

The manufacturing of carbide materials for HVOF

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1. Introduction

Industries are finding new and innovative applications for thermally applied coatings. Surface treatments can now enhance the wear characteristics and life expectancies of a diverse array of parts. Generally these surface treatments must not alter the fit, form, and function of the basic part. Additionally, those surface treatments must also match or exceed the other requirements of the part and the application, e.g. surface finish, corrosion resistance, fatigue strengths, etc. With challenges such as these, each phase of the coating process becomes mission critical.

New ways of manufacturing the materials to be coated are offering industry a way to solve the problem of having one surface treatment meet all the performance requirements needed. Specifically, the formulation of composite materials that are manufactured with individual elements that when combined will fulfil the various requirements. Yet these new material solutions must also comply with the economic requirements. Coatings must be price competitive to the traditional methods being reviewed. In those instances where thermal coatings have elevated process costs, these costs may be more than offset by processing time reductions or life cycle extensions.

The HVOF process is gaining acceptance as the method of choice for line-of-sight application of dependable and cost effective surface enhancements. There are a variety of process techniques from different industry sources. The consumer can pick and choose what type of equipment would fit into their shop environment best. All the devices have the capability to apply materials of unique chemistries that may indeed achieve the required enhancement in the different modes... wear, corrosion, fatigue, etc. But no matter what the choice on equipment type or process uniqueness, they will all require a careful and proper choice in feedstock.

One group of materials with a long history of success are the carbide containing materials. The main constituents are tungsten carbide and/or chromium carbides with the addition of matrix metals, usually Ni, Co and Cr or alloys of these. The coating properties are mainly influenced by the application method technology and the feedstock powder properties. The feedstock properties are influenced by these variables; the type and selection of raw materials, the homogenizing process, the spheroidization methods, the sintering, the screen size distribution, the chemical composition, and the phase structure of the matrix metal.

This presentation will discuss and identify the manufacturing processes and discuss the relationship of these to the performance of the powder material in the application intended. Those involved in the application and/or acceptance of thermal applied coatings should gain from this information information that will allow more informed decisions relative to the selection of powders for critical coatings.

2. Raw materials

2.1 Tungsten carbide

Due to its high hardness and its high wear resistance tungsten carbide is one of the most important materials in wear resistant alloys and coatings. The stoichiometric δ -WC with a carbon content of 6,13 wt.-% and the eutectic cast tungsten carbide WC/W₂C with a carbon content of 3,8-4,1 wt.-% are of technical importance.

The stoichiometric tungsten mono carbide has a hardness of 1800-2000 Hv_{0.5}. At temperatures above 550°C it tends toward oxidation. Under standard conditions tungsten monocarbide cannot be brought to a molten condition by molten metal. Therefore it will not precipitate complex carbide phases. A loss of carbon and the origination of W₂C-phases is required. Tungsten mono carbide decomposes into W-C molten and solid carbon at a temperature of 2785°C. It re-solidifies mainly

into eutectic WC/ W₂C with an accicular structure. This process can and does partially occur during HVOF spraying. It is more known during plasma spraying and plasma densifying, due to the higher temperatures of these processes.

Compared to tungsten mono carbide, cast tungsten carbide has higher hardness and offers the potential for improved wear resistance. Production is performed in induction furnaces at temperatures of 2785°C. The molten product is chill-cast into cooled graphite or copper mold. The quenching retains an accicular structure of precipitated WC in a W₂C matrix. The cast ingots are crushed to the required size distribution by repeated crushing procedures, generally in a hammer mill. The iron elements of the mill wear during the process and an increase of iron contamination up to 1 wt.-% cannot be avoided. Therefore material manufactured by the cast and crushed method is not always suitable for application in corrosive environments. Also, the W₂C phases can be decomposed by molten metals. This results in the formation of η -carbide phases and grain growth of the WC phases can occur.

The previously mentioned η -carbide phases are hard but brittle phases. They originate from tungsten, carbon, and the matrix metal (Ni,Co). They do impart additional hardening of the carbide coating, but with this comes a loss of ductility. Impact resistance as well as resistance against pressure, cavitation and fatigue are decreased. η -carbide containing coatings are also more prone to the formation of fine cracks leading through the whole coating down to the substrate. Penetration of corrosive elements to the substrate. Coating spalling and/or blistering can be the consequence. These failure modes would negatively impact the continued servicability in critical applications like hydro turbines, or aerospace turbines/components.

Generally the stoichiometric tungsten carbide is more suitable for thermal sprayed coatings. The reason is the slower interaction between WC and alloying ingredients of the matrix metals. Therefore the phase structure is more close to the selected raw material.

2.2 Chromium Carbide

Depending on the production process, chromium carbide generally exists in three different compositions, the Cr₂₃C₆ (5,45 wt.-% C), the Cr₇C₃ (9 wt.-% C) and the Cr₃C₂ (13,33 wt.-%). Most common for thermal spraying interest is the Cr₃C₂. This chromium carbide has the highest hardness and wear resistance. The production process and the raw material used can introduce impurities, e.g. sulfur or iron. Depending on the application, especially in corrosive environments, it is often necessary to keep these contaminations below a strict limit.

Chromium carbide can be exposed to oxygen up to a temperature of 850°C without oxidation. Therefore it is used for coatings in high temperature applications >500°C. The specific density of Cr₃C₂ (6,68 g/cc) is lower compared to the specific density of tungsten carbide (15,72 g/cc). The melting point is 1895°C.

2.3 Matrix materials

Matrix metal alloys were successfully developed in the cemented carbide industry and the welding industry and have been successfully transferred into the thermal spraying by use of composite carbide materials. Pure metals such as nickel and cobalt are used as well as alloys. Two typical alloys are cobalt-chromium (70/30) and nickel-chromium (80/20). The ingredients of multi metal alloys are added to the mixing process in element form. The alloying process occurs during the sintering phase. Therefore the metals have to be oxygen free as oxidation during the manufacturing process can prevent the alloying during the sintering. The oxygen shells act as diffusion barriers. If high oxygen levels are present in the manufacturing process, the incompletely alloyed metal matrix materials will not exhibit the same desired properties as if the alloying were complete. Problems could occur during spraying. For example, CrC-NiCr coatings can form dark layers of chromium oxide. The formation of these dark areas is accelerated by chromium rich areas in the powder. If the coating is to be used in a high temperature application, the nickel rich areas may become susceptible to the attack of sulfur. Each application requires unique quality of alloyed matrices. The use of a pre-alloyed matrix material is not viable due to cost. The materials would be required in

1 μ m nominal size that is prohibitively expensive to produce and procure.

2.4 Grain size of raw materials

Experience gained from the cemented carbide industry has shown that the grain size of the starting raw materials is of high importance. Depending on the homogenisation process the tungsten carbides could be milled down, but this is not possible with the metallic ingredients due to their ductility. They should be in a range of 1-2 μ m as a raw material to ensure a complete alloying. The alloying is dependant on a diffusion mechanism. If the metal particles are too coarse, they cannot be alloyed completely. Again, any metal rich areas decrease the wear resistance. The coating would also exhibit non-uniformity in respect to hardness values.

The selection of the optimum carbide size is of extreme importance. The more homogeneous the carbide sizes are the better and more uniform the coating properties can be expected. Therefore, the raw materials should have a narrow distribution prior to inclusion in the manufacturing process. Milling during the homogenizing process should be avoided as to not alter the expected carbide distribution. The required size distribution for the tungsten carbides has to be adapted to the application. As in the cemented carbide production carbide sizes of 0,6 μ m, 0,8 μ m, 1 μ m, 3 μ m and 5 μ m are common. It is necessary that all carbides be within a certain specification. The chromium carbides should be in a range below 5 μ m to avoid a decrease of the deposition efficiency.

3. The homogenizing process

The selected raw materials must be completely and thoroughly distributed through out the production lot before the spraydrying portion of the manufacturing process can be performed. There are different approaches utilized to accomplish this mandatory and critical step.

3.1 Ball Milling

Ball mills are generally horizontal arranged chambers filled with iron or cemented carbide balls. The ball milling process is a dry milling process without any liquids. Depending on the following manufacturing process the raw materials are blended together with an organic binder such as paraffin or PVA. The mixing time and the ball diameter can be altered depending on the type and ratio of the starting materials. Due to the high energy input and the oxygen atmosphere an increase in the oxygen content level cannot be avoided in the standard dry ball milling process. If iron balls are utilized, they will wear similar to the hammer mill elements and impart contamination of the material with abraded iron. The quality of the homogenizing process is depends on the following primary factors; milling time, ball/powder relation, ball diameter, and rotation speed of the chamber.

3.2 Attritor milling

Attritors are special vertical ball mills. They are usually filled with cemented carbides and an organic solvent. The liquid film between the balls and the strictly controlled ball diameters prevent size changes of the base materials. Therefore the carbide size in the finished powder can be tailored by the right choice of the carbide size in the raw material at the beginning of the production process. This allows for a much more controlled and repeatable production method. Attritor milling is the "state of the art" in the cemented carbide manufacturing.

3.3 Dry blending

An old fashion way for homogenizing the starting materials is dry blending. For this process tumbler blender or ball mills without balls are used. There is no forced incorporation of the materials in the dry blending process and the level of homogenizing is truly limited.

4. Manufacturing processes

To produce sprayable granulates out of the pre-blended raw materials a few manufacturing steps are necessary. The blends have to be prepared for the sintering process. A general distinction is made between the "sinter and crushing"-process and the agglomeration and sintering.

4.1 Compressing

For the "sinter and crushing"-process the blended raw materials are pressed into bricks or cylinders. A pressing aid is used to improve degree of compaction. The size of the brick or cylinders must be limited to ensure a homogeneous sintering through the whole block.

4.2 Spray drying in a water based system

For the spray drying in a water based system the homogenized starting materials are mixed together with water soluble binder (glue) and water. The solution is atomised in the spraying chamber either by a lance/nozzle system or a centrifugal impellor style atomizer. Small water drops carrying the solid raw materials are formed. Once exposed to the elevated temperature of the drying chamber the water quickly evaporates in the hot air/water steam atmosphere. The formed micro pellets are held together by the organic binder and the dried shell of the particle. Drying chamber temperature of 180-210°C inlet and 125-135°C outlet are typical.

Spraydrying has the advantage to produce spherical micropellets with a uniform shape. These agglomerates are formed out of a multitude of fine distributed powder particles. The use of an open circuit system with an air/water steam atmosphere has the disadvantage of producing hollow and porous particles. These hollow and porous particles will often fracture into irregular shaped morphologies during later production process phases. Also, since the drying chamber is a oxygen and moisture rich environment, the oxidation of the matrix metals cannot be avoided. For the production of multi metal matrices such as Co-Cr or Ni-Cr this oxidation level can become a significant detriment to the process. The oxide skin on the metallic particles acts as a diffusion barrier and prevents the alloying process during the sintering. The consequences of not completely alloyed powders are manifested as a non-uniformity in the corrosion resistance of the coating or dark chromium oxide layers in a CrC-NiCr coating.

4.3 Spray drying in a closed loop system

In contrast to the spray drying in an open loop system alcohol is used as a solvent in a closed loop system. The atmosphere is an inert gas with an oxygen content below 0.2 wt.-%. The homogenized starting materials are mixed together with the alcohol and an organic binder during attritor milling process step. Actual atomising is comparable to the one in an open loop system. Standard inlet temperatures for the gas are 90-110°C. The outlet temperatures are approximately 65-70°C. This low temperature level ensures a soft evaporation of the solvent without developing a hard skin or the origination of hollow particles. The advantage of this system is to make possible the production of very dense micro pellets with a typical oxygen content of 150-300 ppm. This oxygen content is comparable to the oxygen content of gas atomised metal powders. Due to the preparing attritor milling the carbide grain sizes can be controlled in a narrow range.

5. Sintering

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

For the sintering process different types of furnaces can be used. Generally temperatures are between 1100°C and 1400°C. The temperature and the sintering time influence the cohesion between the carbides and the metallic particles. Too low sintered powders tend to burst or crack when they are injected in the nozzle or the burning chamber. The result in HVOF is nozzle clogging. Too high

sintered powders cannot be sufficiently softened during the spraying process. Internal porosity in the coating and low deposition efficiency are the consequence of too high a sintering level.

5.1 Hydrogen push/pull furnace

The “old fashion“ way for the sintering is by use of hydrogen push/pull furnaces. They are a series of heating chambers arranged in series. The product to be sintered is loaded into carbon crucibles, or boats, and then drawn through the furnace. The sintering cycle is dependant on the temperature and size of the separate chamber areas, and the speed at which the product is moved through the furnace. Original furnaces of this type are generally considered low-tech and are indeed very labor intensive. Through-put is dependant on dedicated manpower to load and unload during any and all times the furnace is operating.

Hydrogen furnaces have the advantage of a reducing atmosphere. Although this reduction is not enough for a complete alloying of compositions such as Co-Cr or Ni-Cr, the hydrogen atmosphere does enable the usage of plastic based binders. These cannot be used in a vacuum furnace due to origination of hydrochloric acid, and subsequent furnace fouling.

5.2 Vacuum furnaces

Vacuum furnaces can be loaded with large lots of materials. They have an internal chamber with a capacity of 400-700 kg of powder. Therefore big lots can be sintered under closely controlled conditions. Actual maximum capacity of this type of chamber furnace is dependant on the specific weight of the material being processed. Temperature is closely and continuously regulated by a cascade PLC control. The whole lot is running through the same sinter cycle and each complete cycle takes 30-36hours typical. The advantage of the vacuum furnaces is the possibility to produce large homogeneous sintered lots. A straight vacuum furnace is limited by the necessity to avoid utilization of some binders, however, modern vacuum furnaces can be run under hydrogen atmosphere during the binder evaporation phase.

5.3 High Pressure Furnace

The construction of high pressure furnaces is comparable to the construction of vacuum furnaces. Only the closing mechanism of the chambers differs to enable a pressure up to 50 bar. This is necessary to sinter alloys or compositions with alloying ingredients that tend to evaporate in the vacuum, e.g. boron. The high pressure prevents this evaporation. These high pressure furnaces represents the “state of the art” in the spray powder manufacturing. All the disadvantages of the other furnaces are solved.

5.4 Plasma densifying

Plasma densifying takes place in an inert chamber. The sintered and crushed powder is injected in a plasma torch and molten. It re-solidifies in a spherical and dense morphology. The flowability of the powders is excellent and they are completely alloyed due to the remelting. This method of spheriodization and densification is difficult to control with a level of consistency that allows manufacturing of follow-on lots to have the same characteristics as previous, especially in relation to the formation of the complex carbide phases formed during re-solidification. Plasma densified tungsten carbide solidifies as eutectic cast tungsten carbide and therefore plasma densified powders can produce coatings with the same characteristics of cast and crushed methods. The morphology of the particles will be more compatible with the equipment, but coating brittleness may lead to cracks in the coating.

6. Crushing, Screening and size distributions

After the sintering process, the bricks are crushed and screened into the required distributions. The

crushing process for the purely sintered powders is done with jaw crushers, hammer crushers and air jet crushers. Contamination of the powder with rubbed-off iron dust from the crushers is a serious problem. The iron dust settles down on the powder surfaces and is not alloyed into the metal matrix. Therefore the corrosion properties of coatings produced with sintered and crushed materials might be poor.

In spray dried powders the sintering causes small sinter bridges between the micro pellets. The destroying of these sinter bridges can be done with less energy. The resultant powder particle size is a result of the spray drying process and not of the crushing process. Therefore the use of heavy crushing equipment is not necessary and there is no iron contamination.

Experience has shown that each HVOF system and each customer require a slightly different screen size distribution. It is very important for the powder manufacturer and the end-user to work together to formulate and commit to the exact specifications for the material that will be supplied. The end user should have an understanding and carefully consider the powder manufacturing process. For example, slight changes in the specified size distribution can result in either higher or lower deposit efficiencies. These efficiencies have the potential to be of much greater value to the coating applicator in terms of total coating application cost that does the specifics of the application device type/fuel used. End users and coating applicators should perform a true cost-benefit analysis in respect to the raw materials they are using. This analysis may prove that slightly higher powder cost can often be more than offset by greater deposit efficiency or possibly lowered finishing costs. Also worth mentioning is the coating consumable parts usage rates (barrel/nozzle wear), or machine down-times due to nozzle loading, or rework and scrap production from a process that has interruption(s) in mid-application cycle. All are points worth serious and further detailed consideration.

7. Conclusion

Having in mind the multitude of powders on the market as well as the multitude of HVOF systems it is clear that there is no powder which will meet all requirements. Powders should be carefully understood and completely justified for the application prior to longterm commitments being made. Many failures in applications are traceable to deficiencies in the powder type selected for the application. These mistakes could be avoided by considering all aspects. Only a few problems and interactions of parameters have been shown in this publication. Each difficult application must be discussed between the end user and the powder manufacturer to find the right solution and to consider all aspects. This publication should give the end user an aid to ask the right questions to his supplier. Working together and completely understanding all aspects of the process will allow a greater potential for mutual success