

ChroSiMol: A Completely Different Coating Against Corrosion and Wear

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ABSTRACT

The paper deals with new layers of the systems Cr-Mo-Ni-Si and Cr-Mo-Co-Si bearing the common name "ChroSiMol". These layers are applied by means of atmospheric plasma spraying on metallic substrates of iron, nickel, cobalt, and titanium-based alloys and serve as corrosion, oxidation and wear protection for these metals at temperatures up to max. 900°C. The layer ChroSiMol is an acid-resistant layer and provides for its substrates a perfect protection against hot sulfuric acid and phosphoric acid in all concentrations. With a hardness of approx. 900 HV and very good anti-friction properties of the molybdenum-containing surface, these layers are optimally suited for use with friction pairs with corrosive loads.

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ARTICLE HISTORY

Received 14-03-2018
Revised 03-04-2018
Accepted 04-04-2018
Published 06-04-2018

KEYWORDS

Plasma torches Axial III,
HV-APS,
Gas-tight layers,
Wear,
Corrosion

Introduction

There are many applications in coating technology that combine high demands on wear and corrosion protection. Classic examples of this combination of requirements are piston rods of hydraulic cylinders, calender rolls, stop valves (ball, slides and housings), extruder screws and cylinders, drill bits and boring bars, valve stems and many other products. All of these parts require hard, wear-resistant coatings that are not only themselves corrosion resistant but must also be impermeable to corrosive media. This last requirement is often the hardest. Thus, for example, the best known most widely used of these layers, hard chrome plating, shows a marked permeability to aqueous solutions, which severely limits its anti-corrosion effect.

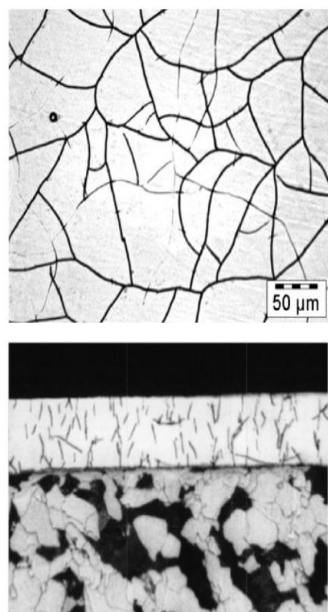


Figure 1: Surface (top) and cross-section (etched) of a hard chrome layer. Source: Gramm Technik GmbH

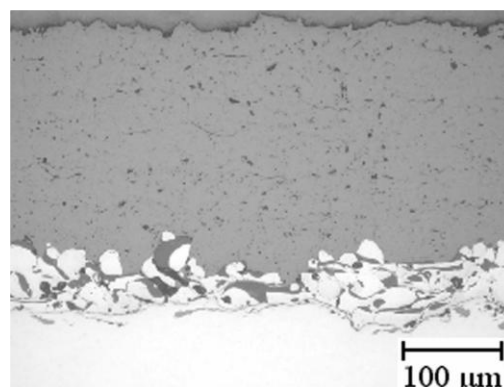


Figure 2: Plasma sprayed Cr_2O_3 layer on Ni-Al bondcoat. Source: HSU Hamburg, Institute for Materials Technology

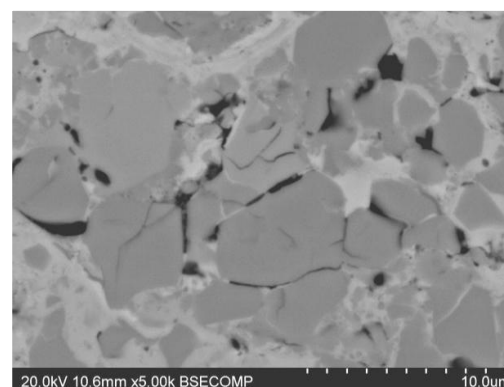


Figure 3: $\text{Cr}_3\text{C}_2\text{-NiCr}$. Source: Faculty of Non-Ferrous Metals, AGH, University of Science & Technology, Kraków, Poland

The layers of galvanic chrome do not provide reliable protection for the base material because they have a crack network (Fig. 1). Similar problem also occurs in many thermally sprayed layers. Virtually all plasma-sprayed ceramic layers (Cr_2O_3 , Al_2O_3 , YSZ, TiO_2 , etc.) are cracked and porous (Fig. 2). The metallic and metal-ceramic

(carbide + metal) layers produced by high-velocity flame spraying (HVOF/HVAF) are usually much denser, but these also often have microcracks (Fig. 3).

In some cases, the porous and cracked layers can be sealed with polymers, but this solution is practical only in room temperature applications.

As you can see, the combination of the three requirements mentioned above (wear resistance, corrosion resistance and impermeability) is already bad enough, but what options for layer selection remain if we add two additional requirements: high temperature resistance and low coefficient of friction during dry rubbing (good antifriction properties)? These additional requirements are not simply theoretically to invent, but are true in many applications: resistance to high temperatures is often important for pure room temperature applications because the coated parts must be heated for various reasons (hardening, welding, brazing etc.). Not always the usual coating on completely finished part of the advantage. Even friction behavior of the layer surface without lubrication plays a very important role in many applications (extruders, valve seats, fittings, etc.). There are good technical solutions for each of the two additional requirements. For example, layers of remelted self-fluxing NiCrBSi alloys (Figure 4) are very suitable for all parts that need to be heat treated after coating.

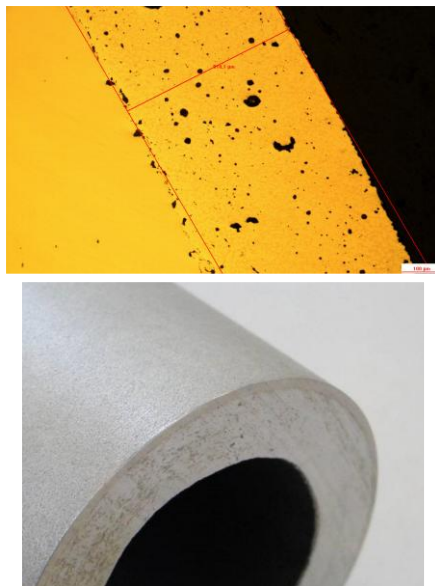


Figure 4: Steel tube with a NiCrBSi layer (Metco 12C). Source: Cremer Beschichtungstechnologie GmbH

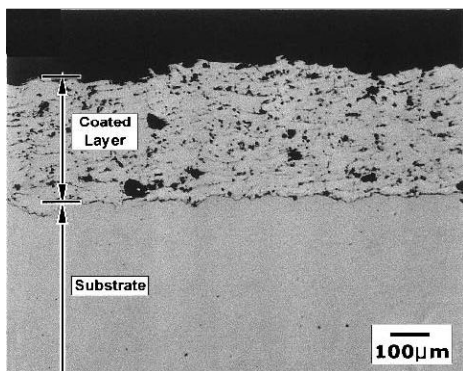


Figure 5: Plasma-sprayed Mo layer. Source: Center for Advanced Aerospace Materials Pohang University of Science and Technology, Pohang, Korea

Molybdenum has gained acceptance as the antifriction layer (Fig. 5). In applications where dry rubbing is to be minimized (e.g., compression rings of internal combustion engine pistons), molybdenum demonstrates its superiority over hard chromium. Unfortunately, in the requirements for impermeability and high temperature resistance, the Mo layers fail.

The NiCrBSi layers combine more of desired properties (four out of five) than any other, but their friction behavior and hardness are not perfect.

Is it even possible to develop a layer that masters all five requirements? Yes, it is possible, and such layers are discussed in this paper.

Experimental

The development of ChroSiMol was based on the invention of chromium-based plasma-sprayed high temperature protective coating according to the patent [1]. The original plasma-sprayed chrome layer had already met the most important requirements: it was gas-tight and had very good adhesion to the substrate (> 200 MPa). In contrast to the galvanic hard chrome, the plasma-sprayed chromium layer according to [1] was not only crack-free, but also temperature-resistant (operating temperature up to 1000°C). In addition, the corrosion resistance of plasma sprayed chromium layer was better than that of the hard chrome. For use as wear protection was missing, however, the necessary hardness (hardness of plasma-sprayed chromium layer was about 600 HV). Frictional behavior of chromium film was also not optimal for use with friction pairs. In order to simultaneously increase friction, corrosion resistance and wear resistance (hardness), a part of the chromium was replaced by molybdenum. In addition, metallic silicon was added to the powder mixture. This created the basis for the ChroSiMol layers: Cr-Mo-Si. To increase the coefficient of thermal expansion of the layer and to improve the spray behavior, a fourth metallic component has also been admixed: Ni80Cr20 or cobalt. Both of these metals can be used for ChroSiMol; One differentiates between NiCr-ChroSiMol and Co-ChroSiMol, which have slightly different properties. The single metallic powders (Cr, Mo, Si, Ni80Cr20 or Co) form a powder mixture for plasma spraying. There is also a coarse-grained cristobalite powder as a carrier for fine-grained metals. However, this cristobalite powder is destroyed during coating and occurs only as a minor side-phase in the layer (more than 98% of the cristobalite disappears during coating).

Results and Discussion

The flowable mixture is sprayed using Axial III plasma torches. Figures 6-8 show the result of plasma spraying.

As you can see from the figures, the individual components of the mixture form corresponding phases in the layer. The short time of the coating process is not enough to form an alloy out of individual metals. The proportions of non-metallic phases (Cr_2O_3 and remains of cristobalite) are < 3%. Thus, the composition of the freshly sprayed layer is shown in Table 1.

Table 1: Composition of ChroSiMol before the heat treatment

Component of the Coating	Proportion, wt. %
Cr	30-32
Mo	30-32
Ni80Cr20 or Co	30-32
Si	3-4
$\text{Cr}_2\text{O}_3 + \text{SiO}_2$	< 3

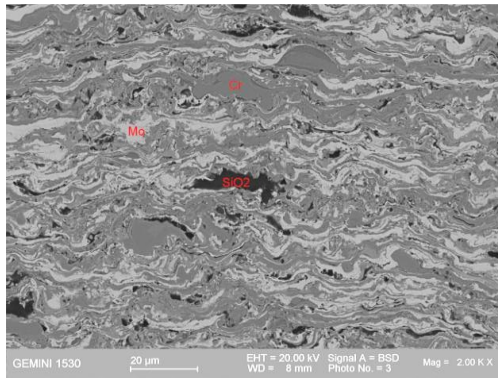


Figure 6: NiCr-ChroSiMol directly after plasma spraying x 2000

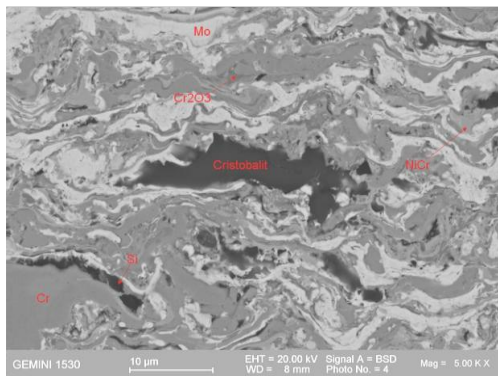


Figure 7: NiCr-ChroSiMol directly after plasma spraying x 5000

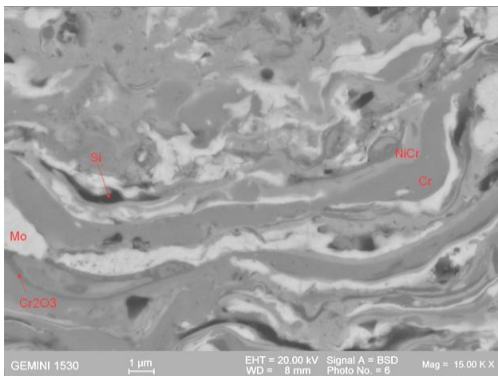


Figure 8: NiCr-ChroSiMol directly after plasma spraying x 15000

In order to form pseudo alloys from individual metallic components, the layer ChroSiMol must be heat-treated together with the substrate. Since the layers are gas-tight after spraying, this heat treatment can be carried out in air. The temperatures of the heat treatment are in the range 750-900°C, duration of the heat treatment: from 1 hour. Besides the formation of hard and corrosion resistant pseudo alloys, the heat treatment serves to improve the cohesion and adhesion of the layer [2-4]. The diffusion processes between the metallic components of the layer during the heat treatment allow a dramatic improvement of the layer adhesion up to > 250 MPa. In addition, stress states are tilted by the heat treatment: after the heat treatment, residual compressive stresses are formed in the layer. The layer structure after the heat treatment is shown in Fig. 9 to Fig. 11.

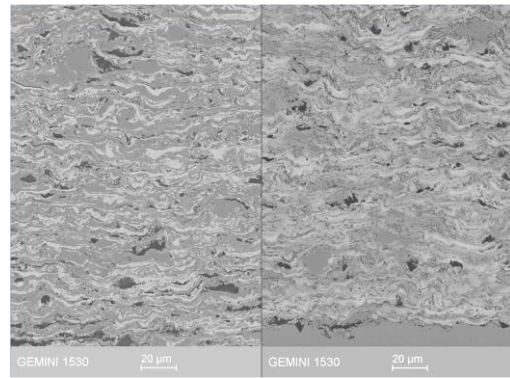


Figure 9: Pre (left) and after (right) the heat treatment at 900 °C, 1h. x 1000

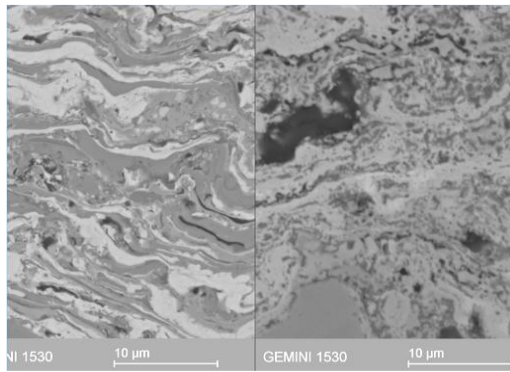


Figure 10: Before (left) and after (right) the heat treatment at 900 °C, 1h. x 5000

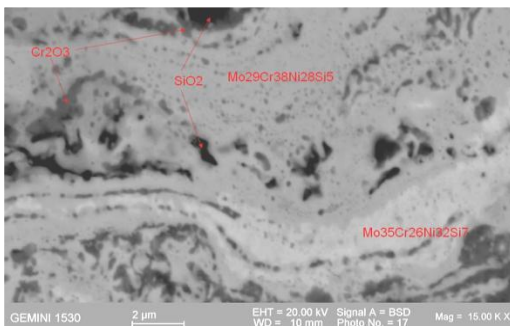


Figure 11: After the heat treatment at 900°C, 1h. x 15000

After the heat treatment, the layers exhibit the following properties as shown in Table 2.

Table 2: Properties of ChroSiMol (both variants)

Property	Value
Hardness at RT	850-950 HV _{0,2}
Flexural strength (4 point) at RT	300-400 MPa
E-modulus at RT	ca. 200 GPa
Adhesive strength to the substrate	> 250 MPa
Thermal expansion coefficient at RT	9-9,5x10 ⁻⁶ K ⁻¹
Thermal conductivity at RT	10-20 W/mK
Density	7,7 g/cm ³
Open porosity	0
Closed porosity	< 0,5%

The corrosion properties were determined in various media (Table 3) and compared with the corrosion resistance of titanium alloy Ti6-4 (samples of Ti6-4 were partially coated with the NiCr-ChroSiMol).

Table 3: Corrosion resistance of NiCr-ChroSiMol compared with Ti6-4

Corrosion medium, temperature and test duration		
10%-H ₂ SO ₄ , 60°C, 48h	No corrosion	Corrosion removal approx. 0,05 mm
20%-H ₂ SO ₄ , 60°C, 48h	No corrosion	Corrosion removal approx. 0,2 mm
40%-H ₂ SO ₄ , 60°C, 48h	No corrosion	Corrosion removal approx. 4 mm
96%-H ₂ SO ₄ , 60°C, 48h	No corrosion	Corrosion removal approx. 1 mm
200-300 g/L CrO ₃ + 2-2,5 g/L H ₂ SO ₄ , 20°C, 72h	No corrosion	No corrosion
200-300 g/L CrO ₃ + 2-2,5 g/L H ₂ SO ₄ , 60°C, 72h	Corrosion through pore formation	No corrosion
30%-H ₃ PO ₄ , 60°C, 48h	No corrosion	Corrosion removal approx. 0,1 mm
5%-HCl, 20°C, 48h	No corrosion	No corrosion
5%-HCl, 40°C, 48h	No corrosion	Corrosion removal approx. 0,1 mm
10%-HCl, 20°C, 48h	Corrosion removal approx. 0,1 mm	Corrosion removal approx. 0,5 mm
20%-HCl, 20°C, 1h	Corrosion removal approx. 0,1 mm	Corrosion removal approx. 1 mm
37%-HCl, 20°C, 0,5h	Corrosion removal approx. 0,1 mm	Corrosion removal approx. 2 mm
15%-HNO ₃ , 20°C, 24h	Corrosion through pore formation	No corrosion
15%-HNO ₃ , 60°C, 2h	Corrosion through pore formation	No corrosion
65%-HNO ₃ , 20°C, 24h	Corrosion through pore formation	No corrosion
HNO ₃ (65%) + 3HCl(37%), 20°C, 24h	No corrosion	Corrosion removal approx. 0,05 mm
HNO ₃ (65%) + 3HCl(37%), 40°C, 24h	Corrosion through pore formation	Corrosion removal approx. 0,2 mm
48%-HF, 20°C, 48h	No corrosion	Not tested because of too fast reaction
5%-HCl + 10%-HF (1:1), 20°C, 100h	No corrosion	Not tested because of too fast reaction
96%-H ₂ SO ₄ + 48%-HF (1:1), 20°C, 48h	No corrosion	Not tested because of too fast reaction
10%-H ₂ SO ₄ + 10%-HF (1:1), 20°C, 100h	No corrosion	Not tested because of too fast reaction
20%-NaOH, 60°C, 48h	No corrosion	Corrosion removal approx. 0,05 mm
3,5%-NaCl, 100°C, air supply, 500h	No corrosion	No corrosion

Applications

The applications of ChroSiMol can be very diverse. Basically it can be said that practically in all applications of galvanic hard chrome, thermally sprayed Cr₃C₂-NiCr, WC-Co, WC-Co-Cr and other wear-resistant layers, ChroSiMol can also be used. Their impermeability to liquid and gaseous corrosive media, high acid resistance and high temperature resistance make ChroSiMol unreachable not only for porous and cracked layers, but also for dense remelted layers of self-fluxing alloys.

Because the coat ChroSiMol is quite similar in chemical properties to well-known alloys of the systems Ni-Cr-Mo-Si and Co-Cr-Mo-Si, ChroSiMol can also be used in the applications of these alloys. Works [5-6] show potential of such alloys in terms of corrosion protection, generally it also applies to ChroSiMol.

In addition to improving the protection of base materials in known, typical applications of protective coatings, ChroSiMol can be used in entirely new areas that are hitherto unknown to coaters. Figures 12-13 show two examples of such new applications:



(a)



(b)



(c)

Figure 12: Corrosion protection for bath warmer of electroplating baths (a-b) Diving depth mark on ChroSiMol layer by sandblasting (dark part - oxide skin after heat treatment); (c) Layer surface before and after the heat treatment at 800°C, 1h



Figure 13: Internal combustion engine valve seat rings: replacement for Stellite armor

Conclusions

1. For all steels and other alloys with $\alpha < 13 \times 10^{-6} \text{K}^{-1}$, the layer of ChroSiMol offers better protection against wet-chemical corrosion in H_2SO_4 and H_3PO_4 than all known layers except precious metals. The need for a heat treatment is often no problem, since it can be done in one step together with the heat treatment of base material.
2. Wear resistance of the layer ChroSiMol is better than that for hard chrome and corresponds to that of $\text{Cr}_3\text{C}_2\text{-NiCr}$ layers (HVOF). $\text{Cr}_3\text{C}_2\text{-NiCr}$ layers are more resistant to abrasion, but the antifriction layer ChroSiMol is more suitable for friction pairs.
3. Due to the very high adhesion and cohesion of the layer, as well as the residual compressive stresses, the impact resistance of ChroSiMol is significantly better than that of all carbide-containing HVOF layers. This allows their use as armor for seat rings instead of stellite.
4. In addition to typical applications of mechanical engineering, the combination of high wear resistance and corrosion resistance can be particularly interesting for the surface refinement of titanium implants of joints. For this application, the cobalt-containing ChroSiMol variant could be better.
5. ChroSiMol is also suitable for high temperature air applications (permanent at 850°C and $> 1000\text{h}$ at 900°C).
6. Manufacturing costs for ChroSiMol correspond to the costs of ordinary $\text{Cr}_3\text{C}_2\text{-NiCr}$ or WC-Co-Cr coatings (HVOF/HVAF).

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