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Coatings of Carbide-Metal Systems (Cr_3C_2-NiCr and WC-Co-Cr) Deposited by High-Velocity Atmospheric Plasma Spraying from Specially Modified Fine-Grained Powders

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ABSTRACT
In this article, the author poses and responds to a provocative question that has practically ceased to be asked in the field of thermal spraying of carbide coatings: *Is the current worldwide trend of using only unmelted metal particles to form coatings (HVOF, HVAF and cold spray methods) correct, and is the deposition of completely melted powders (plasma spraying methods) really outdated?* The results of high-speed plasma deposition of new carbide powders allowed the author to prove that only coatings from molten particles can solve the main problem of such coatings, namely the problem of permeability along the grain boundaries. Through the use of modern Axial III plasma torches combined with optimized fine-grained powders, it has been possible to create Cr_3C_2-NiCr as well as WC-Co-Cr gas-tight layers.

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Introduction

In the last 100 years, the coatings based on chromium and tungsten carbides have attracted attention of researchers in the field of thermal spraying. The first attempts were obtained by the inventor of thermal spraying, Max Ulrich Schoop using a simple flame spraying technique [1].

During time, the quality of such carbide coatings has increased, as new available devices and powders for deposition have been developed [2-7].

One of the first important discovery in this field was the invention of plasma spraying in the 1960s, which allowed the particles of chromium and tungsten carbides to be melted (gas flame spraying does not provide the necessary temperature for melting the tungsten carbide - about 3000°C).

Using the method of plasma spraying, it became possible to obtain coatings from simple mixtures of powders of carbides and metals. However, the quality of such coatings was still very far from ideal. All the old plasma deposition devices were "slow", as they did not allow to accelerate the deposited particles above 200 m/s. In consequence, the low particle velocity was responsible for the high porosity of the coatings. In addition, the powder mixtures consisted of coarse-grained carbide powders, which when are melted, produced a coarse laminar coating structure, respectively.

Another major breakthrough in the field of carbide coatings was the use of detonation spraying (the first installations of detonation deposition appeared in the 1950s) [8]. This method, although it does not allow the melting of tungsten carbides, still gives the particles a temperature higher than the melting point of the metallic cobalt or nickel binder (> 1500°C) and accelerates the particles to very high velocities (>800 m/s). The detonation sprayed carbide coatings were much denser than plasma coatings and were practically inferior to modern HVOF coatings obtained from the same powders. Despite the technological complexity of the detonation spraying process, carbide coatings obtained using this method are still produced, for more than 60 years.

HVOF torches, which nowadays almost completely replaced the detonation spray devices, were intensively used to spray carbide coatings in the mid-1980s [9]. At the same time, modern, agglomerated sintered powders, suitable for these high velocity burners have been successfully developed. The new powders were characterized by the fine particle size of carbides and, in combination with the HVOF method, provided coatings a very high quality. Plasma spraying of new agglomerated sintered powders was also possible, but the quality of such plasma coatings was inferior to that of HVOF coatings. For this reason, in the late 1980s, a tendency to decrease the temperature and to increase the velocity of the sprayed carbide particles appeared. New HVOF devices, and since the 90s, also HVAF burners, have provided a cold and rapid flame, in which carbide-metal agglomerates have been accelerated to speeds above 700-800 m/s at temperatures below the melting point of the metal binder. Coatings obtained with such spraying parameters had very low porosity (nowadays a porosity less than 0.5% is considered the standard) and high hardness (hardness of Cr_3C_2-NiCr coatings is about 900-1000 HV, and WC-Co-Cr coatings - about 1200-1500 HV). In addition, the surface roughness of "fast and cold" carbide coatings decreased to Ra <2 µm.

The tendency to apply "cold and fast" parameters instead of "hot and slow" parameters appeared to be absolutely correct, but one problem of carbide coatings has remained unresolved. This is the problem of particle boundaries.

All the described methods of deposition, forming a coating by deformation of unmelted particles, have one common negative feature: they all have a grid of particle boundaries. This grid is formed because the individual unmelted particles do not mix with each other, but they lie mechanically on each other like bricks in a wall. The oxidized surfaces of individual particles become the

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particle boundaries ("cement interlayer" between individual "bricks" of the coating). These boundaries can be so thin (several tens of nanometers) that they are practically not visible in the cross-section of coatings at magnifications below one thousand, but their influence on the properties of coatings is very high. Particularly, the particle boundaries strongly affect the strength and permeability of coatings. Figure 1 shows an HVOF coating of CoCrWNi powder on a Hastelloy substrate.

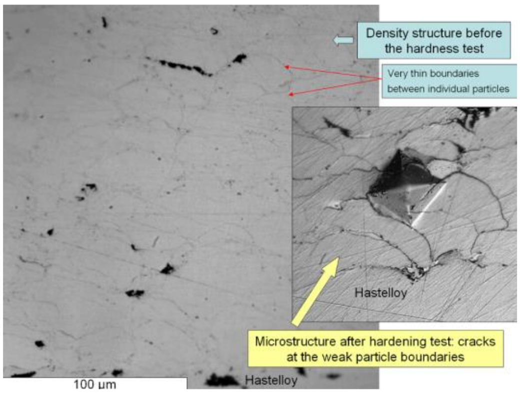
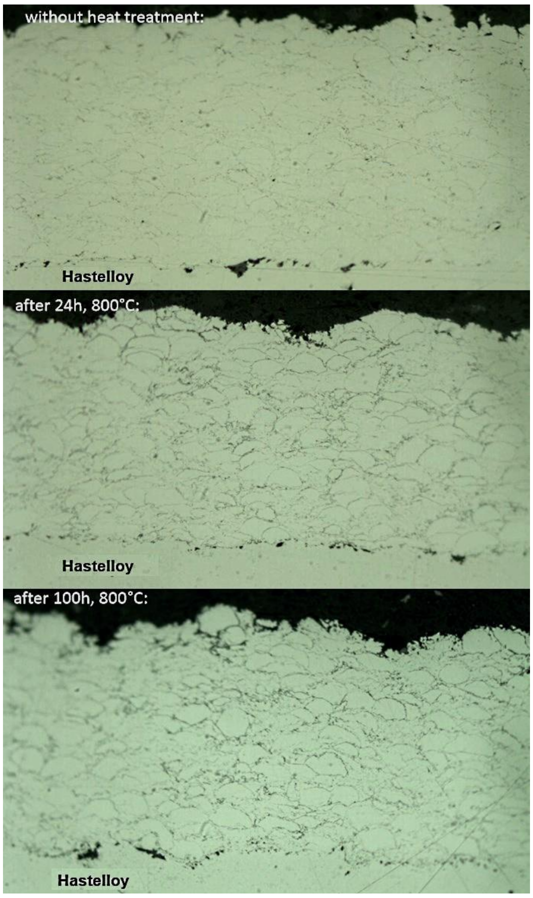
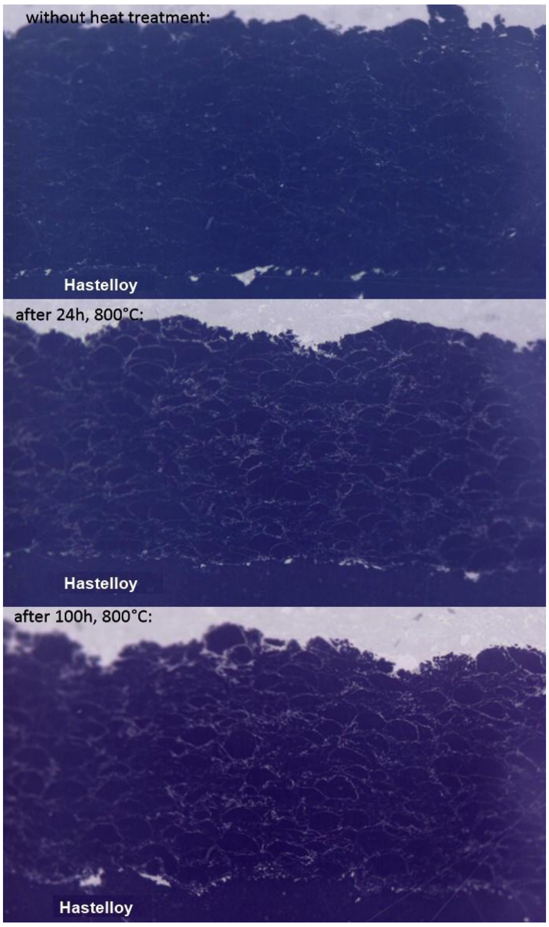


Figure 1: HVOF-deposited CoCrWNi on the Hastelloy-substrate. Source: Thermico GmbH

The coating presented a porosity of less than 0.1% and had no cracks, but despite this, the coating was gas permeable. To prove the gas permeability of the coating, the sample was hold for several hours in an oven, in air atmosphere, at 800°C. Figure 2 shows the optical micrographs of the high-temperature coating after exposure at 800°C for different durations.



(a)



(b)

Figure 2: (a) HVOF-deposited CoCrWNi on the Hastelloy-substrate at x 200, (b) in invert colours: oxidized particle boundaries are more Visible; Source: Thermico GmbH

As can be clearly seen from Fig. 2, the grid of particle boundaries, "magically," becomes progressively clearer on the entire thickness of the coating, as the treatment time in the furnace increases. Only in this case, there is no magic, but a stronger oxidation of the coating material by the oxygen from the air, which penetrates progressively inside the coating along the particle boundaries.

All carbide coatings produced by "cold and fast" spraying methods have the same feature: the particle boundaries are permeable to gases and many liquids, which means that even the densest coatings without cracks and other defects cannot protect the substrate either from oxidation at high temperatures in the air, nor from corrosion in aqueous solutions.

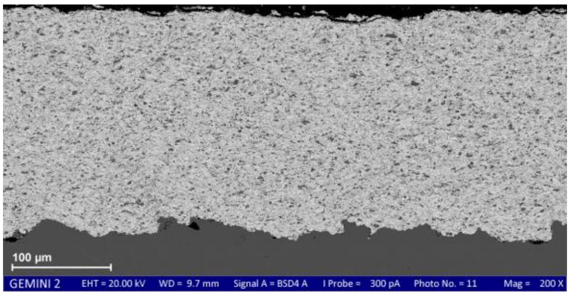


Figure 3: Crack-free HVOF-deposited WC-Cr_3C_2-Ni with a porosity <0.1%, x 200. Source: Thermico GmbH

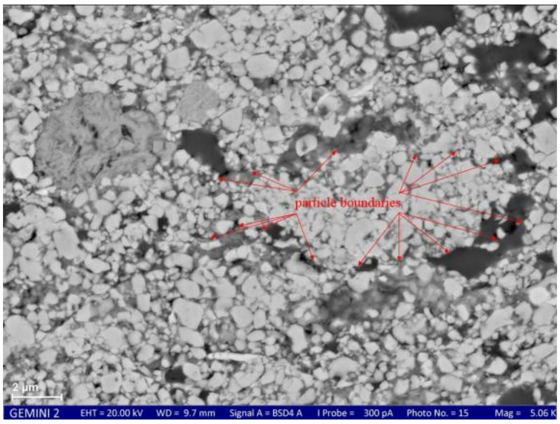


Figure 4: Crack-free HVOF-deposited WC-Cr_3C_2-Ni, x 5000, particle boundaries

The problem of corrosion resistance of carbide coatings is a "painful issue" for all practitioners involved in their application. Although, in some individual cases, the carbide coatings may slow down the corrosion of the substrate beneath them, there is always a fundamental possibility of corrosion of the substrate. Thus, an honest answer to the question of whether the carbide coatings obtained by HVOF/HVAF methods are corrosion-protective, should be No! Exactly the same negative answer should follow on the question about protecting the substrates from oxidation at high temperatures. This also applies to the so-called high-temperature layers Cr_3C_2-NiCr. The layers can withstand the theoretical operating temperature of 800°C only until the substrate under the layer oxidize; after that, these layers can be detached from the surface of the substrate.

How can we cope with the problem of permeability of particle boundaries? The answer to this question is simple: a purely mechanical connection between the individual particles of the coating should give way to a metallurgical connection. To form the metallurgical bond, the processes of wetting and diffusion are necessary, which take place only at high temperatures. In certain special cases (MCrAlY HVOF coatings), using the subsequent high-temperature treatment of the coated substrate, it is possible to start the diffusion mechanisms and turn the permeable coating into a gas-tight coating, but in the case of carbide coatings this is not possible. In other words, it is possible to solve the problem of particle boundaries in carbide coatings only by spraying the molten particles, i.e., by means of plasma spraying.

Of course, this aspect cannot be solved with the plasma spraying techniques used to produce carbide coatings in the 1960s-1980s. Impermeable carbide coatings require not only new, high-speed, plasma spraying devices, but also completely new powders, specially designed for these devices.

Experimental

To obtain a high quality, non-porous layer of molten particles, the supersonic velocity of the particles is imperious necessary. This means, that in principle, this achievement is only possible employing a high velocity burner (HV-APS). Such a burner, called Axial III from Mettech, was used in this project. A second condition for applying successful coatings, is the use of fine-grained particles. Only the particles with a mean size less than 10 µm can gain in the plasma flame sufficiently high temperature to melt and high enough speed to form a dense layer.

Since such fine particles tend to agglomerate, to form lumps and are hardly free-flowing, a temporary carrier, made of coarse-grained cristobalite, was used in the powder mixtures. This technique favours the coating of non-free-flowing fine-grained metallic powder [9]. Cristobalite massively improves the flowability of the fine-grained powder, and almost all of it is removed during the process (large cristobalite particles do not melt in the plasma and during impact, collapse and are blown away by gas streams). More than 98% of the cristobalite disappears during coating.

In the current study, two types of powders for HV-APS were developed. One of them is based on tungsten carbide, and the second one, on chromium carbide. The two powders contain, in addition to cristobalite for flowability, other additives that allow the formation of metallurgically bonded sprayed layer. One of the most important from these additives is flux of silicate glass [10, 11]. The precise chemical composition of both spray powders, deposition parameters and structures of resulting layers are described in the following sections.

Results and Discussion

Gas-tight layer of molten particles based on WC-Co-Cr

As powder base for this layer, a special powder from Thermico named 179-060 (plasma-spheroidized WC86Co10Cr4 powder, -9+1 µm) was used. Additives of the finest metallic cobalt (< 1 µm) and small amounts (about 0.5%) of water glass were added to this powder. After mixing with the coarse-grained cristobalite, a free-flowing spray powder was formed. The coating process by means of Axial III burners was carried out at a short spray distance (80-90 mm), with an electrical power of about 110 kW. After coating, cross sections of the layer were analyzed by optical microscopy and SEM, compared to "normal" high quality HVOF coatings with similar chemical composition (Fig. 5-9). The obtained coating, prepared by means of Axial III, is called WC78Co18Cr4-Plasma or WC78Co18Cr4_Axial-III and the coating used for comparison, prepared by HVOF burner CJS, is called WC86Co10Cr4-CJS. Optical microscopy shows that the both coatings present no pores and cracks, but the state of the particles during spraying (if they are melted or not) cannot be mentioned. To evaluate this aspect, SEM investigations with significantly higher magnifications need to be performed. Fig. 8 and 9 prove that the new plasma coatings actually consist of molten particles and this characteristic really eliminates the particle boundary problem.

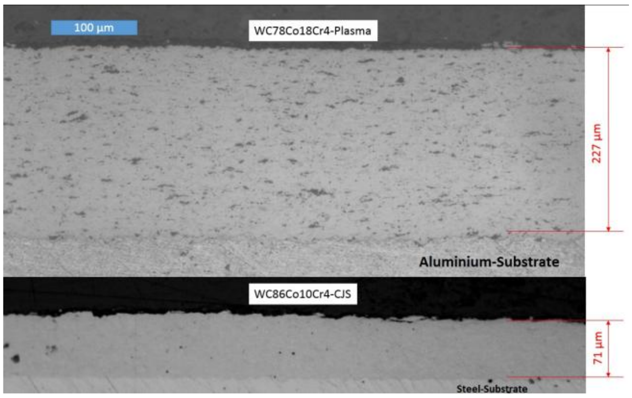


Figure 5: Optical micrographs of (a) WC78Co18Cr4-Plasma, (b) WC86Co10Cr4-CJS at x 200

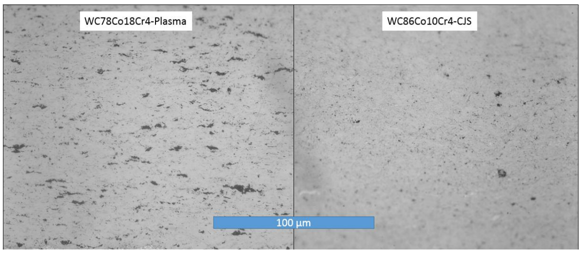


Figure 6: Optical micrographs of (a) WC78Co18Cr4-Plasma, (b) WC86Co10Cr4-CJS at x 500

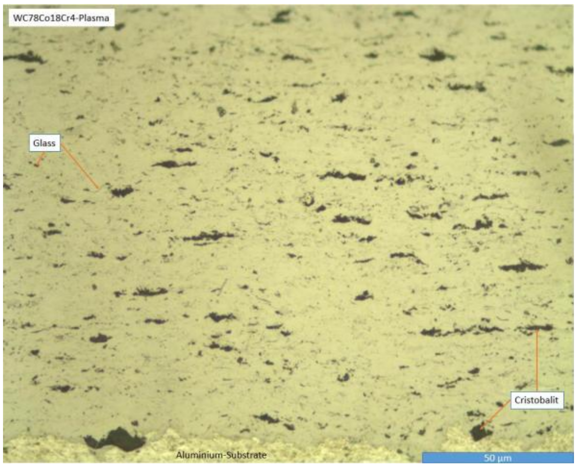


Figure 7: Optical micrographs of WC78Co18Cr4-Plasma, at x 500

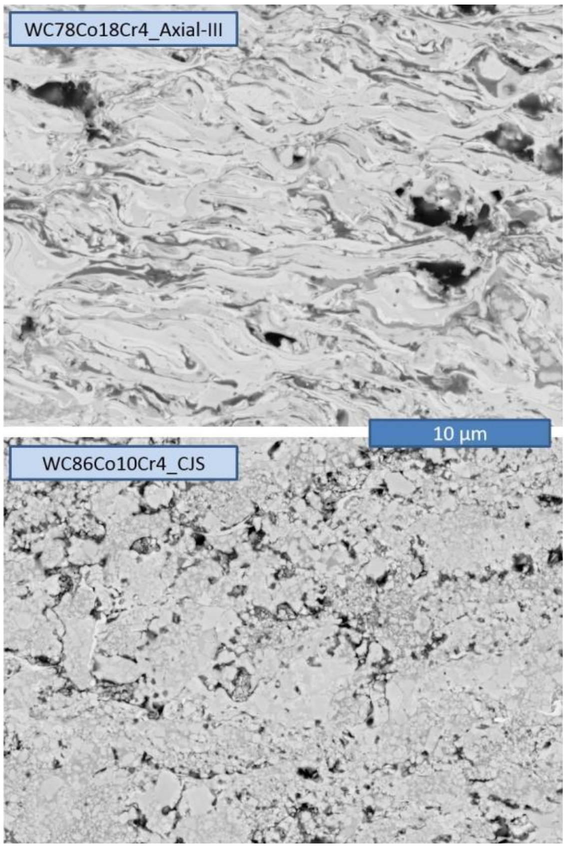


Figure 8: SEM micrographs of (a) WC78Co18Cr4-Axial-III, (b) WC86Co10Cr4-CJS at, x 2000

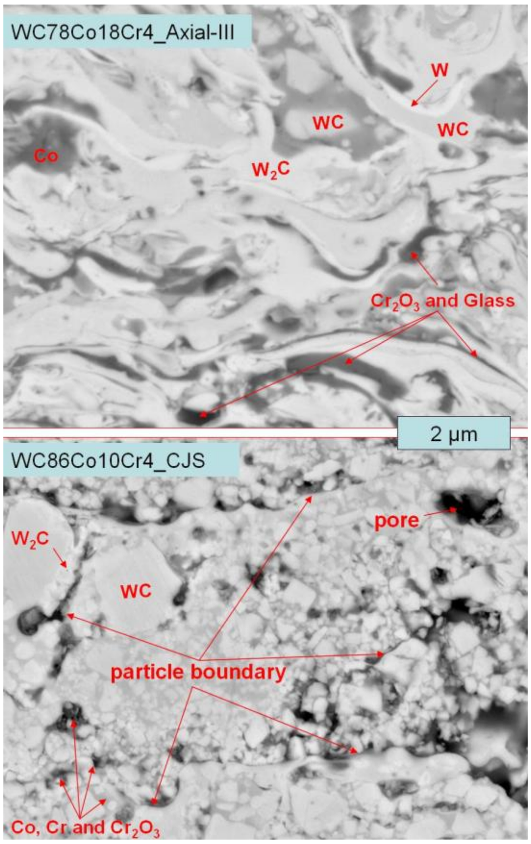
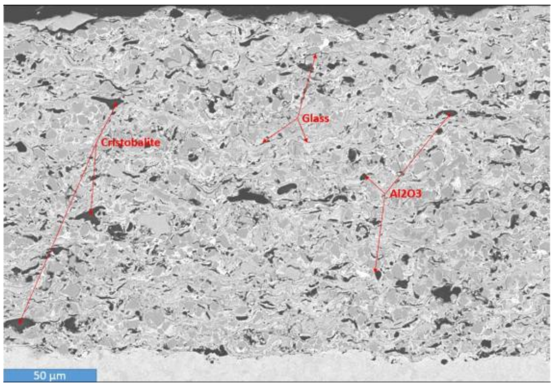


Figure 9: SEM micrographs of (a) WC78Co18Cr4-Axial-III, (b) WC86Co10Cr4-CJS at, x 5000. Layer WC78Co18C4-Plasma has no particle boundaries

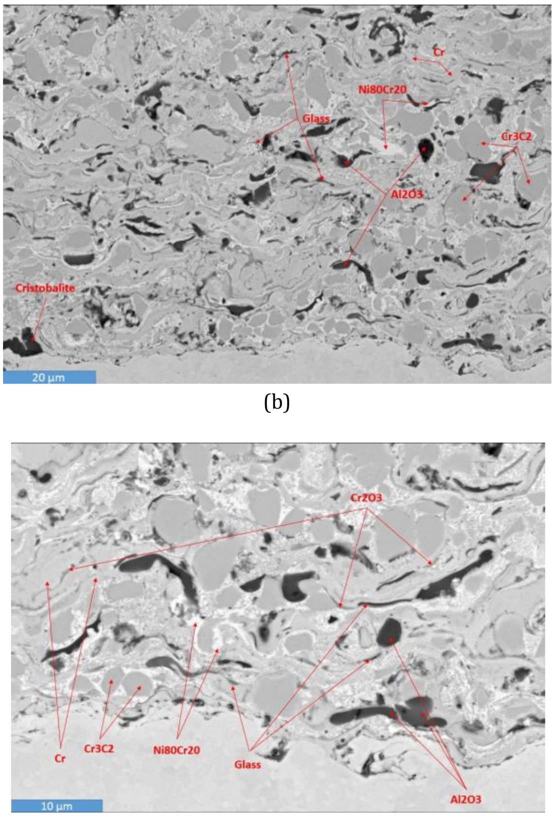
Gas-tight layer of molten particles based on Cr_3C_2-NiCr

As powder base for this layer, a commercial agglomerated sintered $(Cr_3C_2)75(Ni80Cr20)25$ powder, having a grain size of -25+5 µm was employed. Additives of fine chromium (<20 µm), nickel chromium 80/20 (<12 µm), corundum (<10 µm) and small amounts (about 0.5%) of water glass were added to this powder. After mixing with the coarse-grained cristobalite, a free-flowing spray powder was obtained.

The coating process by means of Axial III burners was carried out at a spray distance of 100-110 mm and with an electrical power of about 100 kW. After coating, cross sections of the layer were analyzed using SEM (Fig. 10-11).



(a)



(b)

(c)

Figure 10: SEM micrographs of Coating Cr_3C_2-NiCr-Plasma, at (a)x1000, (b)x2500 and (c)x 5000

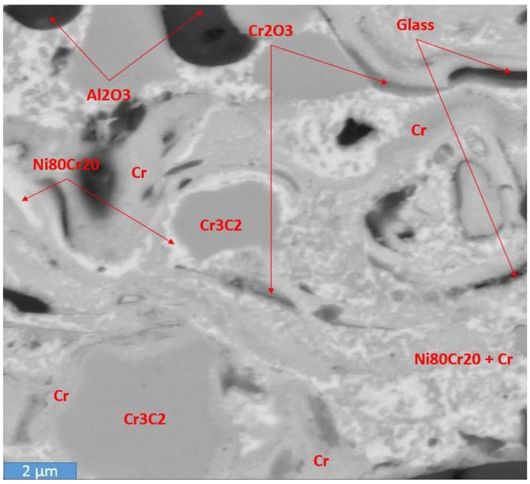


Figure 11: SEM micrographs of Coating Cr_3C_2-NiCr-Plasma, at x10000

Proving of gas tightness for the layers of molten particles

Proof of the gas-tightness of new plasma-sprayed coatings was carried out using the oxidation tests. Unfortunately, this type of evidence can only be used for chromium-carbide-based (oxidation-resistant) coatings, because tungsten carbide oxidizes at temperatures lower as 400°C.

In our tests, we compare the structures of ordinary, high quality HVOF layer of Cr_3C_2-NiCr (CJS-burner) with our new layer of Cr_3C_2-NiCr-Plasma. Both coatings were applied to oxidation-resistant substrate material (steel: X7CrNiMoBNb16-16) and each specimen was tested for 72h at 800°C in air. After the oxidation tests, cross sections were prepared and analyzed by optical microscopy and compared with each other. The clear results are shown in Fig. 12-13.

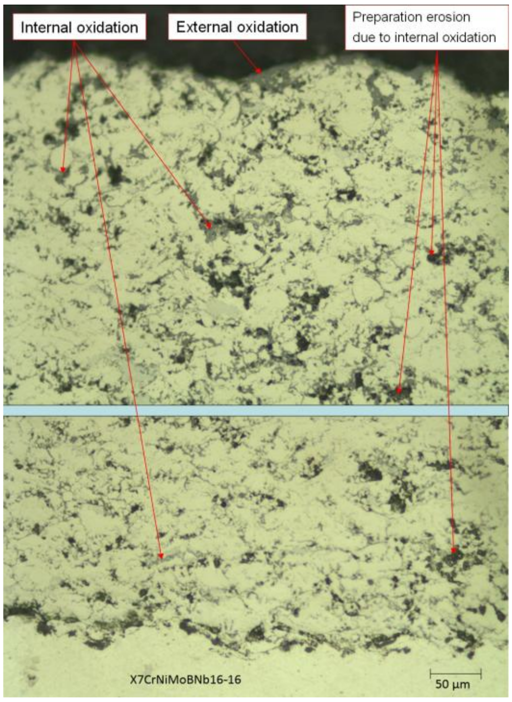


Figure 12: Optical micrographs of Cr_3C_2-NiCr-HVOF coating after 72h at 800°C in air at at x500

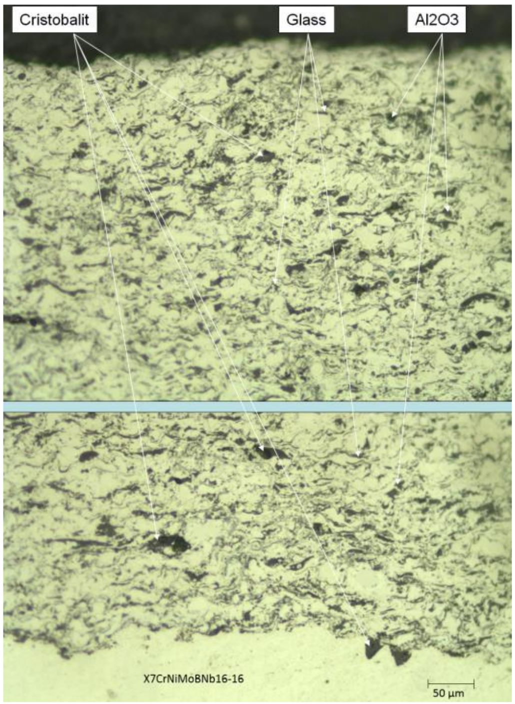


Figure 13: Optical microscopy of Cr_3C_2-NiCr-Plasma coating after 72h at 800°C in air at x 500

To prove that the new Cr_3C_2-NiCr-Plasma coating remains stable even at prolonged maintaining in air at 800°C, the test was extended to approximately 2000 h. The HVOF coating (the reference sample) did not passed this test (the layer was broken), but the plasma coating remained unchanged (Fig. 14).

Figure 14: Optical microscopy of Cr_3C_2-NiCr-Plasma coating after 2000 h at 800°C in air at x 200

Conclusions

Based on the two above-described examples, it has been proven that thermal spraying with molten particles can solve the problem of permeability of particle boundaries. Of course, this technique can be applied not only to the cermet systems with WC and Cr_3C_2, but in general, for all metal-containing coatings.

The main conclusion from our experiments is that the development tendency towards the direction of "cold and fast" spray parameters causes issues related to permeable particle boundaries. To be able to apply really gas-tight coatings, new development direction to "hot and fast" spray parameters is strongly necessary. Since these parameters can only be applied by high-speed plasma spraying, the HV-APS systems must receive more attention.

The second most important conclusion concerns the powder development. Since today's powder development is adapted to the "cold and fast" parameters of HVOF/HVAF burners, the existing HV-APS devices will not receive the suitable commercial powders. A "vicious circle" is formed and normal users cannot take advantage of HV-APS, because the adapted powders are missing, but without increasing the demand for these new powders, they are not developed and produced by the main important powder manufacturers.

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