamental coating in a wide range of industries: aerospace, heavy equipment, automotive, papermaking, and others. Unfortunately, hard chrome plating is toxic and carcinogenic. The accepted emission level for hexavalent chromium Cr^{6+} varies greatly in different parts of the world and become to hard chrome coatings more and more restricted.

"In the USA, the Occupational Safety and Health Administration adopted a permissible exposure limit of five micrograms of Cr^{6+} per cubic meter of air (5μg/m^3) as an 8-hour time weighted average. Many other countries still have a limit of 50μg/m^3, including Japan, Germany, France the United Kingdom and South Africa. Sweden has a limit of 20μg/m^3 and the most restrictive limit among EU member states is Denmark, with the same limit as the USA of 5μg/m^3." [5]

There are two main factors limit the application of hard chrome: the first and vital reason is in the manufacture stage, the hard chrome plating bath contains Cr^{6+}, which induce adverse health and environmental effects. "Chromic acid means lots of hexavalent chrome and the process is quite inefficient, with most of the current going to hydrolyze the water, producing copious amounts of hydrogen and oxygen bubbles. When they raise to the surface these bubbles burst, throwing a fine mist of hexavalent chrome into the air [5]." Cr^{6+} mist air emissions must be trapped in scrubbers, contaminated waste water must be treated before release to public treatment plants or water courses and solid wastes must be disposed of as hazardous waste. The heavy metal effluents lead to high disposal cost.

Another disadvantage is attributable to the long life cycles of hard chromium plated rod surfaces. When used with a hydraulic rod sealing system shown in figure 7 (A), the rod surface will either become smoother or be prone to minute scratching [6]. In the dynamic seal tests, standard hard chrome plated rods from different sources were used. These rods differed from each other in terms of thickness of the hard chrome plating as well as surface roughness and structure, such as grinding pattern. Figure 7 (B) shows the surface values of typical hard chrome plated rods generally available on the market or produced by customers. Consequently, the sealing part could be scratched by the hard chrome surface and the hydraulic cylinder will be completely failure. The search for alternative coatings is also being driven for reduction of seal wear and longer life of hydraulic cylinders.

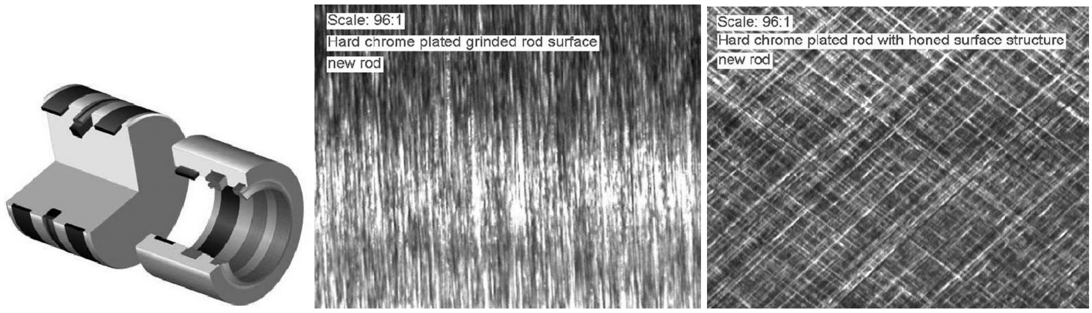


Fig 7.A) Schematic sealing system B) Hard chrome rod with ground and honed pattern [6]

Additionally, there are more demands on the hydraulic cylinders, including: improve the corrosion resistance, reduce fatigue loss and lower overall cost.

1.4 Alternatives to hard chrome

When replacing hard chrome coating, in fact often the total system (substrate + coating + manufacturing method) is designed for the purpose of using the coating that must be replaced. Therefore one must ask a number of questions to ensure that the replacement makes good engineering and economic sense: what are the hard chrome coating functions and what properties does the replacement really need? Does the new coating requires a change in substrate material or component design? For example, a new PVD coating may requires a more temperature tolerant substrate to be effective.
What is the true cost of the process, old and new? Including development, source materials, coating, and finishing, not just the coating part of it. [7]

Through extensive searching for surface treatment methods, there are a large number of potential process substitutions for hard chrome including thermal spray, electro and electroless plate, laser and weld coating, vacuum coating, heat treatment coating as shown in table 3**.**

Among the various alternatives to hard chrome, actually some coating methods have been used for hydraulic cylinder piston rods successfully by piston rods manufacturer: HVOF (high velocity oxygen fuel), electroless tungsten nick alloy plating and plasma spraying. Additionally, as a replacement for hard chrome, stainless liner is a novel promising technique needs to be learned further.

Table 3.Alternatives to hard chrome that maybe applicable to hydraulic cylinders

	Hard chrome alternatives
Thermal spray	HVOF(high velocity oxygen fuel), plasma flame and arc spray, cold(dynamic spray)
Electro and electroless plate	Electro deposition(Ni-W-SiC, Ni-W-B, Fe-Ni-W) Electroless Nickel plating
Laser and weld Coating	Laser cladding, weld cladding, seam welding Impact welding (explosive bonding, electro spark deposition)
Heat treatment Coating	Nitriding, carburizing, Metallurgical rolling bonding, Stainless liner
Vacuum coating	Physical vapor deposition (PVD) Chemical vapor deposition (CVD)

1.4.1 HVOF and coating material Cr_3C_2-NiCr

Due to outstanding characteristics, HVOF coating has been widely used in aerospace, automotive, power generation, transportation, petro chemical metal process, paper industry and heavy equipments.

a) Thermal spraying coatings and HVOF spraying process

Thermal spraying is one of classic fusion process for surface coating. The coating material is melted at a certain distance from the substrate, and projected it towards in fine molten droplet. They are fed in powder or wire form, heated to a molten or semi molten state and accelerated towards substrates in the form of micrometer-size particles as shown in figure 8. [8]

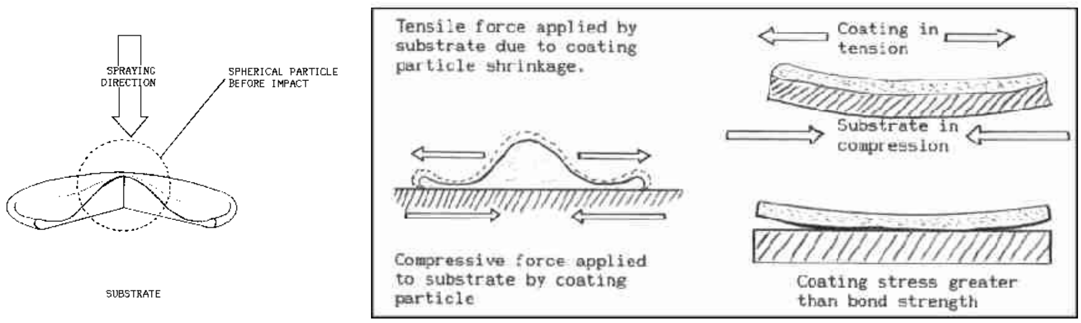


Fig 8.Schematic sprayed particle and compressive stress within the surface of the substrate [8]

Various types of substrate materials could be used for thermal spraying and substrate temperatures remain typically below 200 ^oC. Cleaning and grit blasting are important for substrate preparation. This provides a more chemically and physically active surface needed for good bonding. The surface area is increased, which will in turn increase the coating bond strength. The rough surface profile will promote mechanical bonding.

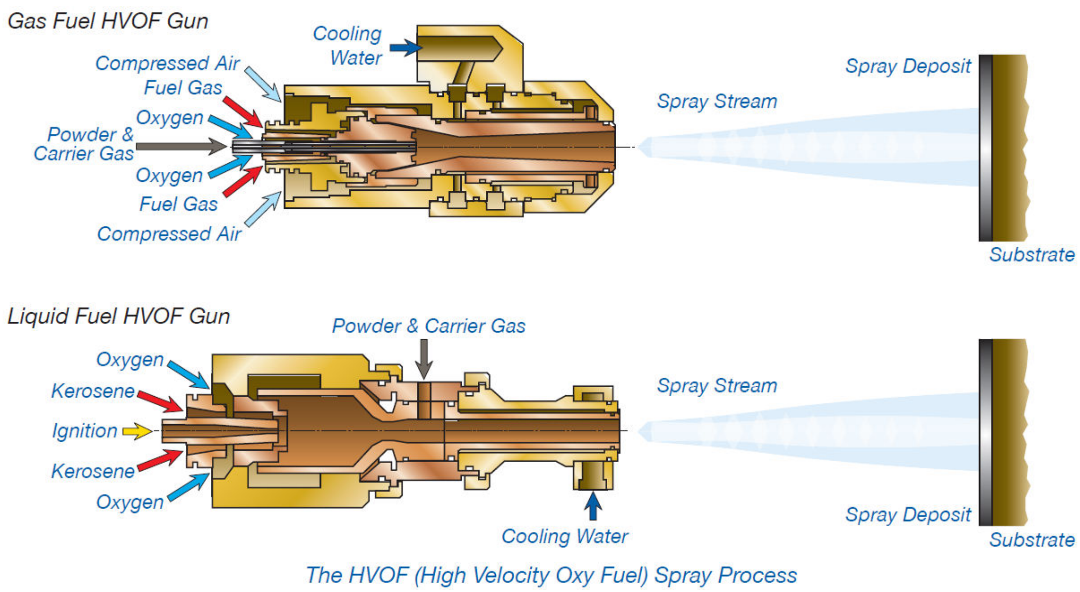


Fig9. Schematic of a typical HVOF thermal spray system [9]

HVOF is an abbreviation for high velocity oxygen fuel, a method of thermal spaying process. A typical thermal spray system consists of the following key components: spray gun, feeder (for supplying the powder), media supply (gases or liquids for the generation of the flame) and spray controller (robot for manipulating the gun or the substrates to be coated). Figure 9 is a schematic of a typical gas fuel and liquid fuel HVOF system. [9]

The properties of HVOF coating depend strongly on the process conditions. The most two important considerations are the strength of coating and the integrity of its bond with the substrate. Strong coatings are associated with complete interfusion between the molten droplet on striking the surface, and low porosity [10].

b) Material study: Cr_3C_2-NiCr

Available materials for HVOF coating include pure metals, alloys, ceramics, plastics and composites according to various demands. The cermet (ceramic-metallic) coating is a conventional composite, consists of hard particles like Cr_3C_2 or WC embedded in a metal binder, which can be a pure metal or a mixture of Ni, Cr and Co.

Table4. Wear and corrosion resistance as priority

A) HVOF coating materials sorted by wear resistance

Product	Composition
Diamalloy 2003/4/5/6 Sulzer Metco5812/5810	WC-12~17%Co alloy
WOKA 360/365/370 Sulzer Metco5843/7,5803	WC-Co-Cr alloy
WOKA 710/720/730 Diamalloy 3004/5/7 Sulzer Metco 5255	Cr_3C_2-20/20/25%Ni Cr Cr_3C_2-25/20/7%Ni Cr Cr_3C_2-50%Ni Cr
AMDRY 4532/4535	Ni-Cr alloy

B) HVOF coating materials sorted by corrosion resistance

Product	Composition
Diamalloy 3001/3002NS AMDRY 4532/4535	Co-Mo alloy Ni-Cr alloy
WOKA 360/365/370 Sulzer Metco5843/7,5803	WC-Co-Cr alloy
WOKA 710/720/730 Diamalloy 3004/5/7 Sulzer Metco5812/5810	Cr_3C_2-20/20/25%Ni Cr Cr_3C_2-25/20/7%Ni Cr WC-12~17%Co alloy

Carbides based cermets coatings are widely used against wear and corrosion in gas and oil industries. Their wear resistance is three to five times that of electroplated chromium, and their manufacturing costs are low. It was pointed out that the wear behavior of coatings depends on the microstructure and the volume fraction of carbides being preserved during the deposition process [11]. Several studies and reviews have already appeared focusing on materials for thermal spraying of wear resistant coatings. Carbides, oxides and cermets have received the majority of interest; in particular, nickel–chromium based coatings containing chromium carbide particle dispersions (hard phase), due to their excellent oxidation resistance and are candidates for continuous service in the range of 550–8158C, with a maximum of 9008C for discontinuous service. [12]

Table 4 shows some HVOF coating materials have been used successfully in surface applications: A) wear resistance and B) corrosion resistance as priority. In order to achieve satisfactory properties, cermet Cr_3C_2-NiCr coating could be a preferable alternative to hard chrome.

The SEM image of sintered Woka 720 and morphology of Cr_3C_2-NiCr powders was shown in figure 10. Cr_3C_2-NiCr powder used in HVOF method, generally sinter crushed, the weight proportion of NiCr is from 7~50% according to the variation of requirements. The powder was in angular shape with angular carbide particles from 10 to 55μm aggregated densely in Ni-Cr alloy matrix. [13]

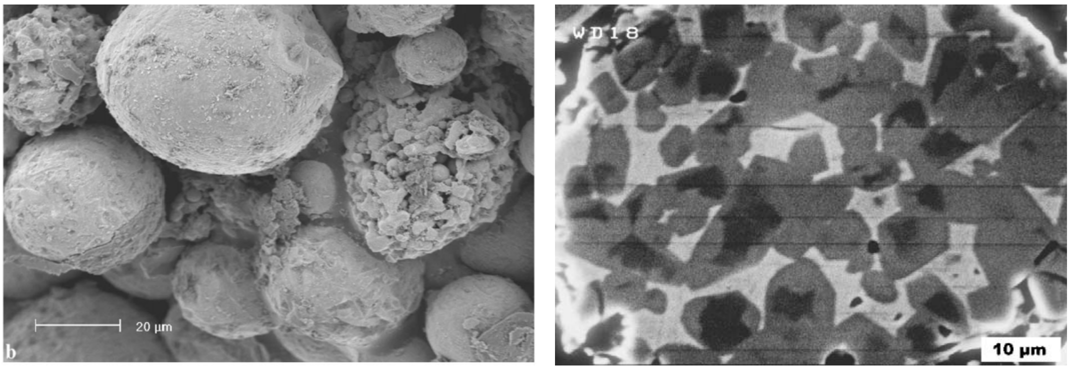


Fig 10.Woka 720 agglomerated sintered powder, morphology of Cr_3C_2-NiCr powder [13]

The powder was commercially available and hardness could reach 1200 Hv, information about conventional used Cr_3C_2-NiCr powders were shown in table 5.

Table5. Information about Cr_3C_2-NiCr powder (provide by Sulzer Metco)

Provider	Composition (Wt %)	Nominal grain size Distribution (μm)	Carbide size (μm)
WOKA 720, Sulzer-Metco	$75Cr_3C_2$–25(80Ni20Cr)	−55/+10	5-10
Diamalloy 3007, Sulzer-Metco	$80Cr_3C_2$–20(80Ni20Cr)	−45/+5	5-10

In the HVOF spraying process, melted and semi-melted particles (the particles are a mixture of Cr_3C_2 in a NiCr matrix) were observed for in the cermet coating. The cross section structure of the Cr_3C_2-NiCr coating which consists of: (A) Nanocrystalline NiCr matrix; (B) carbides; (C) low Cr_2O_3 content; (D) pores; (E) small cracks as show in figure 11. The main phenomena, which occur during spraying, are the thermal decomposition of the chromium carbide and the carbide reactions with the metallic binder. In the Cr_3C_2–NiCr coating, besides Cr_3C_2 particles retained from the starting powder, the carbides, Cr_7C_3 and $Cr_{23}C_6$, were also presented. Among three carbides present in the Cr_3C_2–NiCr coating, Cr_3C_2 retained from the starting powders plays the most important role in determining wear performance of the coating. [14]

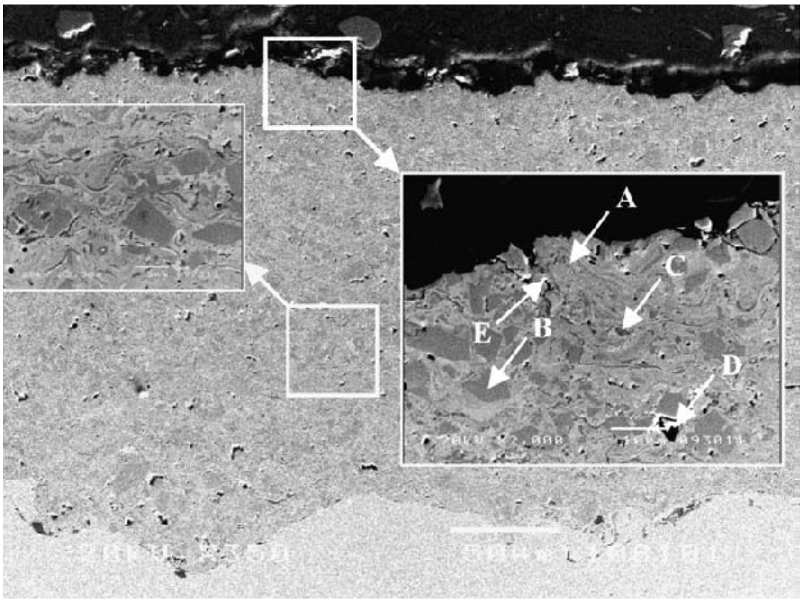


Fig 11.The consist of HVOF Cr_3C_2-NiCr microstructure, SEM cross section image [14]

c) HVOF Cr_3C_2-NiCr coating characteristics

Cr_3C_2-NiCr coating deposited by HVOF process has been studied by various researchers and the wear performance is compared with hard chrome coating. In general, there is no direct correlation between hardness, coefficient of friction and wear resistance, however high hardness, low coefficient of friction often are taken as an indicator of good abrasive wear resistance.

Figure 12 shows microhardness values (HV 0.3) of hard chrome and hard chrome alternatives like Cr_3C_2-NiCr coating that have been investigated and published:
Hard chrome: 800~1000.
Cr_3C_2-NiCr50%: 900, Cr_3C_2-NiCr20%: 1100, Cr_3C_2-NiCr25% 750~ 1300. [15]

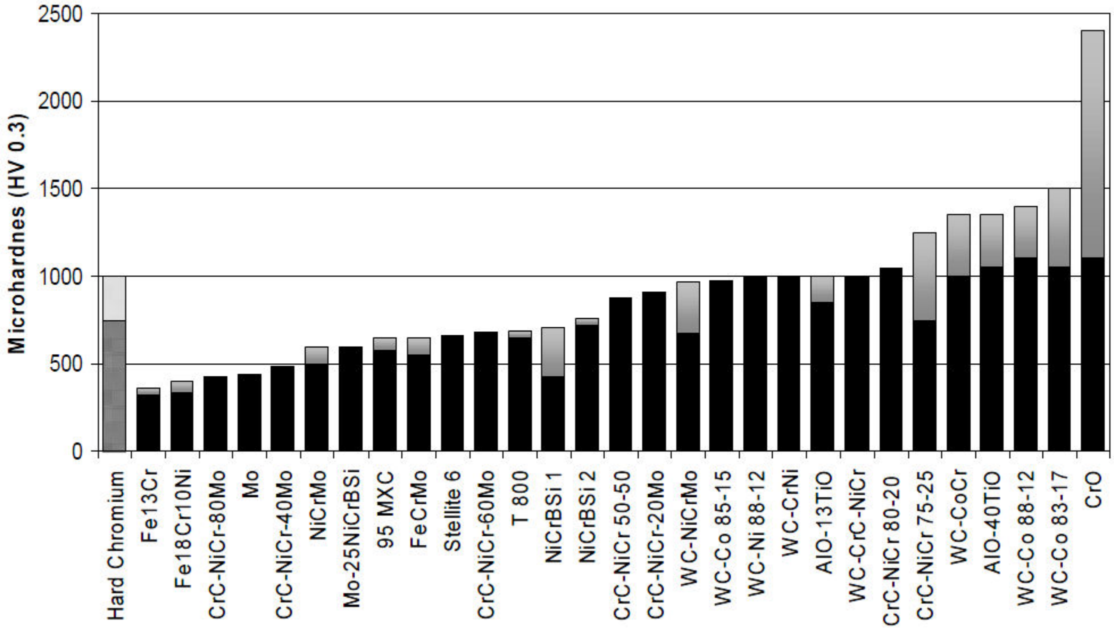


Fig12. Microhardness values as alternatives to hard chrome (published in the literature) [15]

Table6. The conditions of dry abrasive wear test [16]

Normal load (N)	45
Wheel (rpm)	201
Total sliding distance (m)	8657
Total duration of the test (min)	60
Wheel surface speed (m s^{-1})	2.4
Abrasive material	Silica
Particle size range (µm)	150-300
Feed rate (kg/h)	19.32

In abrasive wear test, the coated samples were tested using dry abrasive rubber wheel. The coated sample was mounted in the sample holder and was pressed against the rim of the rubber wheel as shown in figure 13 [16]. The dry silica sand fell freely between the wheel and the coated surface. The test conditions followed are given in table 6.

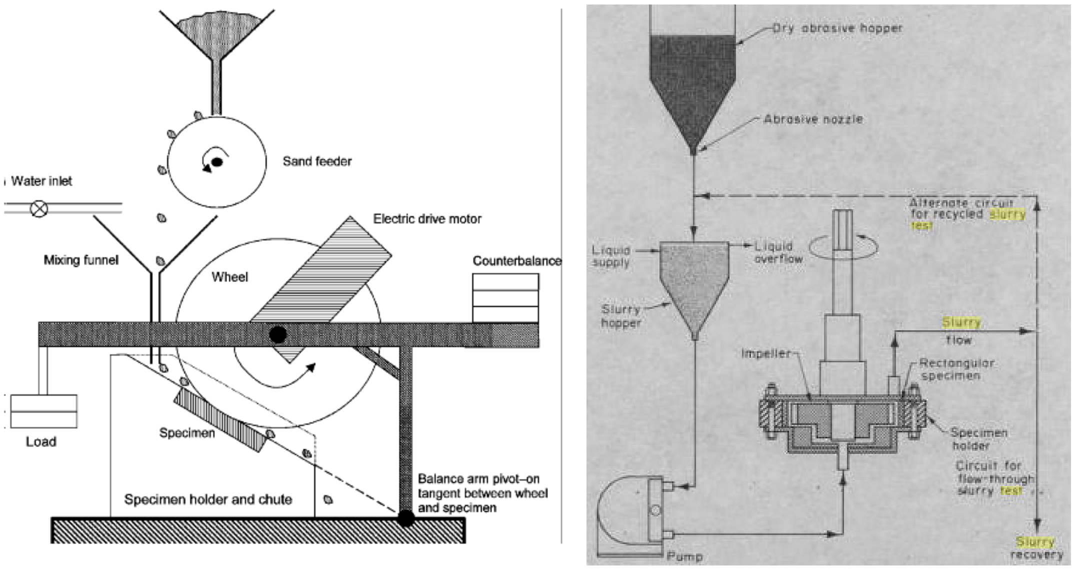


Fig13. Schematic diagram of abrasive test rig and slurry abrasive wear testing [16]

The results of carbide-based thermally sprayed coatings comparing to the hard chrome plating have been shown in figure 14. The wear test on the hard chrome plating had to be discontinued after 20 min as the plating got completely peeled off the substrate at the test region under identical test conditions, indicating the poor adhesion of the plating to the substrate. HVOF Cr_3C_2-NiCr coatings have much better abrasive wear resistance compared to the hard chrome plating. [17]

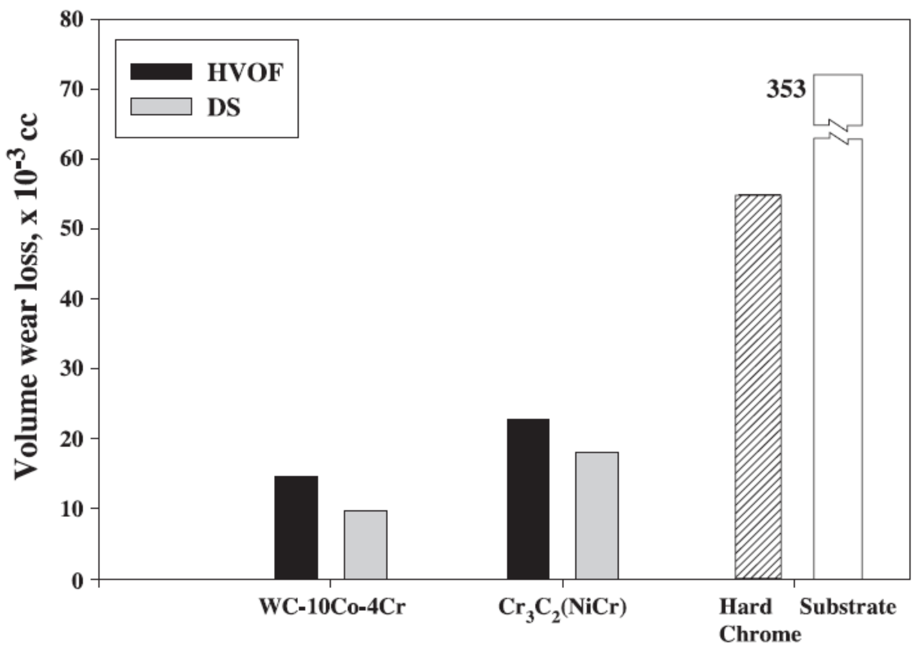


Fig14. The loss volume of thermal sprayed coatings vs. hard chrome plating in abrasive test [17]

In slurry abrasive testing, the material surface was exposed to hard particles moving along and forced against it; hard particles are mixed in a liquid, so slurry could be pumped in the test as shown in figure of 14. Miller Number is an index of the relative abrasion of slurries. The wear damage on the standard wear block is worse as the Miller Number gets higher. The SAR (slurry abrasion response) Number is an index of relative abrasion response of materials as tested in any particular slurry of interest. The SAR Number is a generalized form of the Miller Number. [18]

Experience has shown that slurries with a Miller or SAR Number of 50 or lower can be pumped with minor abrasive damage to the system. It was clearly demonstrated in figure 15 [19]; the SAR number of HVOF coatings like WC-Co and Cr_3C_2-NiCr are below 50, show better performance than hard chrome coating (approximately 100) in slurry abrasive testing.

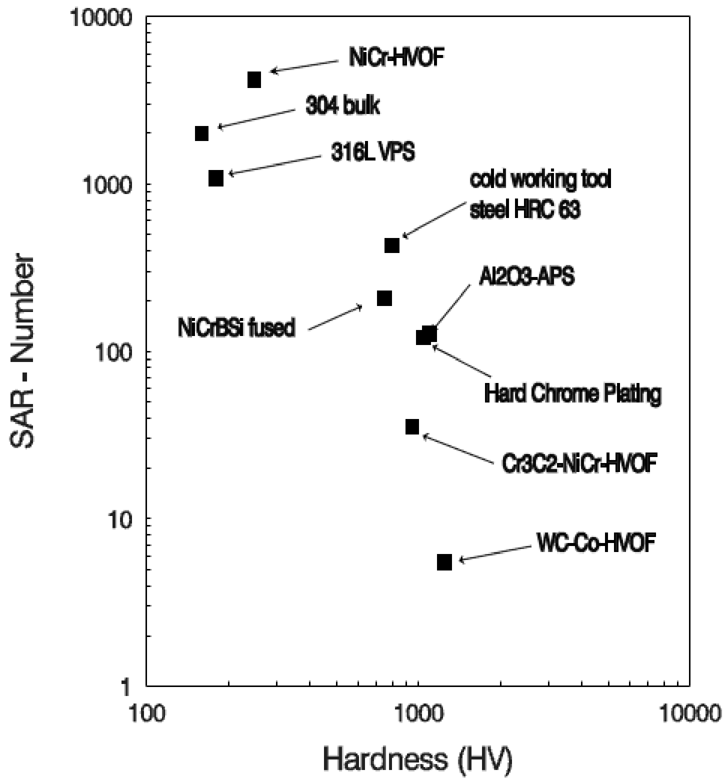


Fig15. The SAR number of different coatings and bulk materials as a function of hardness [19]

Hard chrome and various thermal spray coatings on different substrates have been investigated in salt spray fog testing, the results are shown in figure 16 [20]. On mild steel substrate, hard chrome coating presents excellent corrosion resistance. Comparing to the other alternatives, HVOF WC-Co-Cr and Cr_3C_2-NiCr coatings indicate relatively good corrosion protection.

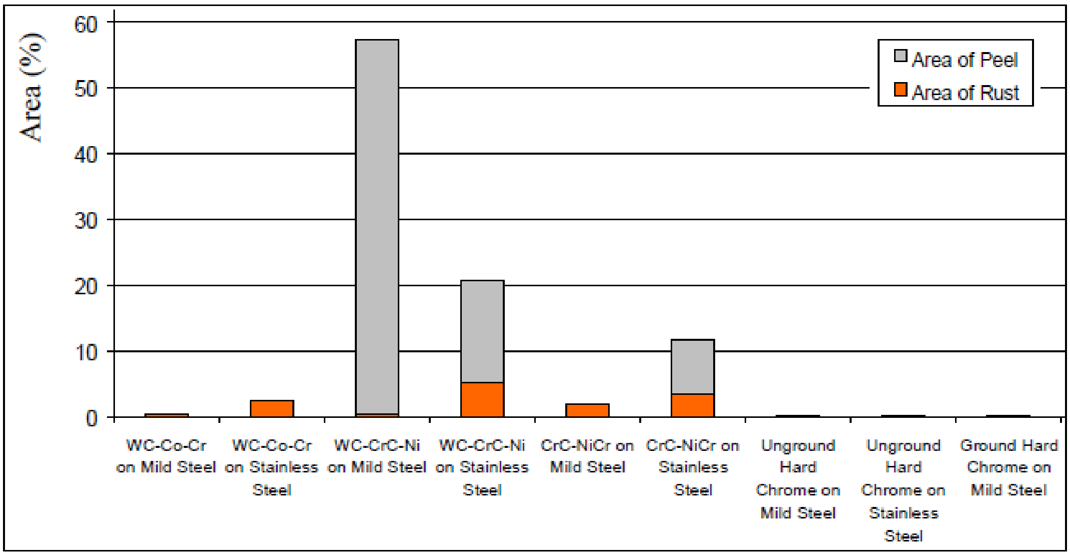


Fig16. Percentages area of coupons corroded after exposed to salt fog for 30 days [20]

Therefore, coatings produced using HVOF have advantages comparing to other hard chrome alternatives that include: optimum hardness and toughness, excellent wear resistance and good corrosion resistance. After preliminary discussion, taking into account of the manufacturer and customer's opinions, HVOF and cermet powder Cr_3C_2-NiCr are probably the most promising material among the competitors.

1.4.2 Other competitors

Plenty of investigations have been done for replacement of hard chrome; actually some alternatives have been approved for producing piston rod coatings on hydraulic cylinder.

a) Nickel based electroplating and electroless plating coatings

Nickel based coatings are applied by electroplating or electroless plating techniques. Examples of these alloys, mixtures and composites coatings are listed in table 7, with proved hardness, coefficient of friction and wear properties. Hard chrome also is given for comparison [21].

Electroplating is a plating process that uses electrical current to reduce cations of a desired material from a solution and coat a conductive object with a thin layer of metal as shown in figure 17. Electroplated nickel itself is not a very hard material, with a VHN of about 230. However, coatings with a nanocrystalline structure have exhibited higher microhardness values. To obtain higher hardness values, alloying also has been investigated, especially with tungsten additions.

Table7 Properties of Nickel based alternative coatings [21]

Coating	Substrate	Application Method	Hardness VHN	Coefficient of friction	Wear resistance
Hard chrome	various	electroplating	800-1000	0.25-0.40	1.0-4.7[1]
Ni-W (25-45%)	steels	electroplating	800-1000*	___	___
Ni-W (< 25%)	steels		500-600	___	___
Ni-Co (50~30%)	steels		860/1150*	___	10-11/8.6[2]
Ni-Co+ WC (25~30%)	steels		850	0.31	4[3]
Ni-B (5%) + Ti (5%)	steels	electroless plating	700/1200*	___	___
Ni-P (6%)	steels		942*	___	15.0[1]
Ni-P (8%)	steels		600/1000*	___	11.6[1]
Ni-P (7-10%) + MoS_2 (<50%)	Steels, Al		675	0.85	> EHC

* After heat treatment

1. Taber (abrasive) wear index, CS-10 wheel, 1 kg load.

2. Taber (abrasive) wear index, CS-17 wheel

3. Pin on disk sliding wear loss, $mm^3/Nm.10^{-6}$

Higher hardness values were obtained with the amorphous or nano structured Ni-W alloy coatings. With less than 25% tungsten in the coating, the measured hardness was 600 VHN, but when tungsten concentration was increased to be in the range of 25 to 45%, a hardness of about 800 VHN could be obtained, as deposited. After heat treatment, values as high as 1,000 VHN were measured. Adhesion was excellent, but wear resistance data for these alloys were not reported [23].

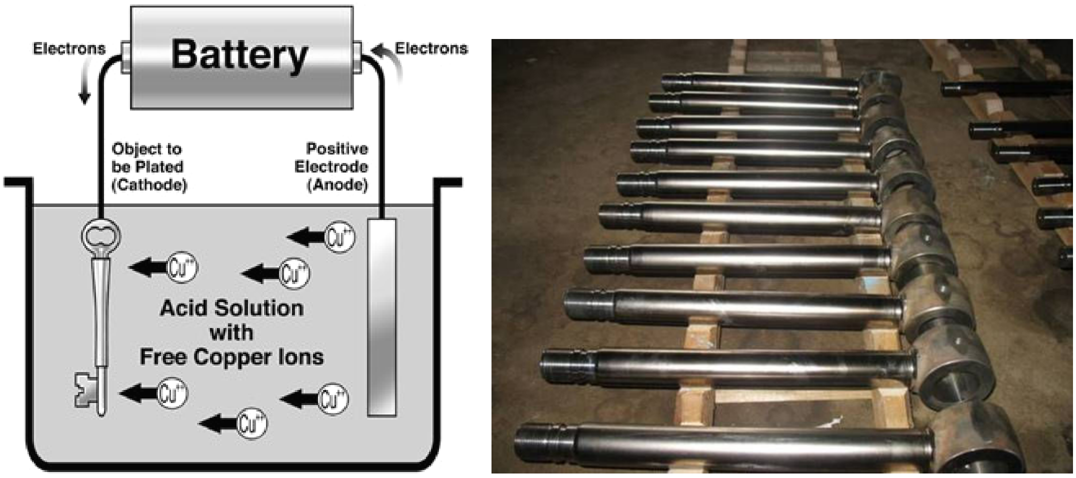


Fig 17.Sketch of electroplating and electroplating piston rods [22]

The addition of nanometer-size particles, such as tungsten carbides, to a nickel-cobalt electroplated matrix has been successful for improving hardness and wear resistance according to the data listed in Table 7. As deposited, the hardness is 850 VHN, and the coefficient of friction and sliding wear resistance compare very favorably with the baseline EHC [24]. For electroless plating, some published quantitative data are given in Table 7 for the most common Ni-P and Ni-B alloys, and others with metals such as cobalt or tungsten. The as deposited hardness of these coatings typically falls in the range of 500 to 800 VHN. When heat treated, most of the coatings listed become harder (900 and1200 VHN) because of a precipitation hardening mechanism. The hardness depends on the composition, concentration of the reducing agent element incorporated (i.e., B or P), and the type of heat treatment.

The Nanofilm has produced hydraulic piston rods with nickel based alloy coatings. The coating processes for different coating materials are similar in that they are electrolytic and deposit a coating of nickel and tungsten with minor percentages of boron or silicon carbide to enhance the coating properties. The nickel-tungsten based alloy electroplating processes are available as alternatives to hard chrome. [22]
Coating materials include:
Nickel-tungsten-boron (Ni-W 46% -B 7.5%)
Nickel-tungsten-silicon carbide (Ni-W 39.5% -SiC 1%)
Iron-nickel-tungsten (Fe-Ni 30%-W 30%)

Ni-W-B electroplating deposits an amorphous alloy. The coating has a bright, silver-white appearance. The coating has favorable chemical and abrasion resistance, high ductility, a low coefficient of friction, and plates very uniformly. A post-plating heat treatment is required to increase the hardness to a level comparable or slightly harder than chrome plating.

Ni-W-SiC composite plating is similar to Ni-W-B, except that it uses silicon carbide particles interspersed in the matrix to relieve internal stress and improve coating hardness. The appearance of the coating is similar to that of Ni-W-B, and heat treatment (- 500' F for 46 hours) raises the hardness significantly to a level that is as hard as or slightly harder than chromium.

Electroplating processes are very compatible with the facilities and equipment used for chrome plating: the tanks can be converted with a liner, stainless anodes, additional circulation and filtration and automatic chemical controllers. Electroplating process uses less energy than chrome plating. Coatings are more uniform than chrome plating, piston rods exhibit good performance like wear and corrosion resistance based on customers' feedback. The major disadvantages associated with these tungsten plating processes are (1) their lack of maturity, (2) potential increased costs over chrome, and (3) their reliance on nickel. [25]

b) Plasma spraying coatings

Hunger, a German company, has developed a coating technology Ceraplate as shown in figure 18, which used in aggressive environment for piston rods. As an alternative to the hard chrome, the ceramic coating improves surface protection significantly against chemical attack and mechanical wear.

Technical facts of Ceraplate coatings: sprayed Ni/Cr base inter layer and Cr_2CO_3/TiO_2 top layer. Layer thickness: interlayer approximate 150 µm, top layer approximate 200 µm. Hardness of top layer 950 HV to 1050 HV. Surface super finished to Ra = 0.15 µm. For piston rods up to a diameter of 1500 mm and a length of 20 m, the coating passed corrosion test (DIN EN ISO 9227, 1500 hours) and was proved good in practical application. [26]

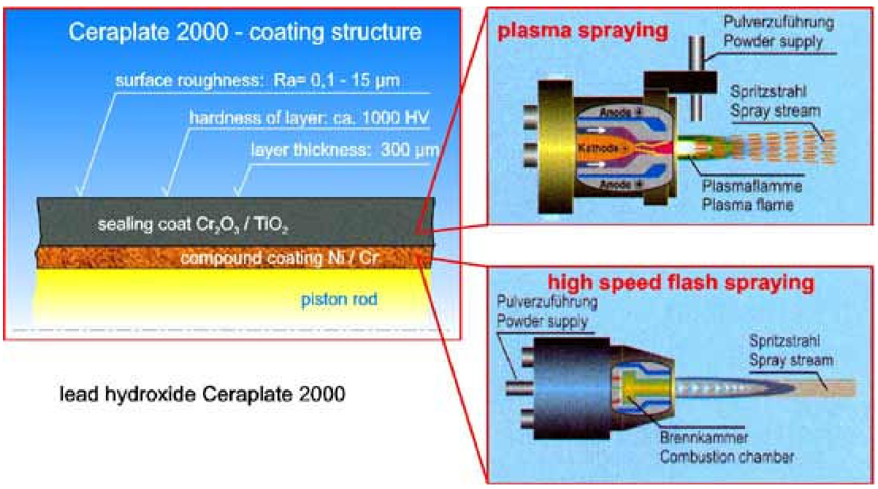


Fig 18.Sketch of Ceraplate coating 2000 for hydraulic piston rods (Hunger Corporation) [26]

c) Stainless steel tube cladding

Additionally, using a stainless steel tube clad on the piston rod substrate is a novel method, which needs to be studied further. A tube could be used as a protective covering liner that protects the piston rod surface. When heat up the tube and cold down piston rod, diameter of tube increase and rod volume contract, if space is adequate, the rod could be put into the tube. After return to room temperature, the rod would be hold tightly by the tube. The liner maybe could replace hard chrome coatings and right choice of liner material is vital.

Since hardness and corrosion resistance are essential criteria, martensitic stainless steel is the most promising material for piston rods' liner. The hardness and chemical composition of martensitic stainless steel are listed in the table 8. The corrosion resistance of these stainless steels is excellent in sea water, weak acids and weak alkalis, acceptable in strong acids.

Table 8.Stainless steel designations and chemical composition (hardness > 500 HV)

Designation (Martensitic)	**Vickers Hardness**
AISI 418 (temper at 260 C)	475-585
AISI 420 (temper at 204 C)	540-590
AISI 440A (temper at 316 C)	500-600
AISI 440B (temper at 316 C)	560-660
AISI 440C (temper at 316 C)	590-690
Semi-Austenitic 17-7 PH (TH 1050)	350-500
Martensitic custom 455 (H 950)	460-500
Martensitic custom 465 (H 950)	459-517

Designation	**Cr**	**C**	**Mo**	**Mn**	**Si**	**Others**
AISI 440A	16-18	0.6-0.75	0.75	<1	<1	<0.04P,< 0.03S
AISI 440B	16-18	0.75-0.95	0.75	<1	<1	<0.04P,< 0.03S
AISI 440C	16-18	0.95-1.2	0.75	<1	<1	<0.04P,< 0.03S
AISI 420	12-14	>0.15	-	<1	<1	<0.03P,< 0.03S
Martensitic custom 465	11-12.5	0.02	0.75-1.2	0.25	0.25	10.8-11.2 Ni, 1.5-1.8 Ti

1.5 Aims of the study

The purpose of this investigation is to study the criteria for piston rods of hydraulic cylinders and alternatives hard chrome coating. After extensive searching for possible competitive alternatives to hard chrome, find out the most promising replacement of hard chrome on piston rods, regarding microhardness and corrosion resistance as top priorities:

(1) Evaluate present alternatives and determine which one is the most promising.

(2) Alternative versus hard chrome as the reference:

Microstructure characterization study
Impact test (appropriate method)
Hardness test
Corrosion test

(3) Seek for appropriate method cladding stainless linear on piston rods

Calculation stainless liner with distinct parameters

2. Test method

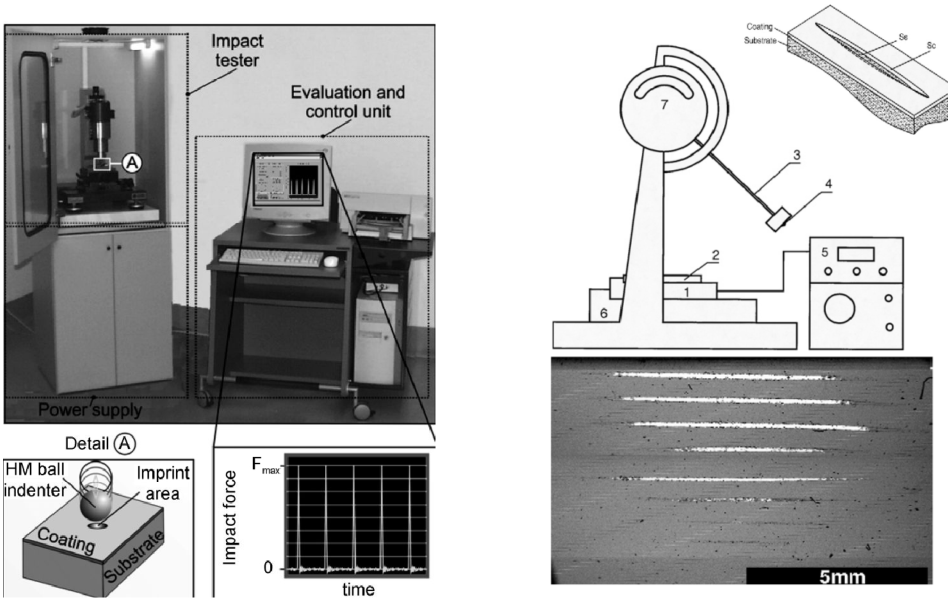
2.1 Methods to investigate mechanical properties of coatings

Coatings are increasingly being used in commercial production and in industrial series processes, for wear and corrosion protection to achieve specific surface properties. The test methods closely related to practical applications can be classified according to the stress mechanisms acting on the surface, the typical test methods are listed in table 9 [27]:

Table 9.Typical coating properties test methods

Coating properties	Test methods
Corrosion	Ageing test, current-density-potential measurement pin on disk test with corrosive intermediate layer Taber abraser with corrosive intermediate layer
Adhesion	Scotch tape test, pin on disk test
Thermal reaction	annealing in defined atmosphere, thermal shock test, heat wave measuring method
Abrasion	Taber abraser, pin on disk test with abrasive intermediate layer
Erosion	Sand blasting, slurry jet blasting
Cavitation	Sonotrode
Fatigue adhesion and crack propagation	impact test: ball indenter impact test, scratch test and Rockwell-C test

Coating fatigue strength and crack propagation could investigate by a ball indenter impact tester, as shown in figure 19 A). During the impact test an oscillating indenter system, a coil-spindle, with a cemented carbides ball, at its front tip, penetrates successively into the coated specimen at an adjustable peak force, which remains constant during the test. Through a parameter variation of the impact test, concerning the applied load and the number of impacts, a diagram of the impact force peak value vs. the number of impacts leading to a coating failure can be elaborated. [28]



(A) Ball indenter impact tester **(B) Pendulum grooving scratch tester**

Figure 19.Coating properties investigating tester

A single pass pendulum grooving has been used for investigating tribological behavior of coatings successfully, such as wear resistance, dynamic hardness, toughness and bonding strength. The device is developed from a common pendulum impact machine, as shown schematically in figure 19 B). The swinging pendulum is equipped with a sintered hard metal stylus at the lower end of hammer and the device has attached a precise specimen holder with an operating system for adjustable incursion depth of stylus in micrometer level. The stylus is finished to form an apex of 90° with a tip radius of 50m.A biaxial force sensor is constructed in the specimen holder for measurement of normal (Fn) and tangential (Ft) forces. The variation of Fn and Ft with time during scratching is recorded by a digital storage oscilloscope attached with an X–Y recorder. [29]

2.2 Coating impact test: use a pendulum machine

Toughness is another significant required property for piston rod coatings; it provides information on the resistance of material to sudden fracture, measures the toughness or energy absorption capability of materials.

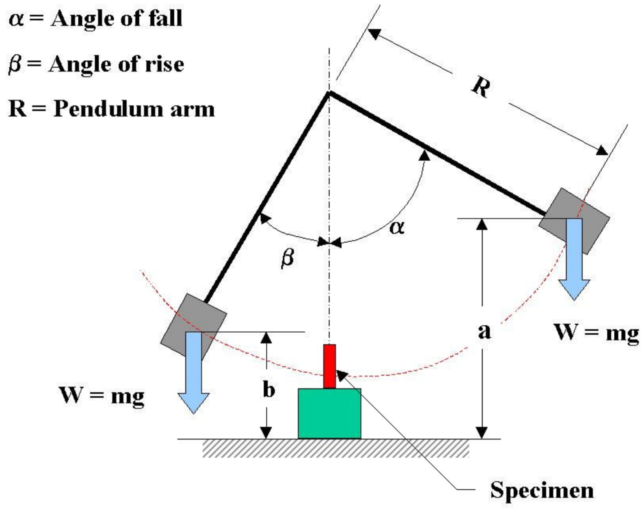


Figure 20.Schematic of impact test theory: use a pendulum machine

A pendulum impact test is a dynamic test in which a selected specimen is usually struck and broken by a swing pendulum. A pendulum machine used in a typical impact test is shown in figure 20. The hammer is raised to a certain height, before the hammer is released, the potential energy will be E_p, after being released, the potential energy will decrease and the kinetic energy will increase. At the time of impact, the kinetic energy of the pendulum E_k equal to potential energy E_p: $E_k = E_p$.

If: hammer mass = m, initial height = a, final height = b

$a = R(1 - \cos\alpha)$, $b = R(1 - \cos\beta)$

So: Initial energy: $mga = W a = E_i$

Energy after rupture: $m g b = W b = E_r$

Energy absorbed during impact: $m g (a - b) = W (a - b) = E_{abs}$

In the present impact test, the notched specimen will be replaced by cylindrical piston rod, the pendulum should stop at the lowest position; consequently the value of b is equal to zero.

So: Energy absorbed by coating and substrate

$$\mathbf{E_{abs} = m\, g\, a = m\, g\, R\, (1 - \cos\alpha)}$$

2.3 Expansion theory for stainless liner

The thermal expansion of pipes and bars could be expressed in a simplified way:

$$\Delta L = L * \alpha * \Delta T$$

ΔL ---- Length change in millimeter, L ---- Length in millimeter, α ---- Linear expansion coefficient, ΔT ---- T max – T min (temperature difference)

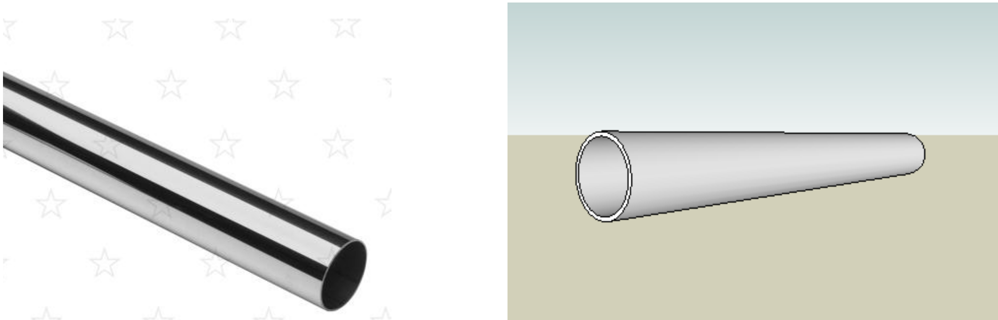


Figure 21.Image and schematic of stainless steel tube for piston rod liner

For stainless steel tube as show in figure 21 and piston rod substrate, the thermal expansion in radius could calculate:

$\Delta R = R * \alpha * \Delta T$ $\Delta r = r * \alpha * \Delta T$ ($2\pi\Delta R = 2\pi R * \alpha * \Delta T$; $2\pi\Delta r = 2\pi r * \alpha * \Delta T$)

R ---- Radius of stainless steel pipe, r---- Radius of carbon steel rod

3. Experimental procedure

3.1 Coating impact test

a) Coating impact test use a pendulum machine

HVOF coating as a promising alternative to hard chrome, various investigation and test have been operated, while knowledge on impact test is still limited because there lacks an efficient and practical method to evaluate. The conventional impact test machine is designed to study material toughness: a small piece of notched specimen will be cut off by the sharp hammer blade.

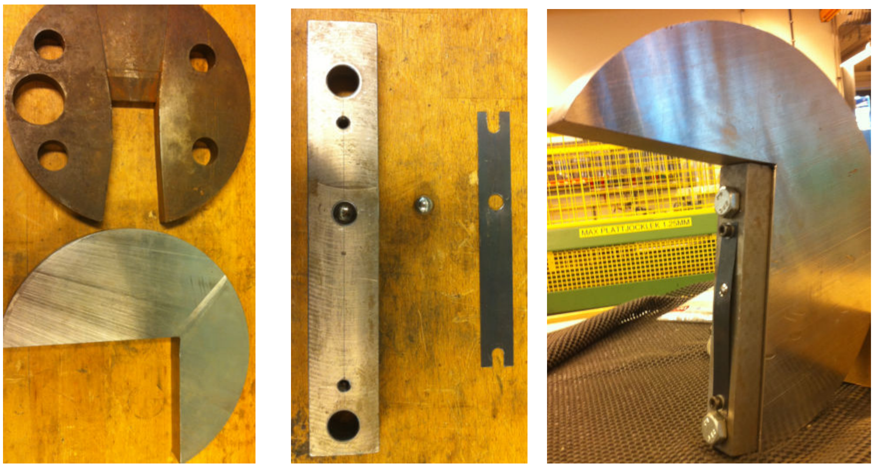


Figure 22.Pictures of modified hammer and blade: a hard steel ball has been used

This coating impact test aims to find out the critical energies of distinct samples, therefore the hammer of pendulum machine must be modified. Otherwise thin piston rod coating will be destroyed by sharp blade.

A new hammer was made for the cylindrical specimen. A 10 mm diameter and 5 mm deep hole was drilled on a steel bar. Then a 1 mm diameter hard steel ball SS45 is placed into the hole, after that the ball was covered by a steel sheet with 8 mm diameter round space preserved, finally the bar was fixed on the new hammer by screw as show in figure 22. Therefore the contact type was switched to spherical against cylindrical area.

The stages and holders for small specimen of the old pendulum machine were also modified, so bigger cylindrical specimen could be clad firmly as shown in figure 23.

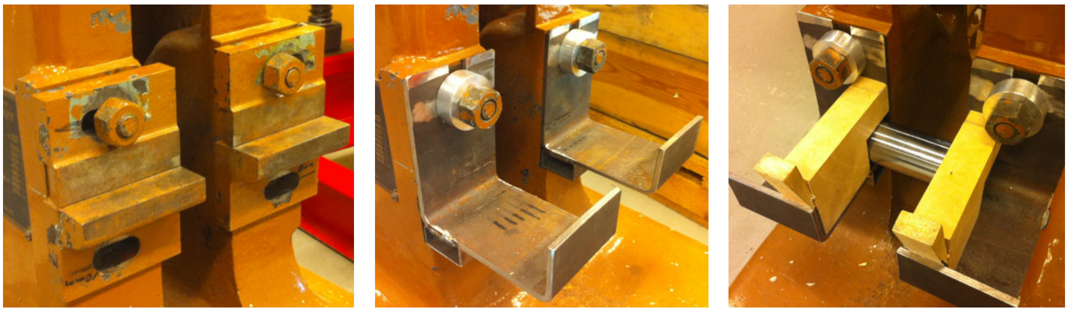


Figure 23.Pictures of modified holders and brackets for cylindrical samples

There are five coating piston rods for impact test:

Hard chrome (reference)

HVOF induction hardening plus grit blasted (h + g)

HVOF induction hardening (h)

HVOF grit blasted (g)

HVOF no pretreatment (no)

Take five distinct energy levels for each sample as show in table 10.

Table 10.Distinct energy levels for five samples

Energy level	**1**	**2**	**3**	**4**	**5**
Angle (degree)	30	60	90	120	150
Joule	11.8	44.1	88.2	132.3	164.6

Angle could convert to joule by the follow equation:

$$\mathbf{E_{abs} = m\ g\ a = m\ g\ R\ (1 - \cos \alpha)}$$

R = 705 mm   m = 9000 g

For each energy level, we plan to test 5 times and every piston rod should have 25 indentations. Once surface damage happened, the lower level of energy will be regarded as the critical energy for the coating as shown in figure 24.

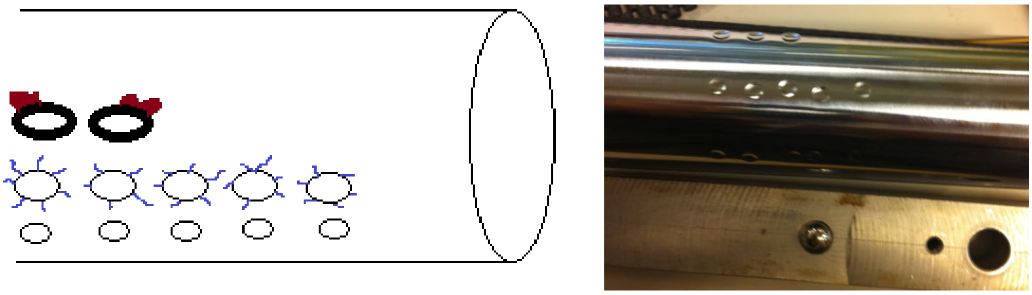


Figure 24.Schematic and photo of critical energy level for piston rod coating

b) Stereo microscope and indentation

The size of indentations was measured by stereo microscope, the resolution is 1 μm. The length along longitudinal and transverse direction was measured, according to contact type, it was spherical ball strike against cylindrical rod; the diameters of indentations refer to the mean value of longitudinal distance.

So the depth of each indentation could be calculated follow the equation:

Depth $\quad d = R - (R^2 - L^2/4)^{1/2}$

R ---- Radius of the steel ball

L ---- Longitudinal indentation length

The original data and indentation depth mean value were recorded, radial cracks (text in blue) and delamination area (text in red) also be measured. Original data recorded from each indentation (mm) was listed in appendix 1.

b) Optical microscope and SEM

As shown in figure 26, the microstructure of coatings cross section was studied using an optical microscope; morphology of coatings surface and indentations were studied by SEM (scanning electron microscope). The specimens were prepared in a normal way. The first step of preparation is cutting. The critical energy indentations were picked to investigate. The rods were cut off along the transverse directions.

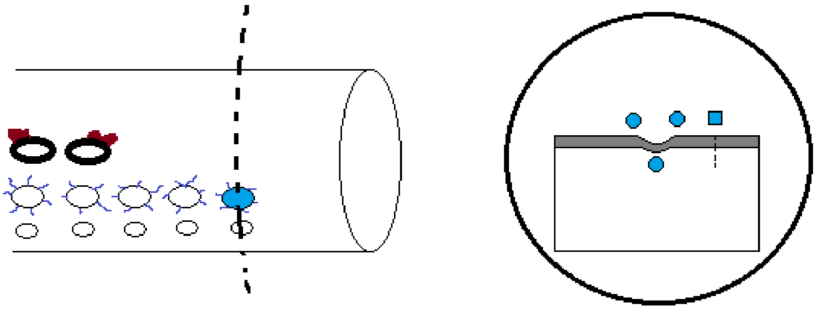


Figure 25.Taking critical energy indentations and cutting off along transverse direction

After cutting the piston rods and washing the samples, the cross section of indentation was plastified as shown in figure 25. Final step is grinding and polishing. The specimens were ground by Pinno using 25N 4 minutes with water, and then were polished as described below:

Alleqvo-20N 5min –blue lubricant-9μm; Dur-20N-6min- red lubricant -3μm ; Plusr-20N-6min- green lubricant -3μm. After each step specimen should be washed to avoid any contamination from the previous steps.

Figure 26.Photos of specimen preparation: cutting and plastify

3.2 Micro hardness test

Two specimens, hard chrome and HVOF (h + g), were selected to do a hardness test by the Microhardness tester. According to coating thickness, hard chrome 10 points and HVOF 20 points, the span is 10 μm. The test follows the straight line as shown in figure 19. The test load is 25 gram.

3.3 Corrosion test

The corrosion test was handled by SP technical research institute laboratory, salt spray test according to ISO 9227 AASS test.

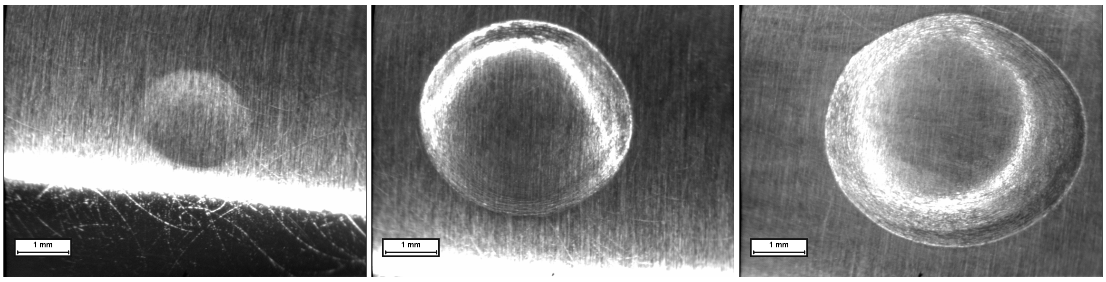
Three hard chrome piston rods Ø100 x 150 mm as the references numbered 1, 2, and 3. Six HVOF piston rods Ø100 x 150 mm marked 850, 851, 852, 853, 854, and 855. The items were cleaned by acetone before the corrosion resistance test. Then they were placed on plastic rackets at an angle between 15^{o} ~20^{o} to vertical. The samples were exposed to acetic acid salt spray for 72 hours. The PH value of used NaCl salt solution is about 3.1~ 3.3.

4. Results

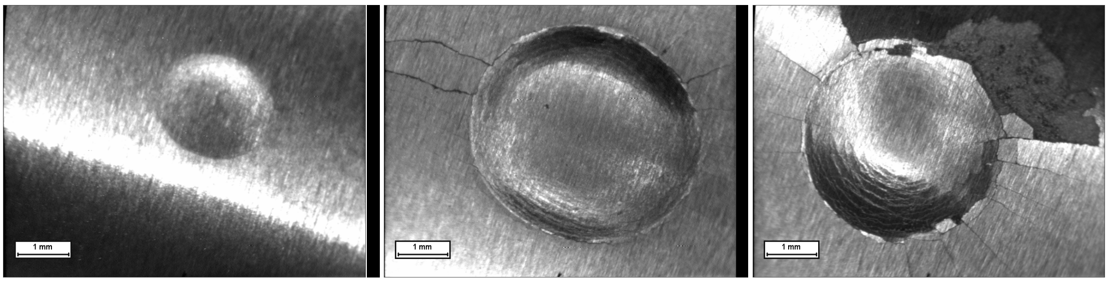
4.1 HVOF and hard chrome coatings

4.1.1 Various energy degree indentations

The diameter along longitudinal and transverse directions of hard chrome and HVOF coating indentations and surface damage could be observed by stereo microscope, as shown in figure 27. According to original data, the indentation depth mean values were calculated. The indentation depth, radial cracks texted in blue and delamination area texted in red are listed in table 11.



(A) 30/90/150 indentations of Hard chrome coating



(b) Indentation and surface damage of various HVOF coatings

Figure 27.Indentation photos of hard chrome and HVOF coatings studied by stereo microscope

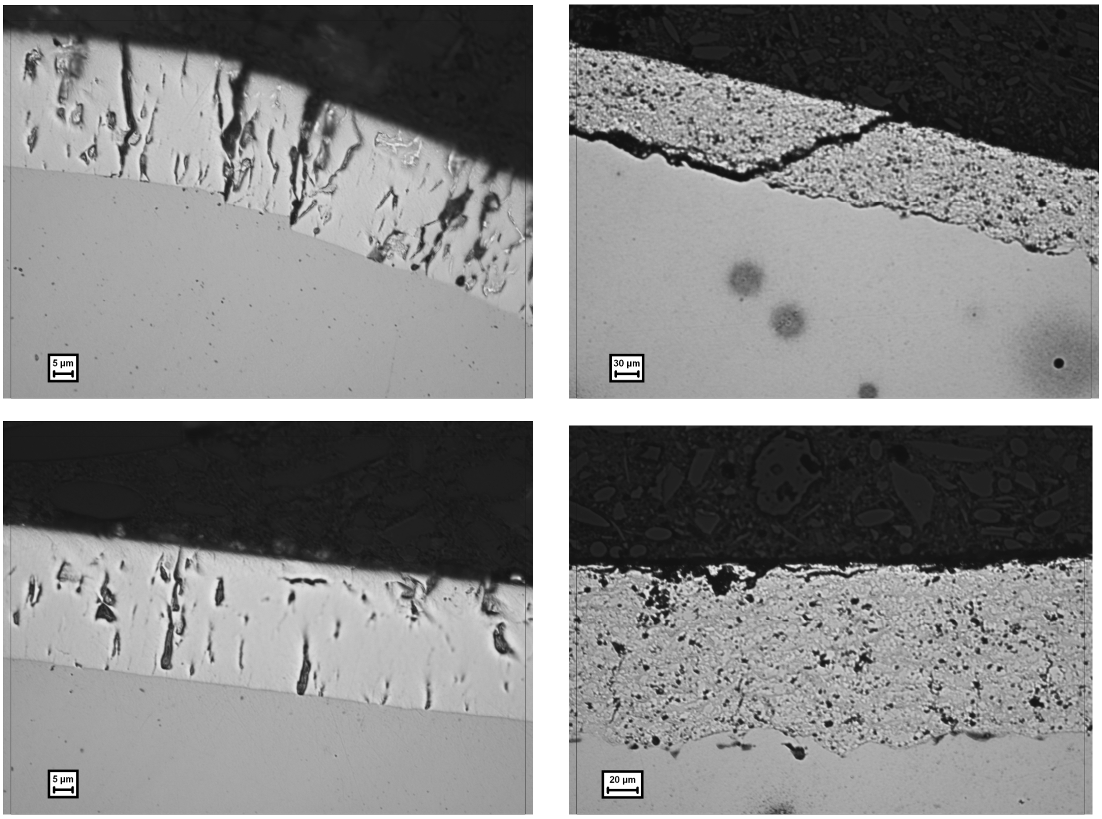
4.1.2 Coatings cross section of indentations

a) Hard chrome versus HVOF (h + g)

Hard chrome (150 energy degree) and HVOF hardening plus grit blasted (90 energy degree) coatings were investigated by optical microscope, as show in figure 28. Coating thickness was measured by optical microscope: hard chrome is 35.64 µm, and the HVOF coating is 119.31 µm.

Table 11.Original data recorded from each indentation (mm).

Depth - Energy **Crack/delamination**	**30**	**60**	**90**	**120**	**150**
Hard chrome	**0.12**	**0.28**	**0.42**	**0.6**	**0.7**
HVOF hardening +grit blasted	**0.13**	0.33 0.45	0.51 0.9	0.63 11.43mm^2	
HVOF Hardening	**0.14**	0.32 0.54	0.49 8.41mm^2		
HVOF Grit blasted	0.19 0.3	0.44 5.26mm^2			
HVOF No pretreatment	**0.12**	0.32 0.64	0.59 10.6mm^2		

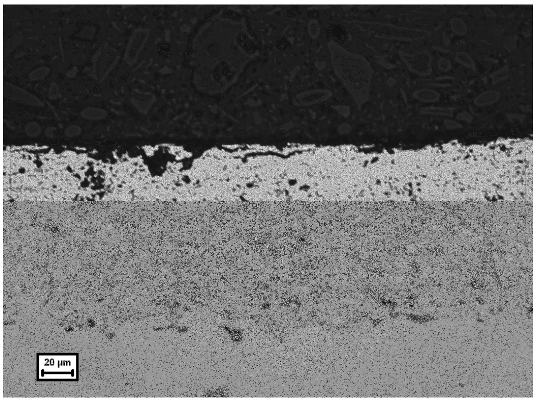


(A) Hard chrome: corner and bottom **(B) HVOF (h+ g): corner and bottom**

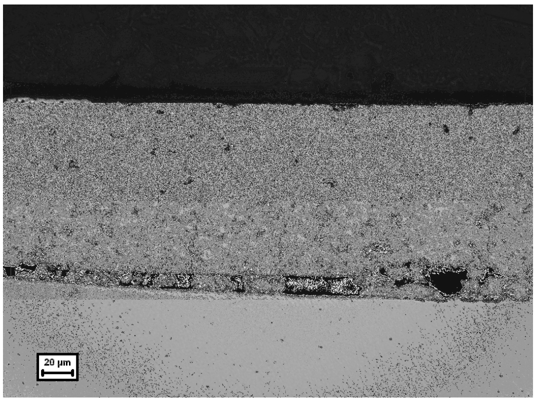
Figure 28.OM cross section images of hard chrome and HVOF samples

b) Pretreatment for HVOF coatings

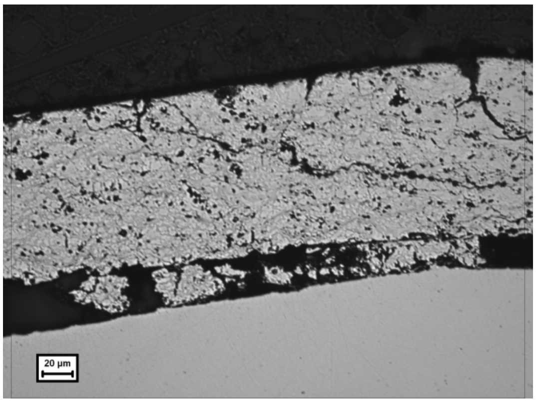
Various HVOF coatings, hardening plus grit blasted (90 energy degree) hardening (60 energy degree) and no pretreatment sample (60 energy degree) samples were investigated by optical microscope, as shown in figure 29.



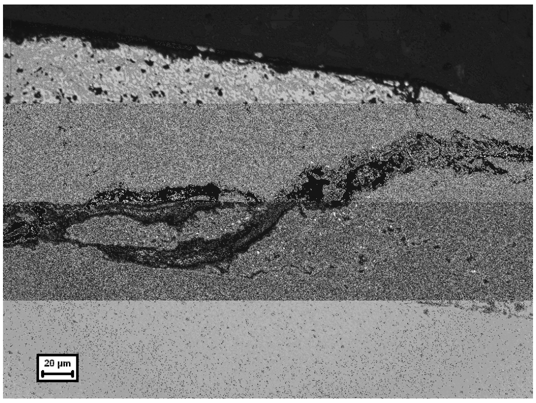
(A) HVOF (h+ g): 90 degree



(B) HVOF (h): 60 degree



(C) HVOF (h): 60 degree

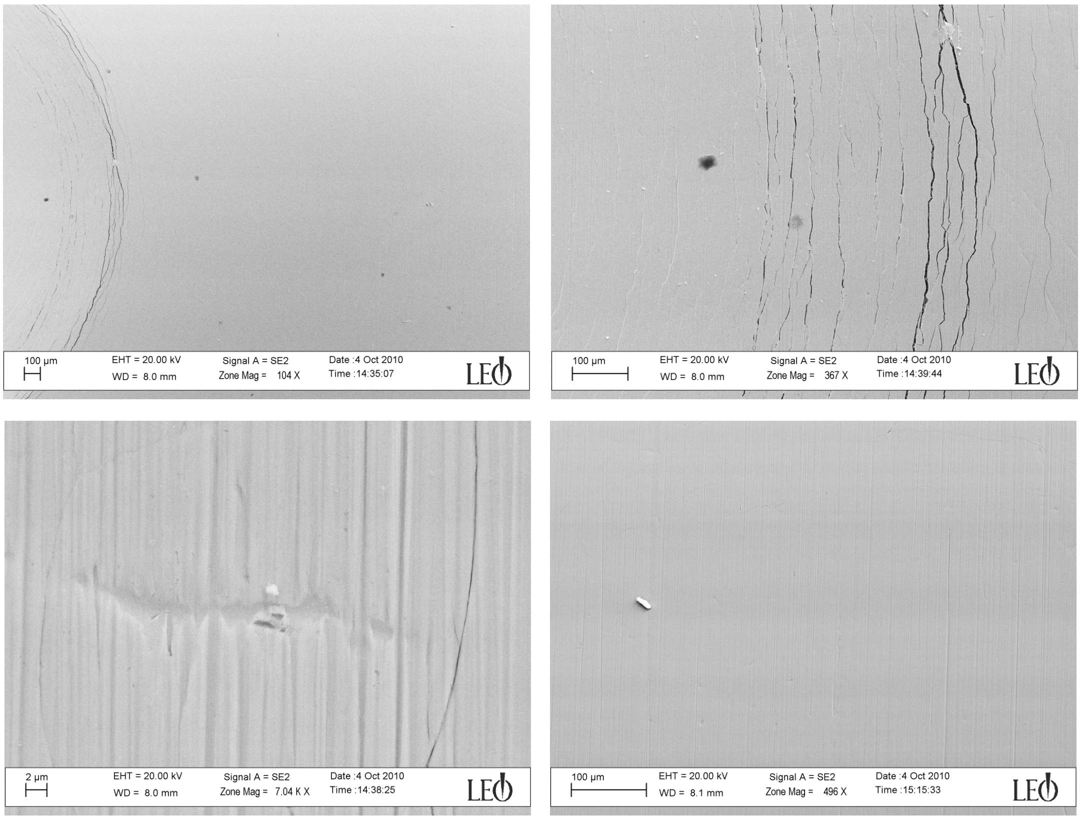


(D) HVOF (no pretreatment): 60 degree

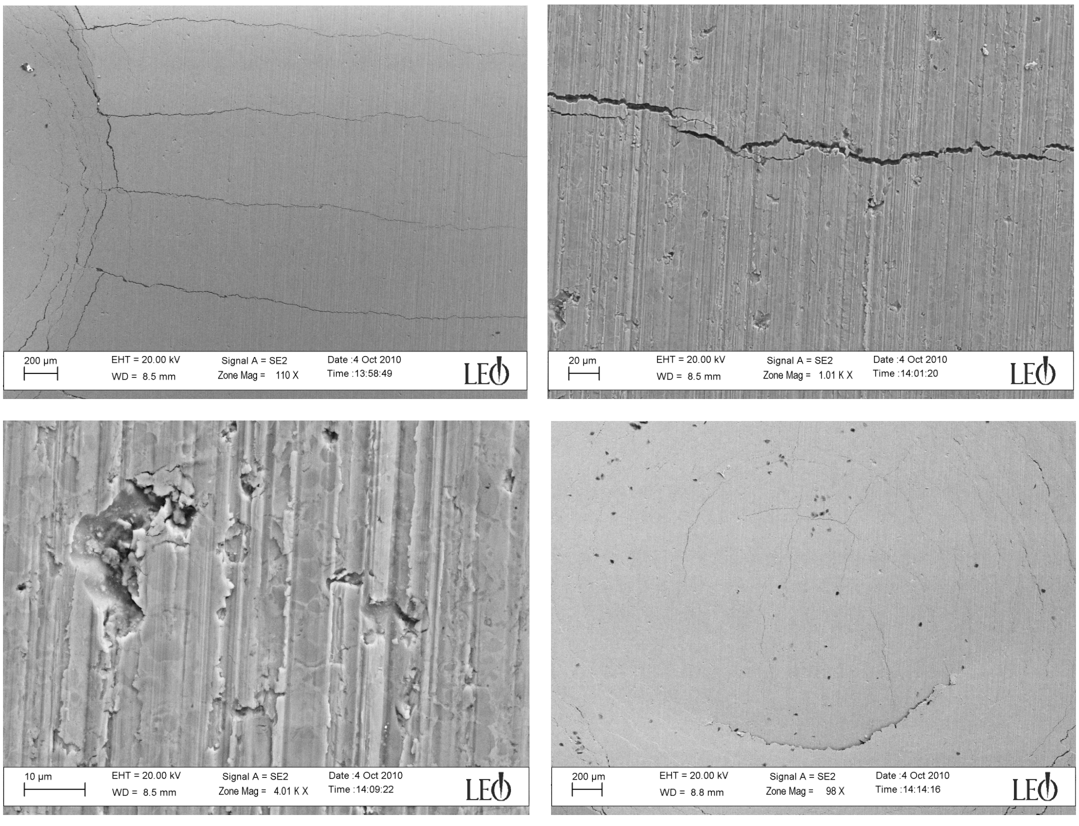
Figure 29.OM cross section images of HVOF samples

4.1.3 Crack patterns

Hard chrome (150 energy degree) and HVOF hardening plus grit blasted (90 degree energy) samples were selected for the investigation of surface morphology by SEM, the impact indentation patterns are shown in figure 30 A and B.



A) Hard chrome 150 degree



B) HVOF hardening plus grit blasted 90 degree

Figure 30.SEM coating surface images

4.1.4 Hardness test

The microhardness test results of hard chrome and HVOF (hardening plus grit blasted) coatings were listed in table 12.

Table 12.Hardness test results of hard chrome and HVOF (h + g) samples.

Test No.	1	2	3	4	5	6	7	8	9	10
Hv $_{0.025}$	**1589**	**1392**	**1223**	**1118**	**873**	**769**	**808**	**789**	**845**	**794**

A) Hard chrome

Test No.	1	2	3	4	5	6	7	8	9	10
Hv $_{0.025}$	**1731**	**1978**	**1969**	**2452**	**1973**	**2282**	**1727**	**1355**	**1213**	**2276**
Test No.	11	12	13	14	15	16	17	18	19	20
Hv $_{0.025}$	**3145**	**1527**	**2119**	**1215**	**754**	**721**	**665**	**640**	**614**	**638**

B) HVOF (h + g)

4.1.5 Corrosion resistance

(A) Hard chrome: ref. 1, 2 and 3 **(B) HVOF: 851, 852 and 853**

Figure 31.Pictures of items after 40 hours of exposure to acetic acid spray

As shown in figure 31, the samples were photographed after 40 hours of exposure to acetic acid spray. Table 11 indicates protection rating of the corrosion test items. Visual examination was carried out after rinsing and drying the samples. After 40 hours AASS test, hard chrome protect rating was No. 10; the protect rating of all HVOF coatings were No. 6 as shown in table 13.

Table 13.Corrosion test results of hard chrome and HVOF coating samples.

The objects	Protect rating after 24 hours	Protect rating after 40 hours	Protect rating after 70 hours
Ref. 1	10	**10**	10
Ref. 2	10	**10**	10
Ref. 3	10	**10**	10
850	7	**6**	5
851	7	**6**	5
852	7	**6**	3*
853	7	**6**	5
854	7	**6**	5
855	7	**6**	5

* No. 852 show flaking off of coating

4.2 Stainless liner

According to the comparison of various designation of stainless steel in section 1.4.2, Martensitic stainless steel is the most competitive material for the piston rod liner.

From equation **$\Delta R = R * \alpha * \Delta T$** and thermal expansion coefficient in table 14:

Three stainless pipes with different inner diameters

D= 50; 90; 150mm so R = 25; 45; 75mm

Assumption: heat up 500 ^{o}C from room temperature

α=9.9*10^{-6} ΔT=500

R = 25; 45; 75mm

ΔR= 0.125; 0.225; 0.375 mm

Three carbon steel rods with different diameters:

d= 50; 90; 150mm so r = 25; 45; 75mm

Assumption: cold down to 200 ^{o}C from room temperature by liquid nitrogen

$\alpha=12*10^{-6}$ $\Delta T=200$

r = 25; 45; 75mm

Δ r = 0.06; 0.108; 0.18 mm

Table 14.Thermal expansion coefficient for materials

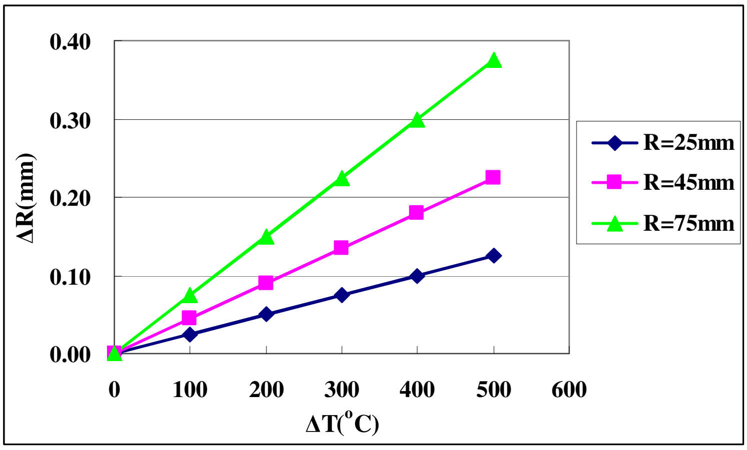
Material	Linear thermal expansion coefficient α (10^{-6} m/m ^{o}C)
Carbon steel	10~13
Stainless steel (Martensitic)	9.9

So for distinct diameter liners and substrates, heating the martensitic stainless steel tubes up to 500 , while cooling piston rod down to minus 200 by liquid nitrogen, space in radius **ΔL** for cladding could obtain as shown in figure 32:

ΔL= ΔR +Δ r

=0.185; 0.333; 0.555 mm

(R = 25; 45; 75mm, r = 25; 45; 75)



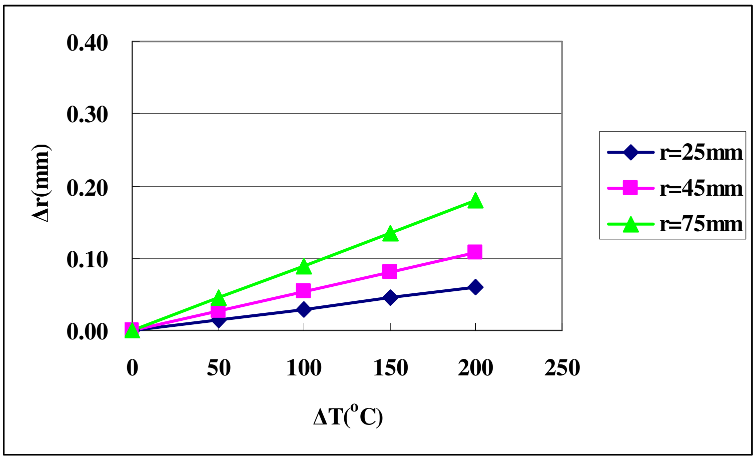


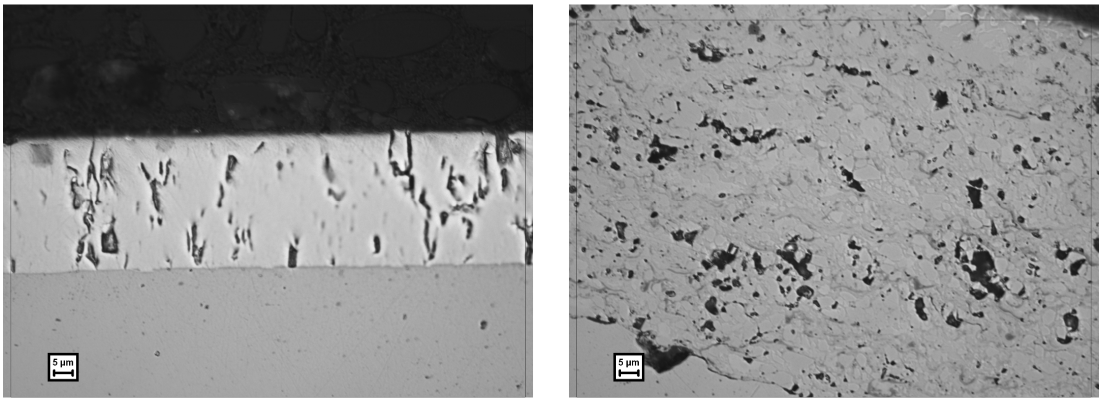
Figure 32.Space in radius for cladding could obtain in distinct tubes and rods

5. Discussion

5.1 HVOF coatings compare to hard chrome

5.1.1 Coating characterization

Coating cross sections were investigated by optical microscope as show in figure 33. Typically, coating thickness of thermal spraying is much thicker than electroplating (hard chrome 150 degree 35.64 µm, and HVOF hardened plus grit blasted 90 degree 119.31 µm), both of them show excellent bonding strength with the substrates.

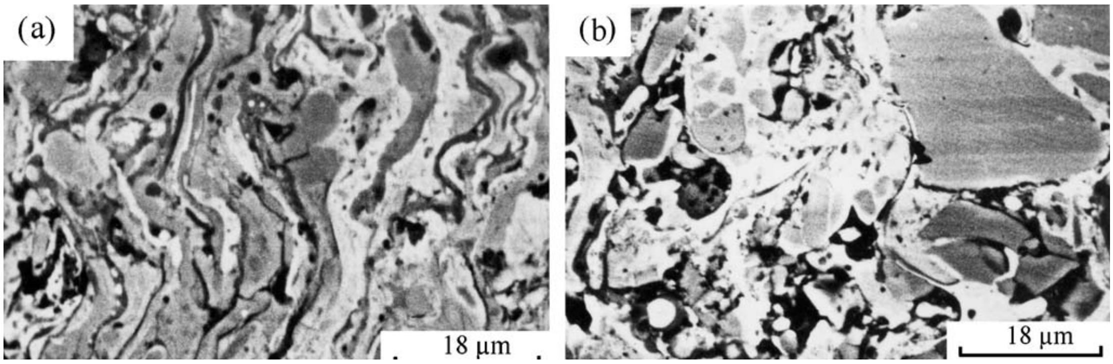


(A) Hard chrome **(B) HVOF hardened plus grit blasted**

Figure 33.OM cross section images of hard chrome and HVOF samples (mag. 500)

In previous study [4], small vertical microcracks were observed in hard chrome coatings, as shown in figure 6A and 33A; the reason for this particular cracked morphology has not been completely understood so far; it is believed that they are caused by relaxation of residual tensile stresses formed in the coating during the deposition. The typical HVOF Cr_3C_2-NiCr coating has lamellar structure parallel to substrate surface with fine carbides dispersed, presents the splats formed during the spray process as shown in figure 33B and 34A.

Furthermore from previous study, it was found that the size, shape and content of carbide particles within the as-sprayed coatings changed with spray parameters. Within the coating deposited at comparatively lower flows of propane and oxygen, as shown in Figure 34B, large carbide particles in an angular shape similar to that in the starting powder were present with an inhomogeneous distribution. On the other hand, the coating deposited at higher flows of both propane and oxygen and a long spray distance contained less carbide particles figure 34A [30].



A) Long distance, higher propane oxygen flows.   B) Lower propane oxygen flows.

Fig34. Microstructure of HVOF sprayed Cr_3C_2–NiCr coatings [29]

A comparatively finer carbide size and higher volume fraction in even dispersed condition may lead to a better bonding of carbide particles to the matrix phase. The fine Cr_3C_2–NiCr coatings present a “bimodal structure” formed by CrC particles with a size greater than 1 μm together with sub-micron carbides in a Ni–Cr matrix. The decrease of the size of the feedstock powder involves the reduction of the superficial coating roughness [31]. The fine Cr_3C_2–NiCr coatings demonstrate superior performance to hard chrome with regard to mechanical and tribological properties. For future successful applications of Cr_3C_2–NiCr HVOF coatings as alternative to hard chromium, many factors like wear resistance, friction coefficient, costs and environmental issues have to be considered collectively [32].

5.1.2 Hardness profile

The results of microhardness test were listed in table 11. The coating microhardness, texted in blue color was in accordance with the finding results in section 1.4.1 c):

Hard chrome: 800~1000 Hv.

Cr_3C_2-NiCr25%: 750~ 1300 Hv.

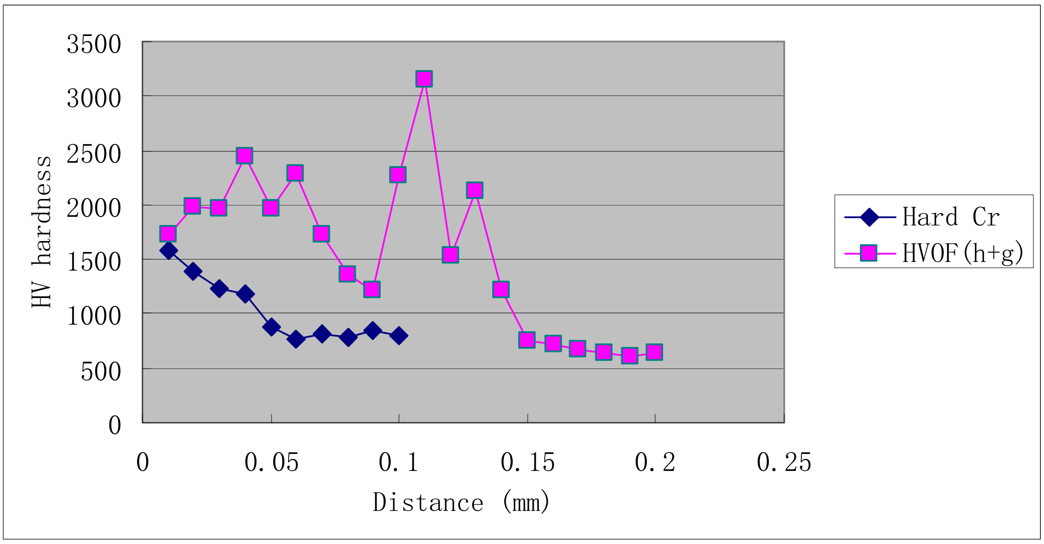


Figure 35.HV hardness diagram: hard chrome vs. HVOF (h + g)

Both of the two coatings show good microhardness, as shown in figure 35; they all could meet the customers' hardness requirement in table 1. HVOF coating presents higher hardness than hard chrome, several hardness value were reach 2000 Hv, perhaps due to the carbides hard particles like Cr_3C_2, Cr_7C_3 and $Cr_{23}C_6$.

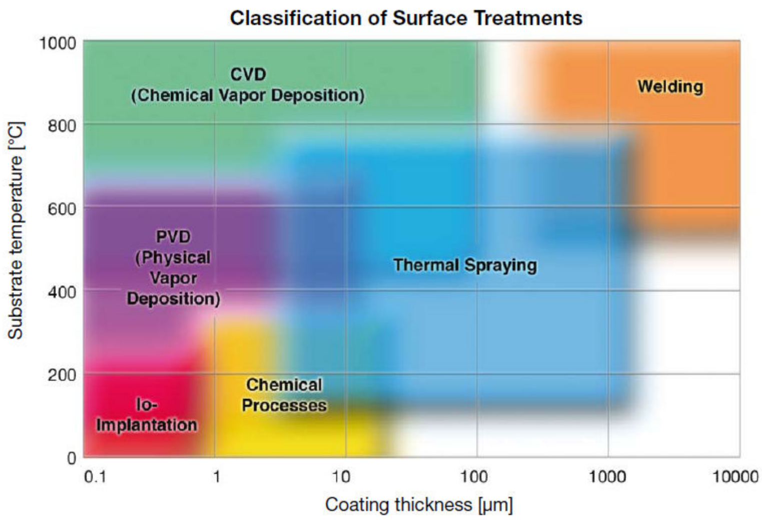


Figure 36.Substrate temperature of various surface treatments. [9]

The substrates of two samples were treated by identical hardening mechanisms: induction hardening. However in the interfacial areas approximate 50 µm to the substrates, the hardness of hard chrome is a little bit higher than HVOF; it was probably affected during thermal spraying, the substrate temperature was elevated above 600 °C by high temperature and kinetic energy particles. Perhaps recrystallization annealing happened at this temperature for medium carbon steel. In this process deformed grains are replaced by a new set of undeformed grains that nucleate and grow until the original grains have been entirely consumed. Since recrystallization is usually accompanied by a reduction in the strength and hardness of a material and a simultaneous increase in the ductility, the hardness of HVOF substrate decreased. On the other hand, for plating process, the substrate temperature could maintain below 200 °C, as shown in figure 36. [9]

5.1.3 Results of pendulum impact test

Toughness of coating can be expressed as ability to absorb impact energy without delamination or cracking. Impact test is a toughness measure method, all the coating energy level showed in this work is generally for comparison, and most of energy was absorbed by substrate. It was found that coating toughness using different test methods were approximately the same. [33]

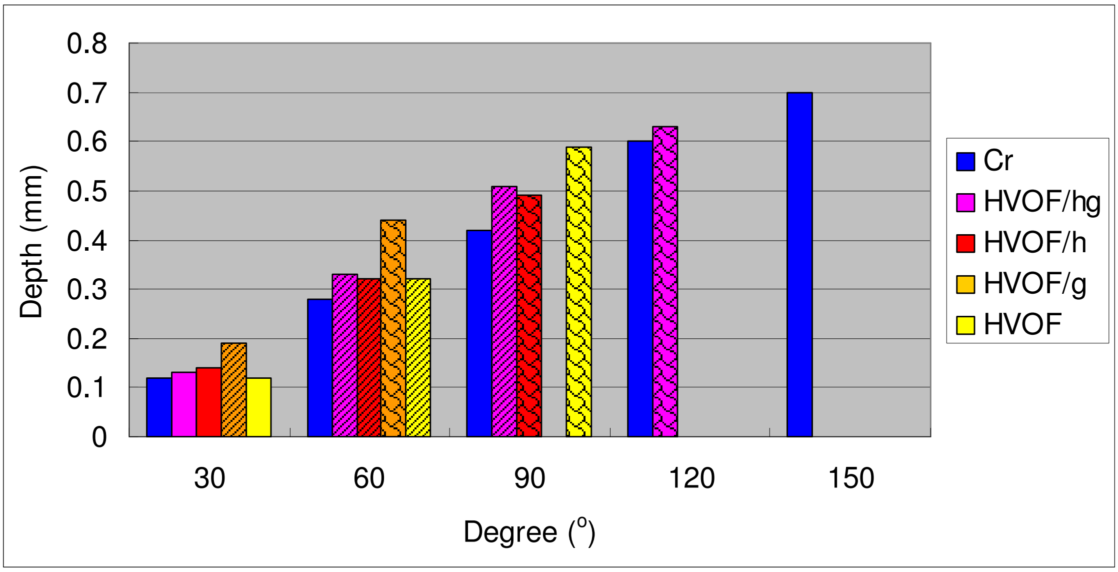
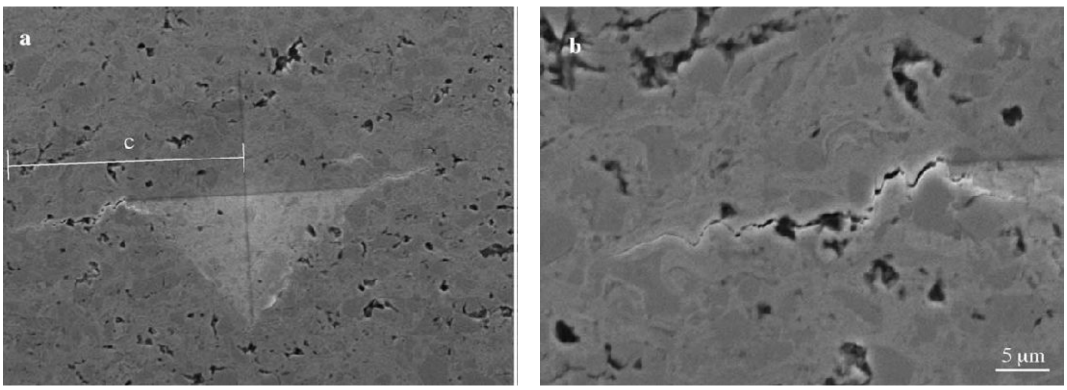


Figure 37.Critical energy diagram: indentation depth versus distinct energy level

The indentations of hard chrome and HVOF coatings formed in distinct energy level were listed in table 10. During the impact test, once the delamination or damage happened, the test was terminated, and the former energy level was regarded as the critical energy degree for this coating, as shown in table texted in blue. From the indentation depth versus distinct energy diagram as shown in figure 37, the critical energy level of hard chrome and HVOF coatings could be easily found out, the bar filled with oblique line. Hard chrome can pass highest energy level 150 degree, no radial cracks and surface damage was obtained.

a) Coating characters and impact results

Du to different process of formation, coating microstructure and bonding mechanisms, in ordinary engineering applications HVOF coatings are much thicker than hard chrome. In this present, the thickness of HVOF is 3.3 times against hard chrome, as show in figure 33. Coating thickness, hardness, ductility and toughness are related, but the ductility is the key parameter for coating toughness. Even HVOF is thicker and harder than hard chrome coating, the ductile hard chrome coating shows excellent toughness, as show in figure 28(A) no radial cracks or delamination was found from 30 to 150 angle degree. Most of HVOF coatings show good quality at low angle degree as shown in figure 28(B), with increasing impact energy, flaking off and the radial cracks happened, and the crack direction was not perpendicular to the substrate.



A) Cracks and crack length c **B) Crack propagation path**

Figure 38.The indentation cracks in HVOF Cr_3C_2–NiCr20 coatings [17]

Figure 38 A) shows the typical indentations on the transverse section with cracks for Cr_3C_2– NiCr20 coatings. In the thermal sprayed coatings, the cracks parallel to the coating substrate interface are more easily formed in comparison to the perpendicular direction. This has been attributed to the characteristics of the thermal sprayed coatings have discussed in section 1.4.1 a). Further, examination of the crack features show that the crack propagates along a region between the carbide particles and the binder phase in Cr_3C_2–NiCr20 coatings as shown in figure 38 B). [17]

b) Substrate grit blasting, adhesion strength and coating performance

In order to a dense strong coating to enhance the tribological property, surface preparation before coating is very important. The bonding mechanisms of HVOF coating is more depend on mechanical interlocking, surface preparation by cleaning and roughening, for instance grit blasting, is particular important in before HVOF.[10]

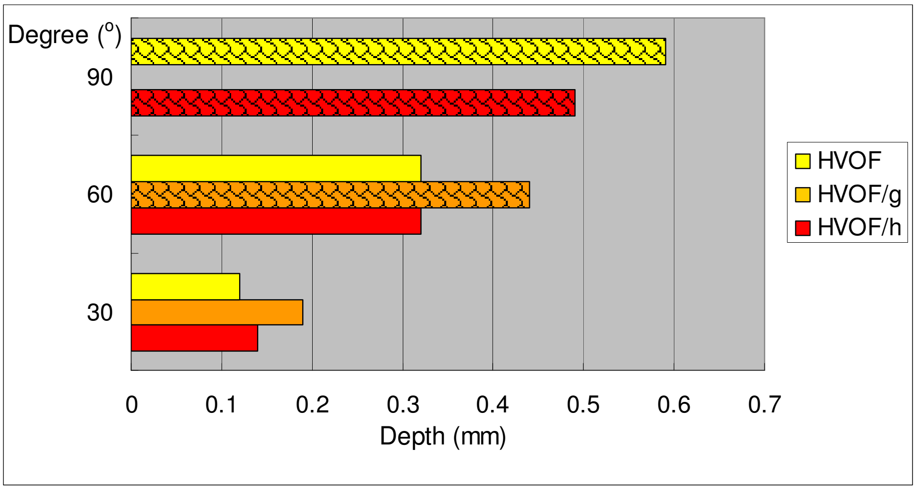
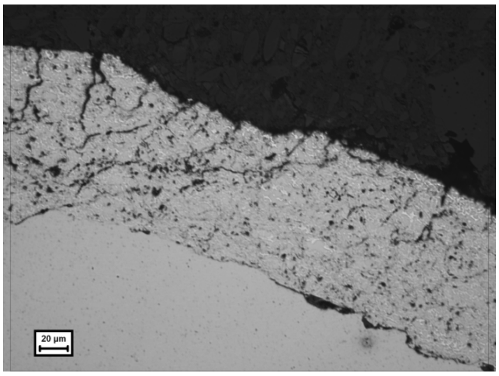
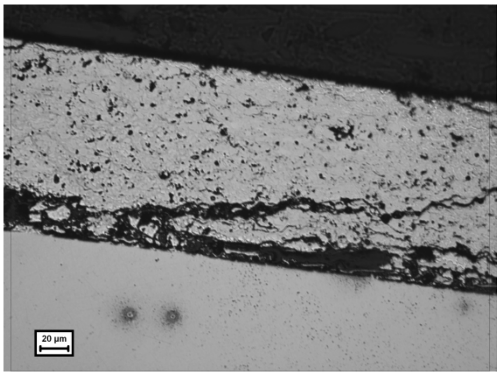


Figure 39.Coating disintegration energy diagram: indentation depth versus distinct energy level

The HVOF coating performance of samples in this impact test, among four HVOF samples, grit blasted sample reached higher energy than without substrate preparation as show in figure 39, and the bars filled with wave are the disintegration energies for different coatings. Delamination and coating cracks occur in HVOF coating without substrate grit-blasting in 60 degree energy level as show in figure 40B), and the substrate grit-blasting coating reach 90 degree without damage as shown in A).





(A) HVOF (h+ g): 90 degree (B) HVOF (h): 60 degree

Figure 40.OM cross section images of HVOF samples (corner)

In the Rockwell-C adhesion test, the impact indention causes layer damage adjacent to the boundary of the indentation. After indentation, an optical microscope with a magnification of 100:1 was used to evaluate the test. On each sample three indentations were produced. The damage to the coating was compared with a defined adhesion strength quality shown in Fig 41. HF l-HI; 4 define a sufficient adhesion whereas HF 5 and HF 6 represent insufficient adhesion. This test method is very easy to perform and is especially useful for quality control during manufacture. [34]

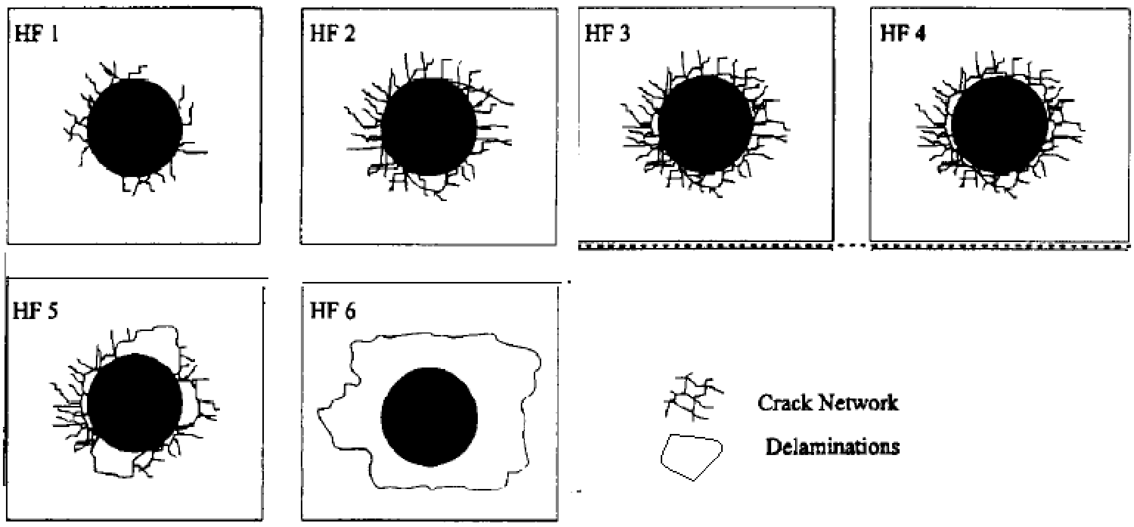
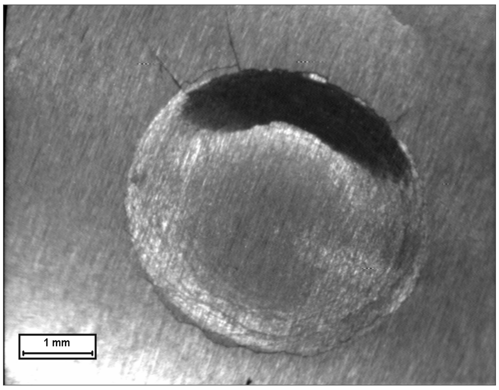
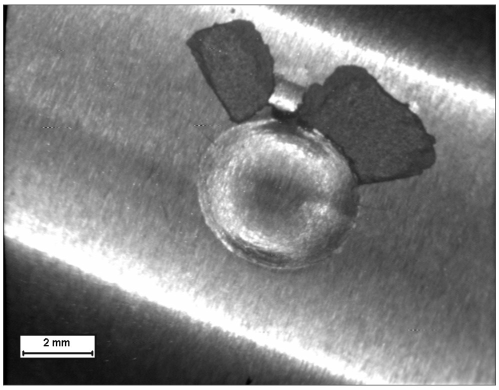


Figure 41.Coating adhesion strength quality HF 1 to HF 6 [34]

* HF is the German short form of adhesion strength

Figure 42 indicates that during 90 degree energy impact test, substrate hardening and grit blasting samples present good bonding strength HF2-HF3 A); On the contrary, substrate without grit blasting shows poor adhesion HF 6 as shown in B).





(A) HVOF (h+ g): 90 degree **(B) HVOF (h): 90degree**

Figure 42.Stereo microscope: impact indentations images of HVOF coatings

c) Substrate hardness and coating performance

The physical properties, such as hardness, of the substrate may have evident influence on the properties and performance of the hard coatings.

Practically, hard coatings need to be deposited on different kinds of substrate materials in different application areas. For instance, despite the excellent CVD coating properties, the poor quality of the substrate would prevent industrial applications where the coating-substrate compound has to withstand high load as shown in figure 43A). After induction hardening, microstructural gradients are generated in substrate. As a result, hard layers are obtained, which is an excellent load support of coating, while the core of the substrate remains tough as shown in figure 43B). Nevertheless, induction hardening have many more advantages due to generation of compressive residual stresses in substrate and only very low distortions resulting from the surface treatment [35].

From the former study the influence of substrate hardness on the properties of the hard coatings was investigated. It was found that the substrate hardness has little influence on the crystalline structure, nano-hardness, and tribological properties (friction coefficient and wear rate). However, it showed a significant effect of the toughness and adhesion of the hard coatings. And adhesion between coating and substrate increases linearly with the increasing of substrate hardness. It can be concluded that hard coatings need to be supported by hard substrates. [36]

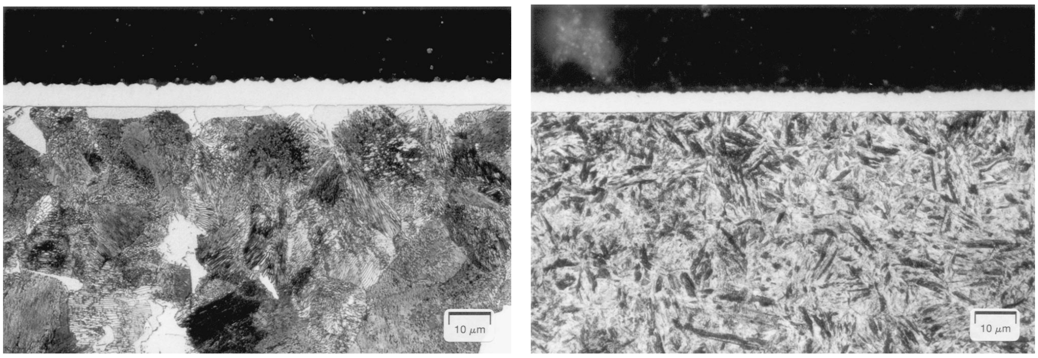


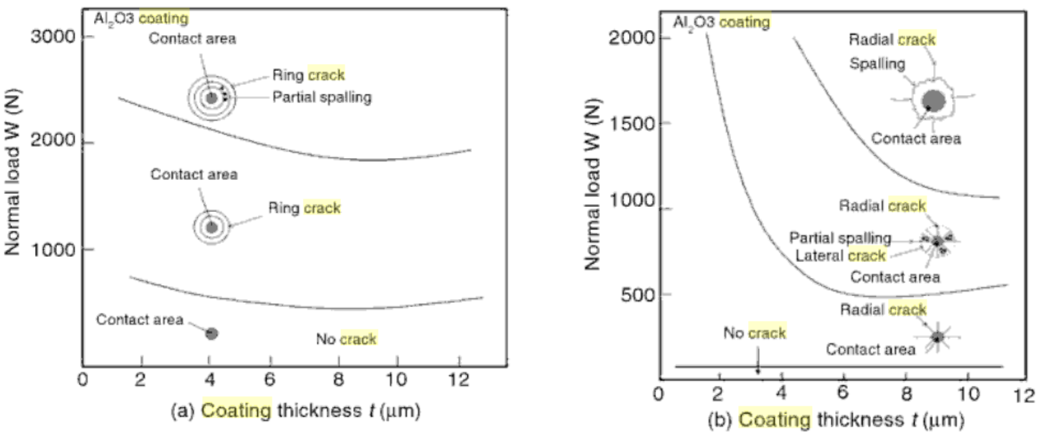
Figure 43.A) AISI substrate plus TiN coating B) AISI substrate after induction hardening

In this thesis, in accord with literature, substrate induction hardening samples show much better performance: hard chrome 150, HVOF (h + g) 120 and HVOF (g) 60 degree, as shown in figure 42.

d) Crack patterns and failure modes

Hard chrome and HVOF coatings with distinct characteristics, during the pendulum impact test, show different mechanisms in crack propagation and damage.

Cracking and delaminating mechanisms of various coatings by distinct indentation have been studied as shown in figure 44. The patterns and development of crack is a function of coating thickness **t** and normal load **W**. A partial delamination of coating can be generated only by the indentation of a hard pin if the indentation load or depth is large enough. For ductile coating, when load increasing, ring cracks more than three are generated around the indentation mark, and partial delamination takes place between the neighboring rings as show in figure 44 A): 1. Elastic contact, without cracks; 2. Maximum tensile stress exceeds the critical value of coating, the ring cracks propagated downward to form a shape of cone, the ring cracks concentrated around the indentation; 3. Partial delamination takes place between neighboring rings. For brittle coating as shown in figure 44 B): 1.The radial cracks generated in the contact area since partial plastic deformation; 2. Maximum tensile stress exceeds the critical value of coating, the lateral cracks propagated downward to form a shape of cone; radial cracks, lateral cracks, and partial delamination take place; 3. Large area general delamination happened around indentation mark. [37]



A) Indentation by a SiC ball of radius 1.5mm B) Indentation by a diamond pin of 0.2mm tip

Figure44. Indentation mark and crack pattern: Al_2O_3 coating on WC-Co substrate [37]

The hard chrome coating indentation marks and crack patterns in 150 degree impact test were similar with the indentation of Al_2O_3 coating on WC-Co substrate by a SiC ball in region two, as shown in figure 30 A): ring cracks appeared around the contact area and no partial spall was observed. The metallurgical characteristics of HVOF Cr_3C_2– NiCr20 coatings influence the crack propagation path. The HVOF (h + g) coating indentation marks and crack patterns in 90 degree impact test were similar with the indentation of Al_2O_3 coating on WC-Co substrate by a diamond pin, between region two and region three as shown in figure 30 B): radial and lateral cracks appeared around the contact area, small parts of delamination was observed. In the higher energy level 120 degree, the indentation patterns developed from region 2 to 3, and the flaking was observed.

From literature it was found that the ductile coatings, such as TiN layers, presented with relatively small delaminations whereas the high microhardness coatings like CrN and Cr_2N layers, showed brittle behavior with large delaminations and relatively early coating failure [34].

Two main failure modes can be found during the impact test: adhesive (interfacial) and cohesive. Adhesive failure is associated with bonding strength of coating, and cohesive failure is associated with toughness [38]. Figure 27 shows that adhesive failure had happened in HVOF various coatings; with energy level increasing, cohesive failure mode probably could be found in hard chrome coatings, due to excellent coating toughness.

5.1.4 Corrosion resistance in AASS

Table 13 indicates after 40 hours AASS test, the protect rating of hard chrome items were No. 10, no corrode area was found by visual examination. However the HVOF is No. 6, were not qualified.

As shown in figure 31, the samples were photographed after 40 hours of exposure to acetic acid spray. Perhaps the brown rust in the figure 31B) was obtained from the substrate corrosion, due to the porosity of HVOF coating is much higher compare to that of hard chrome as mentioned in section 1.4.1. In figure 16, the corrosion resistances of various HVOF coatings have been listed, the Cr_3C_2-NiCr coatings on mild steel substrate indicate relatively good corrosion protection in AASS test.

Published corrosion data exist for a wide range of coating materials deposited by different techniques; for instance HVOF and hard chrome coatings. However not all corrosion resistance data can be compared directly because of variations in substrate material and surface preparation, the deposition parameters, coating thickness, coating porosity and surface finish, sometimes the use of bond coatings and intermediate layers, and sometimes the use of post treatments [38]. All of these reasons could affect the testing results. Finally, the salt fog test providing results in a short time period, however cannot be related to in service use in most cases: for hydraulic cylinders, most of time the coatings of piston rods were immersed in hydraulic oil.

5.2 Stainless liner

For hardness and corrosion resistance requirements, perhaps martensitic stainless tube could be a competitive alternative to hard chrome. According to thermal expansion theory, if heating up the tube (R = 25/45/75mm) to 500°C and cooling down the substrate piston rod (r = 25/ 45/ 75mm) to -200°C, space in radius **0.185/0.333/0.555 mm** could be acquired.

However, perhaps martensitic stainless liner for hydraulic piston rod is not a practical method. Due to high hardness and brittle behaviour, almost no commercial martensitic thin pipes or tubes in reality; moreover, for custom martensitic stainless steel have low carbon content, which makes it highly prone to occur micro-cracking during heat up the tube to 500°C. [40]

6. Conclusions

Cr_3C_2-NiCr20% HVOF as a promising alternative to hard chrome has been studied:

1. Pendulum impact test showed that substrate pretreatments, induction hardening and grit blasting are very crucial for HVOF coatings; coherently HVOF (h + g) presents the highest critical energy level among HVOF samples. Hard chrome and HVOF coatings present distinct cracks propagation and delamination mechanisms. Hard chrome shows higher toughness more than 40% and adhesion strength compare with HVOF; cracking and delaminating take place more easily in HVOF coatings due to brittleness.

2. Hardness test demanstrated that HVOF coating indicates higher hardness than hard chrome, which is a key parameter for wear resistance (mean value: 1784 Vs. 1244 Hv); however the hardness of HVOF substrate is a little bit lower than hard chrome, perhaps it was affected by thermal spray process.

3. Corrosion resistance showed that HVOF rating number 6 and hard chrome rating 10 after 40 hours in AASS test: the substrates of HVOF coating were corrode since the coating porosity.

While as hard chrome alternatives on hydraulic piston rods, besides HVOF there are several viable processes have been investigated.

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