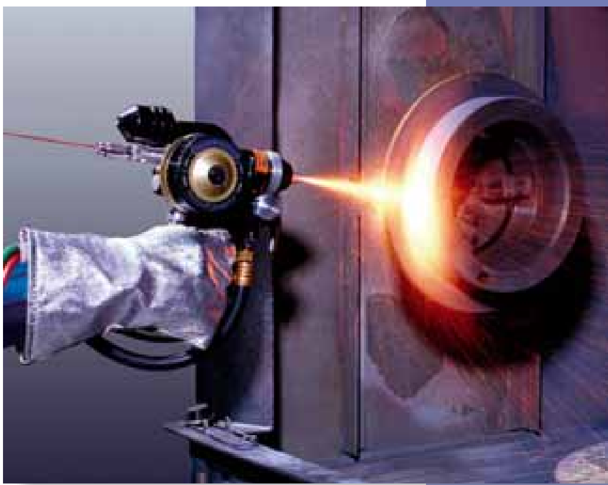
Metallographic preparation of thermal spray coatings

Application Notes

Thermal spraying was invented in the early 1900s using zinc for „metallizing" substrates for corrosion protection. The development of the plasma spray gun in the late 50s and 60s made it commercially viable to use high temperature materials such as ceramics and refractory metals for coating materials. In addition to flame and plasma spraying, today thermal spray methods include high velocity and detonation spraying using a multitude of different spray materials for the most diverse and demanding applications.

Thermal spray coatings are applied to a substrate to give a specific surface quality, which it originally does not have. Thus the bulk strength of a part is given by the substrate, and the coating adds superior surface qualities such as corrosion, wear or heat resistance.
Therefore thermal spray coatings are widely used in the aerospace and power generation industry for new and refurbished sections and parts for jet engines and gas turbines, compressors and pumps. The properties of some coatings can only be fabricated by thermal spraying, using mainly metals, ceramics, carbides and composites as well as mixtures of various materials.



Metallography of thermal spray coatings can have several purposes:

- To define, monitor and control spraying conditions for quality control
- For failure analysis
- For developing new products.

The procedure normally involves coating a test coupon to define and optimize the process for the part to be sprayed. Sections of this test coupon are then metallographically prepared and examined to assess coating thickness, size and distribution of porosity, oxides and cracks, adhesion to base material, interface contamination and presence of unmelted particles.

Electric arc metal spray coating, showing grey oxides and round, unmelted particles

Difficulties during metallographic preparation

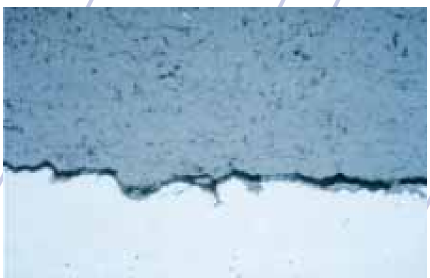
Cutting: Cracks in the coating due to clamping the sample and using coarse cut-off wheels;
Delamination from substrate

Mounting: Insufficient penetration of mounting resin

Grinding and polishing: Because of smearing of soft materials and pull-outs in brittle materials, it is difficult to establish and evaluate true porosity

Solution:

- Precision cutting
- Vacuum impregnation with epoxy resin
- Standardized, reproducible preparation methods for thermal spray coatings



Crack between a plasma spray coating and the substrate. The crack originates from cutting *500x*

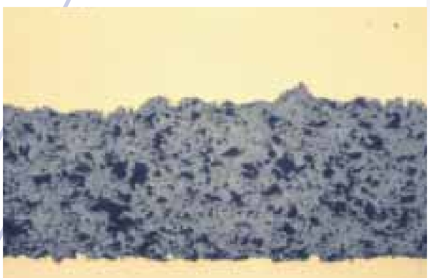
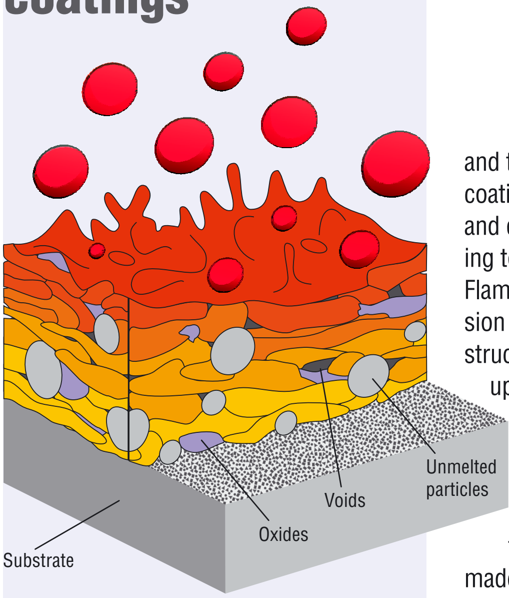


Fig.1: Ceramic spray coating, insufficiently polished *200x*

Fig. 2: Same coating as Fig.1, polished correctly *200x*

Spray methods and applications of thermal spray coatings



In the spraying process the coating material, wire or powder, melts in a high temperature heat source in a spray gun and is accelerated by the flame or plasma jet and projected towards the substrate. A stream of molten and semi-molten particles impinges onto the substrate and forms a coating. When the particles hit the workpiece they mechanically lock onto the surface, deform and cool rapidly. The bonding of single particles is through mechanical interlocking, or in some cases metallurgical bonding or diffusion. High velocity of the particles leads to better bonding and higher density of the coating. For good adhesion to the substrate it is essential that the surface is roughened by sandblasting and thoroughly degreased and cleaned before spraying.
The various spraying techniques display different temperatures at the heat source and different particle velocities, which, together with the economical aspect, need to be taken into consideration for specific applications. In the following the main spraying techniques are briefly described and some of the most well-known applications of the resulting coatings mentioned:

Flame spraying is the oldest method of applying thermal spray coatings. The coating material is either wire or powder, which is fed into an oxygen-fuel gas flame. The molten and atomized particles are ejected in a directed stream through the spraying gun nozzle. Due to the relatively low particle velocity the oxygen exposure is increased and therefore the oxide content in these coatings is relatively high (Fig. 3); adhesion and density are moderate (subsequent fusing to increase the density is possible). Flame sprayed coatings are used for corrosion protection and/or wear protection of structures and components, surface build-up and repair of worn shafts, for coating small parts and spots.

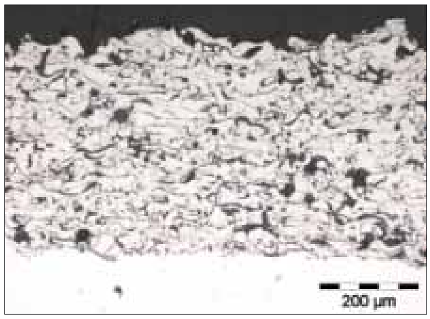


Fig. 3: Flame sprayed coating; Ni5Al

Brass synchronising rings flame-sprayed with molybdenum for wear resistance

Electric Arc spraying uses the heat of an electric arc between two continuous consumable wire electrodes made of coating material to melt the wires. The wires intersect in front of a jet of compressed air. As the heat from the arc melts the wires, the compressed air blows the molten droplets of the coating material onto the substrate. The high arc temperature and particle velocity gives this coating a bond strength and density superior to flame sprayed coatings. However, because of the use of compressed air the arc sprayed coatings have a higher percentage of oxides (Fig. 4).
The advantage of arc wire spraying is its high deposition rate which makes it suitable for large areas or high volume production applications: spraying of large structures like bridges and off-shore structures with corrosion resistant zinc or aluminium coatings, reclamation of engineering components and spraying of electronic component housing with conductive coatings of copper or aluminium.

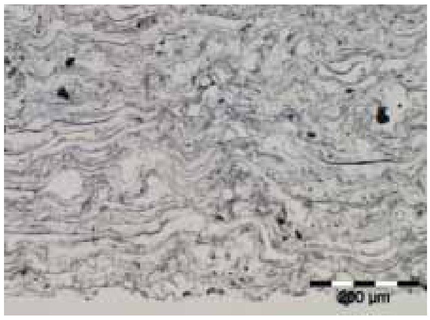
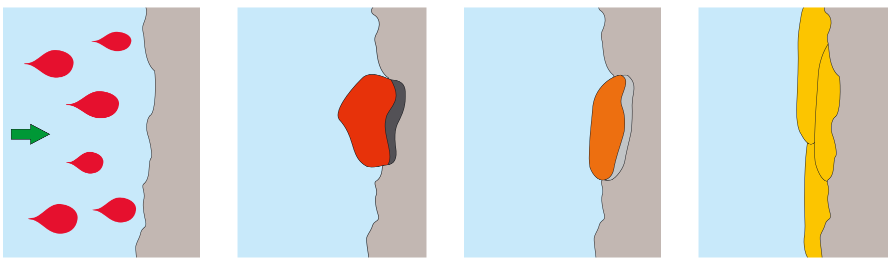


Fig. 4: Electric arc wire-sprayed metal coating FeCrSiNi and Mn

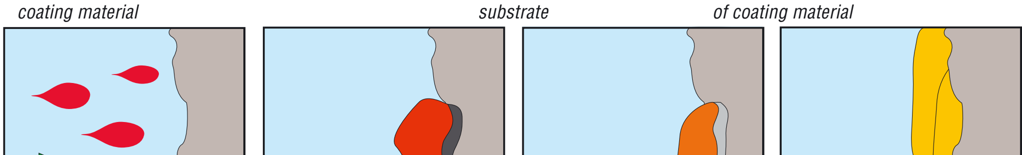
For **Detonation spraying** small amounts of carbide powder, fuel gas and oxygen are introduced in a closed tube and exploded. The detonation ejects the powder with multiple sonic speed and shoots it onto the workpiece with extremely high kinetic energy. These coatings have an excellent density, integrity and adhesion to the substrate. Due to the process conditions this method is limited to the application of carbide coatings, mainly in the aerospace and aviation industry for wear-resistant coatings.

In **High Velocity Oxy-Fuel Combustion spraying (HVOF)** fuel gas and oxygen are fed into a chamber in which combustion produces a supersonic flame, which is forced down a nozzle increasing its velocity. Powder of coating material is fed into this stream and the extreme velocity of the particles when hitting the substrate creates

Principle of layer formation



Flying drops of molten coating material — *Impact on substrate* — *Heat dissipation to substrate* — *Solidification and shrinking of coating material*



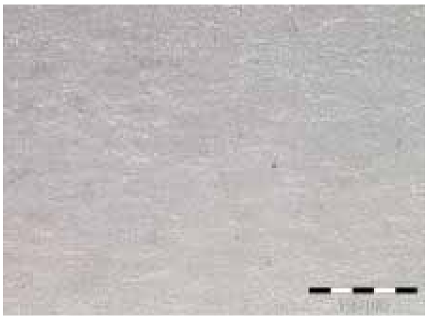


Fig. 5: HVOF coating of WC/12Co

a very dense, strong coating (Fig. 5). The very high kinetic energy of the particles when striking the substrate ensures an adequate mechanical bond even without the particles being fully molten. This makes this spraying method particularly well-suited for spraying of coatings with carbides. Typical applications are tungsten carbide coatings on air engine turbine components and valves, and nickel-chromium coatings for oxidation resistance.

Plasma spraying is the most common method for thermal spray coatings, and is applied as Air Plasma Spraying (APS) or spraying under controlled atmosphere. An electric arc is formed between a cathode and the concentric nozzle of the spray gun. A mixture of gases with a high flow rate along the electrode is ionised by the arc, and forms plasma. This plasma stream is pushed out of the nozzle, where the powder of the coating material is injected into the plasma jet. The heat and velocity of the plasma jet rapidly melts and accelerates the particles so that they are propelled onto the substrate and form a coating. Plasma sprayed coatings have a denser structure than flame sprayed coatings (compare Figs. 3 and 6).
Plasma spraying has the advantage that it can spray materials with high melting points such as ceramics or refractory metals. It is a versatile spraying method for

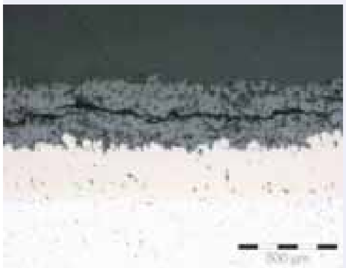
Combustion chamber with APS thermal barrier coating, bond coat NiCrAlY, topcoat $ZrO_2 + Y_2O_3$

Fig. 6: APS coating with NiCr bond coat and titanium oxide top coating

high quality coatings and used for a wide range of applications, including coatings on traction surfaces, thermal barrier coatings on turbine combustion chambers, vanes and blades, biocompatible hydroxylapatite coatings for implants and ceramic coatings on print rolls.

Difficulties in the preparation of thermal spray coatings

Cutting: Clamping of spray coated workpieces for sectioning can introduce cracks in brittle coatings or compress very soft coatings.



Cracks introduced through sectioning

Mounting: Cold mounting resins with high shrinkage can cause damage to coatings with weak adhesion to the substrate; due to the shrinkage gap the coating is not supported by resin, which can lead to delamination of the coating during grinding and polishing.

Grinding and polishing: Edge-rounding can lead to uneven polishing and subsequent misinterpretation of the coating density (Fig. 7). Relief between coating and substrate creates a shadow that can be misinterpreted (Fig. 8).

How to estimate the true porosity in a metallographically prepared spray coating is still a reason for debate, as metallographic grinding and polishing, if not carried out

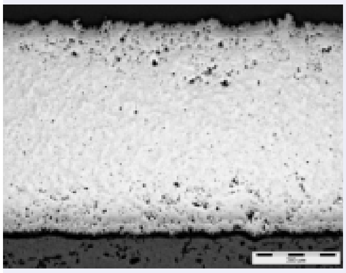


Fig. 7: Incorrect polish suggests less porosity in the middle of the coating

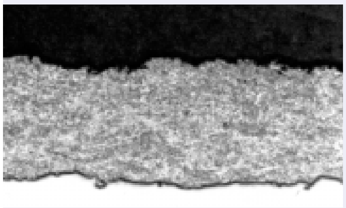
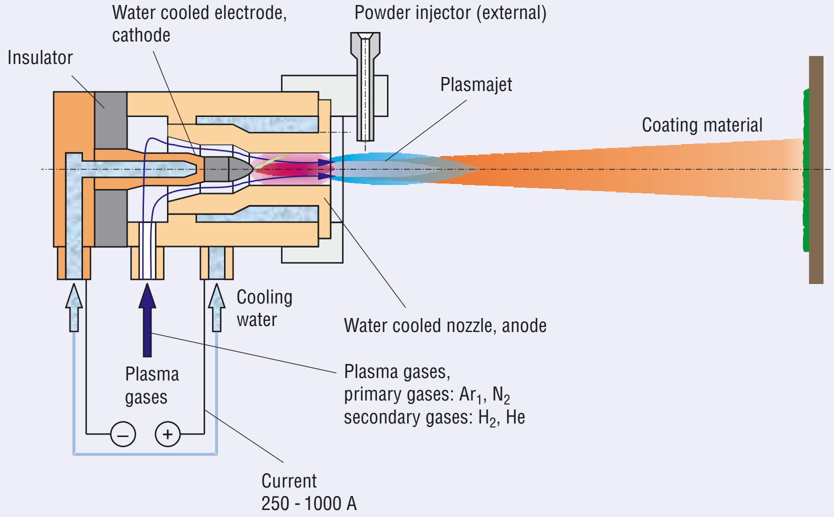
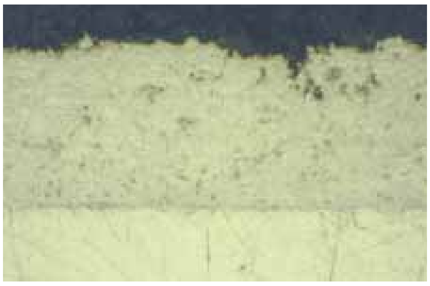


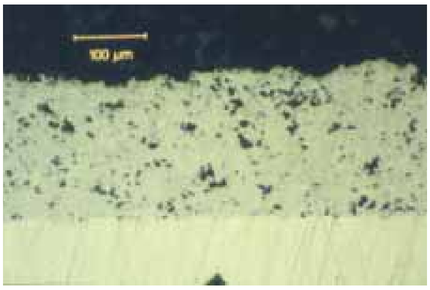
Fig. 8: WC/Co spray coating with relief polish shows dark line at resin/coating interface. Can lead to misinterpretation.



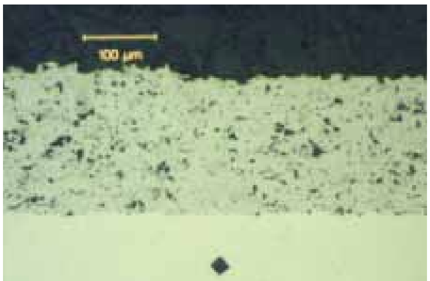
Schematic drawing of plasma spray gun



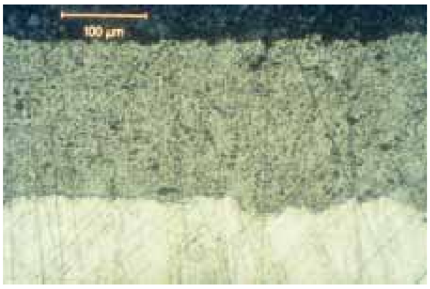
a) Metal spray coating after fine grinding



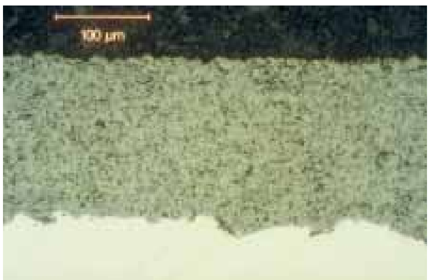
b) Same coating as in a) polished with 3 µm



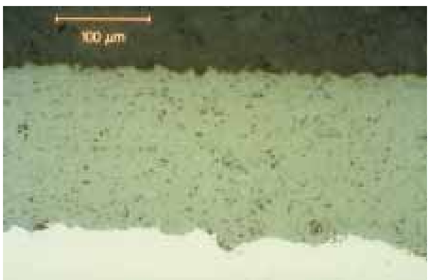
c) Same coating as in b) after final polish



d) Ceramic spray coating after fine grinding

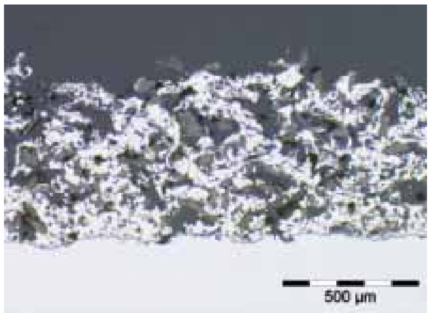


e) Same coating as in d) polished with 3 µm



f) Same coating as in e) after final polish

Nickel flame spray coating with 15% graphite



correctly, can introduce artefacts which are not part of the coating structure. For example, in metal or metal/ceramic coatings, the softer metal is smeared into pores during grinding and if not polished properly can cover up the true porosity (see Figs. a-c). In comparison, ceramic coatings are brittle and particles break out of the surface during grinding. If not polished thoroughly, these break-outs leave an incorrect impression of a high porosity (see Figs. d-f).

Recommendations for the preparation of thermal spray coatings

As there are many different spraying materials with sometimes unusual combinations, it is important to know the correct spraying and substrate material. It facilitates to estimate how the materials will behave under mechanical abrasion. As different spraying processes result in different coating densities and structures it also helps to know the spraying method used on a particular sample in order to estimate the expected porosity and oxide content.

Cutting: Selection of the cut-off wheel is based on the substrate material, which is usually metallic. A wheel with a looser bond (soft) is preferable to a denser bond (hard) as brittle particles of the coating are dragged out by a hard cut-off wheel. This is particularly important when cutting parts with ceramic coatings. Even if the coating is ceramic, it constitutes only a small percentage of the total cross sectional area and does not need to be cut with a diamond cut-off wheel. Usually sectioning is possible with a soft aluminium oxide wheel. If the ceramic coating is very thick and dense a resin-bonded diamond cut-off wheel can be used as an alternative.

A thin piece of styrofoam between clamps and sample can help to protect brittle and very soft coatings from being damaged.

When cutting pieces other than test coupons, for instance samples for failure analysis, it is important to ensure that the workpiece is clamped into the cut-off machine in such a way that the cut-off wheel is cutting into the coating towards the substrate, and not from the substrate into the coating. As the bond of the coating is mainly mechanical, it can delaminate from the substrate due to the drag of the cut-off wheel.
Particularly fragile or thin coatings can first be vacuum impregnated with cold mounting epoxy resin, and then the micro sections are cut and remounted for grinding and polishing. This ensures maximum support to the coating during sectioning.

The appearance of cracks in a coating after final polishing may or may not be the result of cutting. It is recommended to regrind and polish the sample. If the crack is from cutting it will usually disappear, if it is inherent in the coating it will reappear, or cracks will surface in other areas of the coating.

Mounting: Cold mounting with epoxy resin (EpoFix, CaldoFix) is recommended as spray coatings are very easily damaged during hot compression mounting (Figs. 9 and 10).
In general, vacuum impregnation is recommended for all coatings. The depth of impregnation varies with the degree of open porosity and interconnections between the pores. Very porous coatings can be easier impregnated than denser ones, and coatings with less than 10% porosity can not be impregnated successfully. As it can be difficult to distinguish voids filled with transparent or translucent mounting resins from the structural elements of the coating, it helps to mix a fluorescent dye (Epodye) into the cold mounting resin. Viewed with a long pass blue filter and a short pass orange filter in the microscope, the fluorescent dye

Fig.9: Damage to ceramic spray coating due to hot compression mounting *200x*

Fig.10: Same coating as in Fig. 9, cold mounted *200x*

Fig.11: WC/Co plasma spray coating in bright field

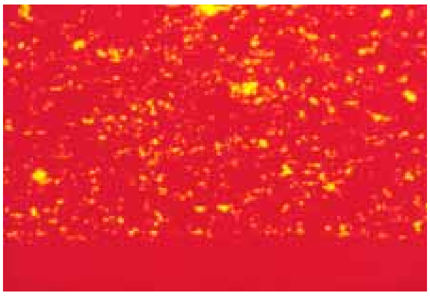


Fig.12: Same coating as in Fig.11 in fluorescent light

will colour those voids yellow which have been filled with resin by the impregnation (Fig.11 and 12).
Unfortunately this method is not always applicable for ceramic coatings, because ceramics are translucent and the whole coating appears fluorescent.

Grinding and polishing: As a general rule plane grinding should start with the finest possible silicon carbide paper to avoid creating artificial porosity by fracturing brittle particles. Exceptions can be very dense or thick ceramic coatings, which are plane ground more efficiently with diamond (with e.g. MD-Piano 220). For high sample volumes or large parts, which need to be examined as a whole, plane grinding with a stone may be preferred as it is faster. Whichever method is use, one must always be aware that the first preparation step should aim to remove any cracks that arise from cutting without introducing new damage from coarse grinding.

To retain flatness and assure a good material removal rate, fine grinding is preferably done with diamond on a composite fine grinding disc. For ceramic coatings the fine grinding disc MD-Allegro is recommended, and for metal coatings MD-Largo. A thorough polishing on a silk cloth (MD-Dur or MD-Dac) will retain the flatness of the sample and guarantee the removal of smeared metal.

Metal coatings can be fine polished either with 1 µm diamond or a colloidal silica (OP-U) on a soft cloth. It is not recommended to use the colloidal silica suspension OP-S for polishing metal spray coatings as it creates too much relief. However, OP-S is suitable for the final polishing of ceramic coatings as it gives a good contrast to the structure.

In the trial stage for establishing preparation methods both silicon carbide and diamond grinding can be tried to find out which is the more suitable plane grinding method. The same applies to the final polishing step, for which 1µm diamond might in some cases be preferable to colloidal silica.

In general it is recommended that, if possible, a standard procedure is always used for all coatings. With automatic preparation equipment it is possible to control preparation parameters, which guarantees consistent results and excellent reproducibility. By keeping the preparation conditions constant, it can then be assumed that sudden differences in the microstructure in most cases reflect differences in the spraying process and not in the preparation process.

Standard preparation method for thermal spray coatings

Grinding

Step	PG	FG
Surface	SiC-paper 220#	MD-Largo
Suspension		DiaPro Allegro/Largo*
Lubricant	Water	
rpm	300	150
Force [N]	180	180
Time	Until plane	5 min.

Polishing

Step	DP 1	DP 2**
Surface	MD-Dac	MD-Nap
Suspension	DiaPro Dac*	DiaPro Nap B*
rpm	150	150
Force [N]	180	120
Time	5 min.	1 min.

Valid for 6 mounted samples, 30 mm diam. clamped in a holder.

Remarks:

**Alternatively DiaPro diamond suspension can be replaced by DP-Suspension, P, 9 µm, 3 µm and 1 µm respectively, applied with blue lubricant.*

***Alternatively, this diamond polishing step can be replaced by a polishing step with colloidal silica (OP-U for metal, OP-S for ceramic coatings) for 30-60 sec.*

The preparation method in the table above has successfully been used for the most common coatings. The data are for 6 mounted samples, 30 mm diameter, clamped into a holder. DiaPro diamond suspension can be replaced by DP-Suspension 9 µm, 3 µm and 1 µm respectively, applied with blue lubricant.

Etching: In general, etchants that are recommended for a specific material can also be used for spray coatings of this material. It can be expected that the more similar the substrate and coating materials are, the more even the etching attack will be.

Thermally sprayed acetabular cup shell

Coatings sprayed in a controlled atmosphere have few or no oxides and it is difficult to recognize the coating structure. Therefore these types of coatings need to be contrasted with chemical etching.

Vacuum sprayed coatings on nickel and cobalt based superalloys can be etched with the same solutions used for the substrate, or electrolytically with 10% aqueous oxalic acid.
The structure of coatings containing molybdenum can be revealed by using the following etchant:

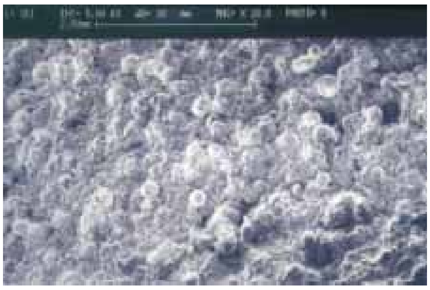
50 ml water
50 ml hydrogen peroxide (3%)
50 ml ammonia

Caution: Always follow the recommended safety precautions when working with chemical reagents.

Summary

Thermal spray coatings are widely used to give or improve a specific surface quality or function to a workpiece. Different spraying methods result in different characteristics of the coatings, and they are mainly applied for corrosion, heat and wear resistance. Metallographic examination of spray coatings includes estimation of porosity, oxides and unmelted particles as well as adhesion to the substrate. Because incorrect grinding and polishing procedures can influence the evaluation of the true porosity it is very important that metallographic preparation is carried out systematically and that the results are reproducible. Precision cutting with the correct cut-off wheel is recommended to avoid cracks in the coating. Mounting should follow with slow curing epoxy. Coarse grinding introduces the most damage to the coating and should therefore be carried out with the finest grit possible. To avoid relief fine grinding with diamond on a rigid disc is recommended, followed by a thorough diamond polish on a silk cloth.

It is particularly important to be aware that metal coatings behave differently to ceramic coatings under mechanical abrasion



SEM photomicrograph of thermally sprayed surface of acetabular cup shell

and that the diamond polish needs to be long enough to reveal the true porosity.

The recommended preparation procedure is based on experience and gives excellent results for the majority of common thermal spray coatings. However, it should be noted that for some specific proprietary coatings the polishing times may need to be adjusted.

Application Notes
Metallographic preparation of thermal spray coatings

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Acknowledgement
We wish to thank Sulzer Metco AG, Wohlen, Switzerland, for its cooperation and supplying information material. Special thanks go to J. Hochstrasser and P. Ambühl for sharing their extensive knowledge with us and supplying the following images for reproduction: photo of spraying process and large micrograph on page 1; drawing: Principle of particle movement, photo synchronising rings and micrographs on page 2; drawing, photo combustion chamber and all micrographs on page 3 and micrograph of nickel flame sprayed coating on page 4. We thank Richard Compton, Zimmer, Inc. USA, for the photo of the acetabular cup shell and the SEM photomicrograph on page 6.

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