Neue Technologien zur Kesselbeschichtung für den Schutz gegen Korrosion und Verschleiß

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Abstrakt

Die Wanddickenabzehrung von Kesselrohren aufgrund der schweren Betriebsbedingungen kann zu vorzeitigem Rohrbruch und ungeplanten Ausfällen führen. Es gibt immer höhere Anforderungen, um Müll und Mischabfälle bei höheren Temperaturen mit einer verbesserten Zuverlässigkeit der Kesselrohre zu verbrennen. Muhlverbrenung Anlagenbetreiber sind immer stärker dazu gezwungen kostengünstige Lösungen für eine höhere Verführbarkeit von Flossenwänden und Überhitzerrohren im Vergleich zur großflächigen Schweißplattierung mit Inconel 625 zu finden.

Thermisch gespritzte Beschichtungen etablieren sich als zuverlässige und kostengünstige Lösungen. Diese können mit einfach Mitteln auf der Baustelle eingesetzt werden, mit dünnen Beschichtung und mit einer Reihe von Legierungen und Prozessen die auf die unterschiedlichen komplexen Korrosions- und Verschleißsituationen abgestimmt sind.

Es wurden neuartige Legierungen mit verbesserten Korrosions- und Verschleißschutzeigenschaften gegenüber der Legierung 625 entwickelt. Jedoch ist es nicht möglich, diese Fülldrahtlegierungen zu verschweißen, aber sie können mit den thermischen Spritzverfahren aufgebracht werden. Mehrere neue Beschichtungsmaterialen und -verfahren (HVOF, ARC, Spray & Fuse, Laserschweißen) haben sich in langfristigen Kesselrohr-Untersuchungen gegen Erosion und Korrosion bewährt und eine neue Art von "verdichteten" thermische Spritzschichten haben ihre technischen und kommerziellen Daten nachgewiesen.

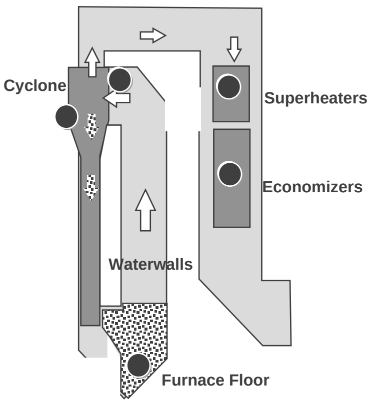
Der Beschichtungsprozess kann in Fachwerkstätten auf neue Rohre und Flossenwände mit einer Vielzahl von Durchmessern und Geometrien durchgeführt werden. Auch eine vor-Ort- Beschichtung direkt im Kessel ist möglich, um bereits geschädigte Kesselrohre und Wärmetauscher flächig zu sanieren und zu schützen. Die theoretischen und praktischen Aspekte der Beschichtungen und wie sie angewendet werden wird im Detail zusammen mit einigen Fallstudien vorgestellt und diskutiert.

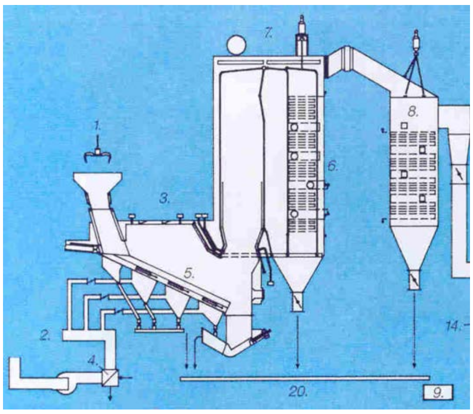
1. INTRODUCTION

The typical power generation boiler associated with a Mullverbrenunganlage (MVA) represents an aggressive environment in terms of erosive wear and high temperature corrosion for the heat exchanger tube materials. The many forms, sizes, designs, makes, etc. of boilers, together with the diversity of fuels used (coal, oil, municipal waste, industrial waste, biomass, etc.) and operating regimes gives rise to a broad and complex range of wear/corrosion problems. However, some patterns do emerge and general problem areas typically found are illustrated in Fig. 1. To this can be added the erosion/corrosion wastage problems (1,2) of in-bed heat exchanger tubing found in the various forms of Fluidized Bed Combustors; Atmospheric-AFBC, Circulating-CFB and Pressurized-PFBC.

1.1 Different types of boiler design and fuels lead to different types of corrosion/erosion regimes requiring different types of solution including on site and workshop coatings

In relatively clean burning waste boilers (separated waste or mixed fuel), oxidation and sulfidation can be problematic depending on local oxygen and sulphur levels (3,4). Burning fuels with significant amounts of chlorine or elements such as sodium, potassium, vanadium, etc. can cause the formation of ash and salt deposits having very low melting point substances. If the metal surface temperature is above this temperature very corrosive conditions can develop with the molten salts fluxing the protective oxide scales or directly dissolving the metal. Such corrosion is often encountered in waste incinerators (5) but also in black liquor recovery boilers in the pulp and paper industry (6).





Fluidized Bed

Waste burning

Fig. 1 Schematic of typical boilers and corrosion/wear sites

The corrosion is not just a high temperature phenomena. During a period of boiler shut down acids can condense from the flue gases (below about 120 °C) to cause direct attack of heat exchanger tubing. In addition, these acids can react with the surface products (oxides, scales, slags, coatings, etc.) to accelerate high temperature corrosion after the MVA start up.

The key issue is that the erosion or corrosion of the boiler tube leads to a thinning of the tube wall cross-section of what is a pressure vessel. When the tube wall thickness becomes too thin, the tube bursts and operations have to be closed to replace it. The rate of section loss in critical tubes is monitored and expensive outages to replace thinning tubes needs to be planned. Many times the rate of wear and consequent schedule for replacement does not correspond with scheduled outages, which leads to large additional costs of an unplanned boiler stoppage. The cutting out and replacement of boiler tubes is also an expensive job, as not only is the plant not running, but tubes need to be cut out and new tubes welded, inspected and pressure tested before operations can resume. With increasing cost and performance pressures on the operators of all boilers (Figure 2), tube replacement is an increasingly costly and unwanted maintenance operation.

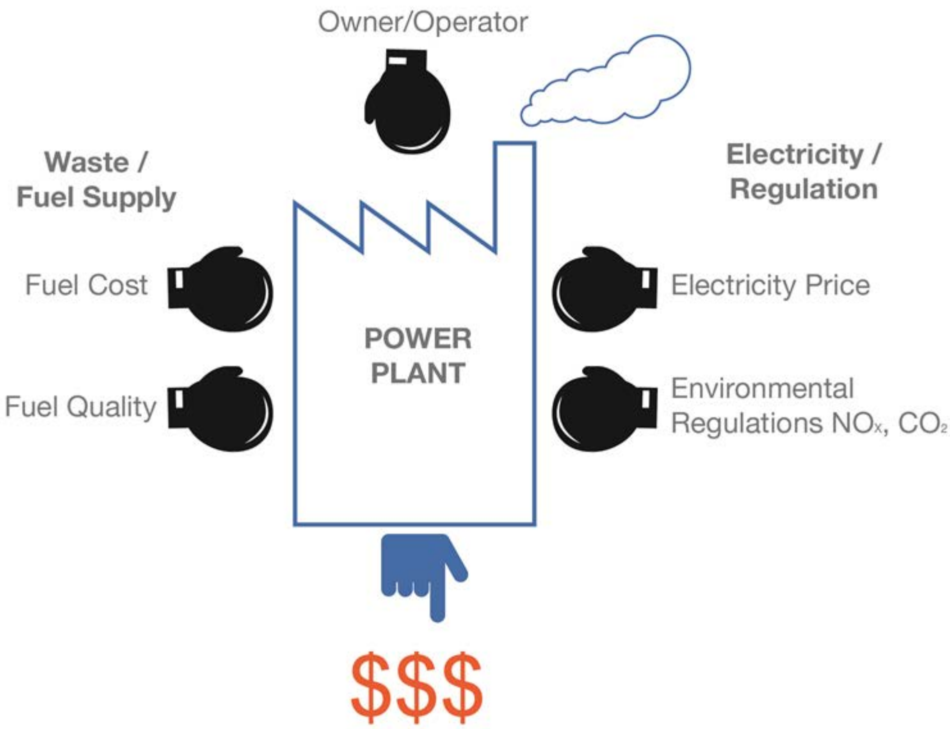


Fig. 2 Schematic of typical constraints for a MVA operator

The erosive element varies dependent on the fuel being used, but it is generally a by-product of the original fuel or created during the combustion process. However, the erosive element has the general feature of being harder than the boiler tube, traveling at a high velocity in the gas stream and impacting the boiler tube at a range of angles. In low grade coal this erosive product is typically fine quartz, which is extremely hard and very erosive, also due to its angular form. In Biomass, quartz can also be present in cut straw from entrapped soil. In waste/biomass incineration, the hard particle can be formed during combustion, or could be oxides created from metallic impurities (such as nail, screws, etc.).

Erosion wear of boiler tubes is an old problem in coal fired boilers and solutions have been developed over the years to protect these tubes. These solutions can also be used in MVAs where corrosion is the predominant wear. The normal solution is coating the boiler tubes with a thin material that is considerably harder than the relatively soft boiler tube material. A range of deposition techniques and alloys have been developed depending on the restraints of access to the effected tubes and whether the tubes are new (and can be coated in a specialist workshop) or whether the worn tubes need to have immediate protection with a hard coating (performed in-situ).

In conclusion, there is a wide range of requirements for the MVA protection and the choice is not just made regarding cost or performance, but also maintenance planning and on-site coating requirements that fit best to the plant operator.

1.2 Past and current solutions to reduce boiler tube wastage

There are various philosophies to reduce tube wastage to acceptable levels (1,2,7,8). These include design, operating temperature and gas flow modifications (which can reduce boiler efficiency) or tube material changes (which can be expensive and usually mean sacrificing other properties). As the wear/corrosion is only a surface attack phenomena of an otherwise mechanically functioning tube, many boiler producers have preferred some form of protective surface treatment/coating approach. Methods available include co-extrusion, calorizing, nitriding, chromizing, borizing, pre-oxidizing, weld-overlay and thermally sprayed coatings.

Today, against corrosion in MVAs, the overwhelming technology used and trusted is weld overlay (usually 2mm thick) of a nickel-based complex alloy (usually Inconel 625). This solution has given protection to hundreds of boiler and enabled them to reliably manage the boiler corrosion. This solution is performed on single tubes and also large panels mainly with specialist equipment in specialist workshops. Weld overlay can also be performed on site on large panels such as waterwalls, but not single tubes. Weld overlay is not used to apply alloys that are protection against erosion. Consequently, thermal sprayed coatings developed in parallel to tackle the inherent drawbacks of weld overlay which are:

- Inherent thick coating, which has a poor thermal conductivity and takes a long time to deposit (important for in-situ work)
- Inherent high dilution with substrate tube material (best 5%), which reduces the corrosion protection efficiency by adding iron to the 625 chemistry
- No erosion resistant materials available which also have good corrosion resistance

- Rough, uneven surface that can accelerate corrosion through easier sticking of slag or produce lower coating thickness areas that concentrate heat flux.

The typical characteristics of thermal spray coatings are that they are thin (0.3-1.0mm), are fast to apply, can have unique chemistries and can be applied like paint to complex shaped parts including worn tubes. Thermal sprayed coatings have had a mixed success in the past due to adhesion problems, porosity or unsatisfactory resistance to corrosion and erosion. This has focused development activities to produce new coating technologies and new coating materials. Today, thermal spray coating solutions have achieved an important position in combating high temperature corrosion/erosion and have become the preferred solution in many boilers for erosion and corrosion protection.

The main advantages of coatings are:

- alloy composition flexibility to also include very hard, wear resistant alloys
- multi-layer structures combining optimal corrosion and wear properties
- unique microstructures due to various coating processes and high rate of coating cooling
- thinner coatings, so better thermal heat transfer performance and lower coating costs per square meter
- no dilution of substrate, as usually mechanical or diffusion bonding, so no dilution of corrosion performance of alloy
- high deposition rate process compared to welding (time to coat a square meter of tube panel)
- possibility of on-site application of single tubes and repair of components

The spray processes that have been used in boiler protection are: Flame Combustion (with powder or wire), Electric Arc Wire, Air Plasma (APPS), High Velocity Oxygen Fuel (HVOF), Spray and Fuse (S&F) and finally painted coatings of inorganic ceramic-based compounds (slurry coatings).

Today, all these thermal spray solutions are still being used as each process and its associated optimised alloy have found a niche success in terms of performance, price and practicality.

1.3 The technical problems are intensifying

In Europe and also increasingly Asia, the increasing move to alternative energy producing sources plus demands for lower CO_2 and general cleaner emissions have lead to stricter boiler operations for low NOx performance plus the use of alternative fuels (municipal waste, biomass) in incineration power plants. However, the focus on reducing the already high costs of generating electricity have also pushed traditional large coal fired plants to burn low grade coal (with its high sulphur and high particulate content). All these trends have increased the amount of corrosion and wear that is being seen in the boiler tubes.

1.4 The plant economic factors, limitations and issues

In addition to the increasing technical problems, all plant managers with fixed fuel prices and delivered electricity prices plus pressure to improve the economics of their plant are looking at a) reducing their maintenance spending including outages b) generating more electricity with the same plant (increased operating temperatures and longer availability). Coating quality and performance, coating cost, reduction in downtime to apply coats on site, new tubes vs repair on site worn tubes, etc. are now becoming critical issues in the economics of many power plants (Fig 2).

Thin Thermal Sprayed coatings can also be used to extend the lifetime of existing solutions (such as weld overlay 625) for a few years at a reduced total cost to meet the planned major overhaul scheduling at a plant. Many addition solutions over weld overlay are offered (Fig 3).

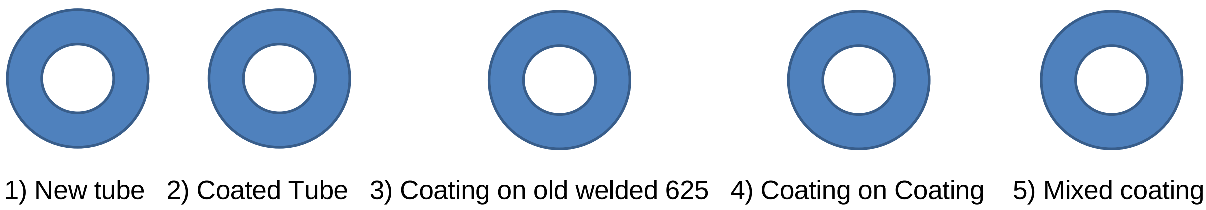


Fig. 3 Schematic of the variations of coatings possible with on-site applied Thermal Sprayed BTCs

1.5 New economical solutions

Through numerous development programs, Castolin Eutectic continuously improves its technologies. Well controlled processes, densification technology, new alloys and on-site automation all combine to form economical solutions that Castolin Eutectic can offer to solve its customer’s problems.

In addition to the experience in boiler coating development since the 1970s with S&F, Flame, Arc Wire and Densification, the portfolio of solutions has been recently expanded with the addition of the USA-based company, WherTec, to the Castolin Eutectic group. WherTec have boiler coating experience with weld overlay of 622, laser cladding of 622, HVOF, arc wire spraying and slurry coatings on-site and in specialist workshops, since 1996. An overview on our range of on-site and workshop processes in addition to the spray & fuse process is given in Figure 4.

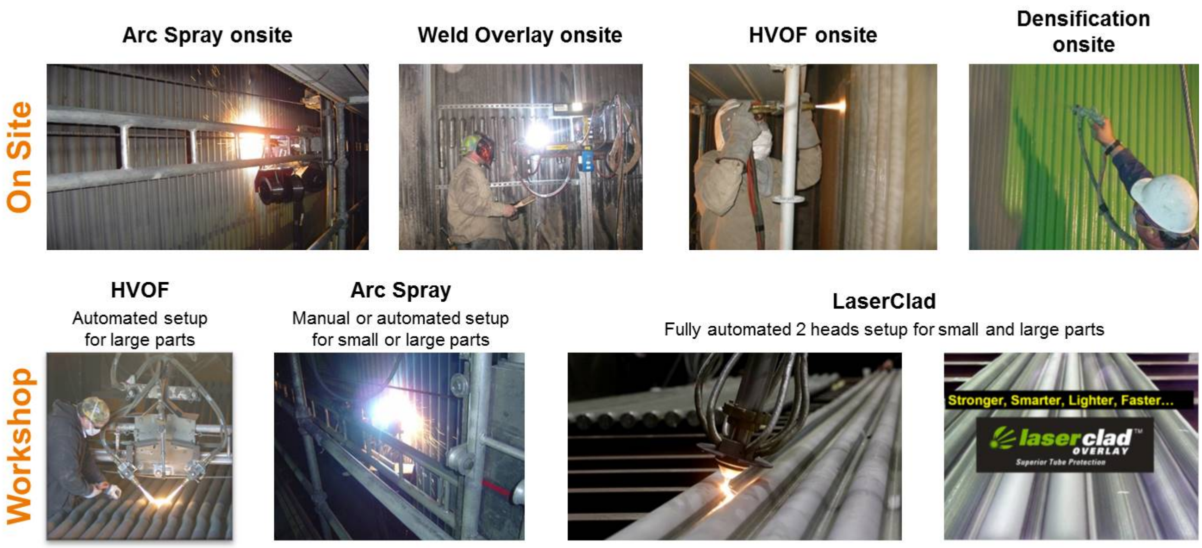


Fig. 4 Overview of boiler coating technologies in the workshop and in-situ in addition to the established spray & fuse process.

2. IDEAL SOLUTIONS

Success in these environments has been due to a careful tuning of alloy, process equipment and application procedure to the specific corrosion/erosion environment as illustrated schematically in Fig. 5. Each of the three elements is critical and if not controlled or optimised can lead to poor coating performance in a boiler.

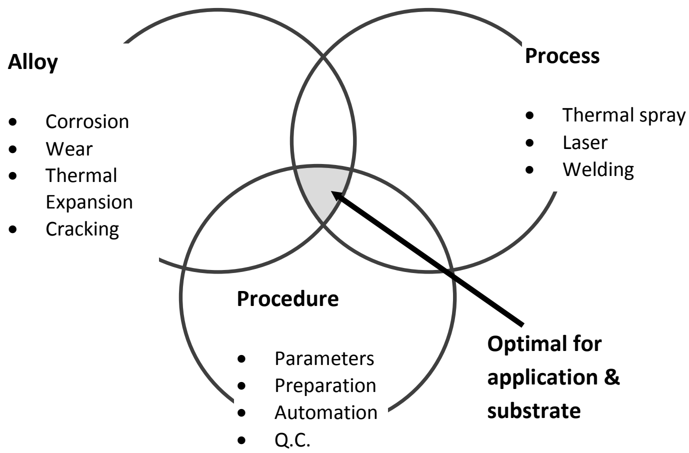


Fig. 5 Development elements involved in producing optimal boiler coatings

Consequently, a range of materials and processes have been developed which is available to the waste incineration industry. However, the waste incineration is still demanding the following advancements in technology and service above the standard solutions of weld overlay of Inconel 625 and arc wire spray of long established iron based alloys:

- Improved corrosion resistant nickel based coating, but with a higher hardness to resist erosion
- Dense, high bonding thermally sprayed coating
- Lower cost quality coating and faster on-site processing for shorter outages

3. THERMAL SPRAY COATINGS AND PROCESS TECHNOLOGIES

For many years thermal spraying a layer of protective material has been successfully used as a coating method to improve or repair a part's surface properties.

The protective material sprayed in the form of wire, powder or ceramic rods are melted in a gas flame, electric arc or a plasma jet. The melt is atomized into a gas or air stream and then sprayed towards the object to be coated (Figure 6). Metals, ceramics, carbides and plastics are examples of coating materials that can be applied by thermal spraying.

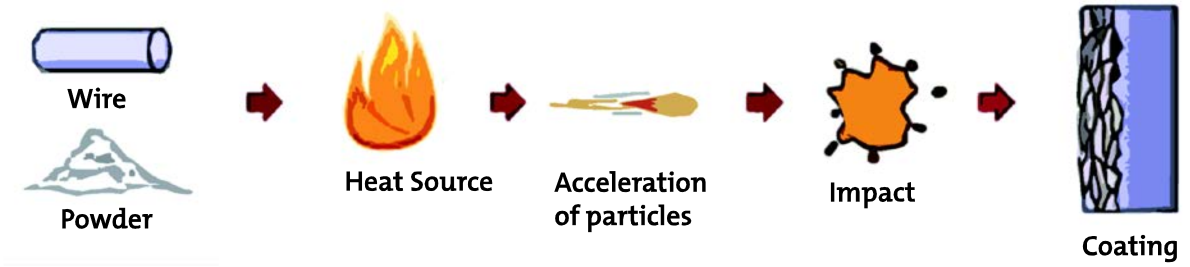
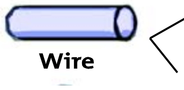
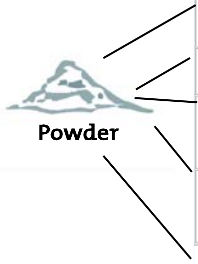


Fig. 6 Schematic of the thermal spray process to produce coatings

There exists a broad range of thermal spray technologies that have been developed by Castolin Eutectic and other pioneers over the years, based on optimization of feedstock, heat source, particle acceleration and densification method, as illustrated in Figure 7 below:



Heat source	Acceleration	Process name	Post treatment	Coating name
Arc	Medium	*Arc Wire*	- Densification -	**- Arc Wire - BTC**
Flame	Medium	*Arc Flame*		**Arc Flame**



Heat source	Acceleration	Process name	Post treatment	Coating name
Arc – PTA	Slow	*PTA*		**PTA**
Plasma	- High - Medium	*- LPPS - APPS*		**LPPS APPS**
Laser	Slow	*Laser cladding*		**Laser cladding**
Flame	Medium	*Flame spraying*	- Non - Fusion	**- Flame Spray - Spray & Fuse**
Flame	High Velocity	*HVOF*	- Non - Fusion - Densification	**- HVOF - HVOF Spray & Fuse - HVOF Densified-Monitox**

Fig. 7 Overview of thermal spray processes

3.1 Established spray & fuse, arc wire and HVOF processes

Spray & Fuse

Spray and fuse coatings are the oldest and most successful thermal sprayed coatings against corrosion and erosion and have been used since the 1970s.

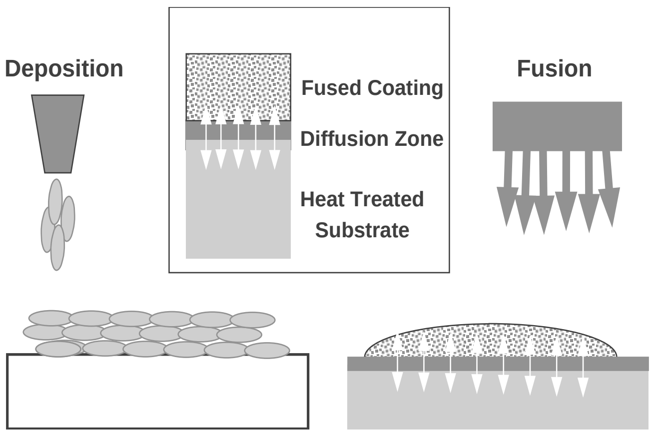


Fig.8 Schematic of spray & fuse process

The spray & fuse technique is a two-step process (Figure 8) comprising the deposition of a coating (by combustion spraying) followed by a fusing procedure in which the coating material is heated above its fusion temperature. The boiler tube is also heated to a higher temperature than any other “cold “ thermal spray process. The high temperature and fluid nature of the coating during the fusion step give rise a uniform microstructure and chemistry, plus zero open porosity, a very smooth surface and also a diffusion bonded interface, which are critical for effective corrosion resistance. Against corrosion it is recognised as the ultimate thermal spray coating and has been used non-stop since 1973 in severe industrial corrosion/wear applications. Spray and fuse coatings have proven a better solution than welded 625 in many MVA in Germany over the last 15 years. However, this excellent performance has not overcome the inherent limitations for large scale commercial MVA applications, which are: high heat input to base tube and not possible to coat on site.

Arc Spray

Arc wire spraying is a simple, cost effect solution for large surfaces, that doea not heat the tube and can be done on site. The special feedstock is in the form of 2 wires which are short circuited to melt the wire tips. Compressed air is used to atomize the molten tips and propel the droplets towards the substrate.

The spray rate can be up to 20 kg/hour are possible and the process is used both in workshops and on-site (Figure 9).

The characteristics of the arc wire spray coating are that it has a rough surface but a good adhesion (usually above 35 MPa). Its porosity content is typically below 2% when the spray parameters are optimized.

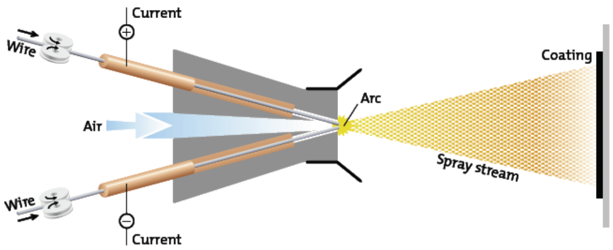


Fig. 9 Arc wire spray process and modern Eutronic ARC spray systems for coatings on large surface areas

HVOF

HVOF (High Velocity Oxygen Fuel) spraying is a relatively new process giving the densest (less than 1%), hardest coatings with very high bond strength. During HVOF spraying the ignited kerosen/oxygen mixture produces a hot gas stream into which powder is injected (reaching velocity up to 800 m/s). This creates high impact energy particles and the highest quality coating. It can also spray very hard tungsten carbide coatings having hardness of over 1300 HV. Therefore it is often used to protect against extreme erosive wear and for corrosion resistance with nickel-based complex alloys.

3.2 New Processes: densification and laser cladding

Mindful of the industry requirements from the plant operators for improved protective coatings having corrosion resistant, higher erosion resistant, denser and faster to deposit on-site (lower cost), Castolin Eutectic have developed new alloys and processes.

<u>Densification</u>

Castolin Eutectic have developed a proprietary process that “Densifies” the thermally sprayed coating which effectively blocks all the paths in the coating that would allow the corrosive species to reach the steel substrate. A chemical reaction between the “Densification” component with the applied coating alloy creates this exceptional barrier against corrosion. It is mainly used in combination with our optimized arc spray coatings but can also be used on HVOF coatings.

This densification process coupled to the arc spray process (the BTC coating product range) is well suited to coat waterwalls in waste-to-energy and biomass boilers where corrosion is an important wear mechanism. In cases where corrosion is not so severe, an inorganic self “densifying” coating can be applied directly onto the boiler tube, without the use of the applied thermal spray coating. Here, there is a significant cost and time saving but coating performance is also not at the same level.

In the Castolin Eutectic family of companies (Monitor Coatings, WherTec) there is now the largest global experience in using “Densification” technology in a broad range of boilers.

<u>Laser Cladding</u>

The advent of High Power Diode Lasers (HPDL) technology has allowed the previously promising, but expensive, laser cladding technology to become a cost effective corrosion solution for large boiler surface areas. This state-of-the-art technology allows efficient cladding of tubes and panels in our workshops. Inconel type materials can be applied at a range of thickness also down to 0.7 mm. This technology competes well against the traditional weld overlay while giving better properties such as a lower dilution, a smaller heat affected zone and smooth coating surface.

We use laser cladding machines which are coupled with diode lasers up to 8 kW and the high deposition speed and coating thickness flexibility finally allow these excellent coatings to be competitively priced for the boiler coating market. In the USA, several hundred square meters of our laser clad boiler tube are installed in boilers (Figure 10).

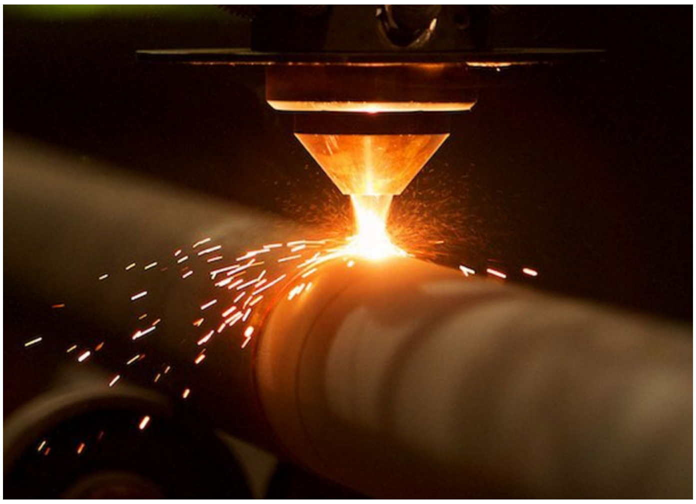


Fig. 10 Laser cladding process on a single boiler tube at WherTec workshop

3.4 Alloys available

Castolin Eutectic is a leader in self-fluxing nickel-based alloys since the 1970s and a patented alloy that can be deposited with sprayed & fuse, arc spray or laser cladding is currently available. Its corrosion resistance is even better than Inconel 625 (results of field tests performed in many waste-to-energy boilers in France, Austria and Germany) while it is much harder. Indeed, its 58 HRC hardness is an excellent feature against erosive conditions that may be found in a corrosive environment.

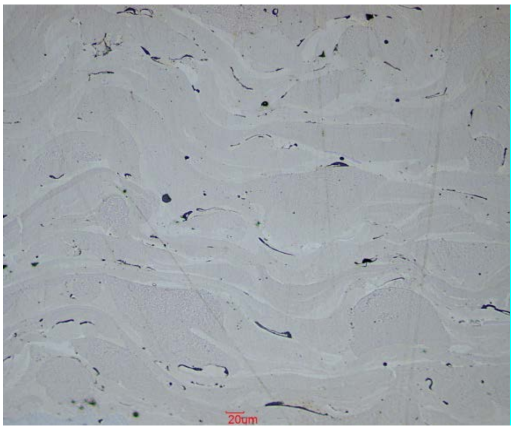


Fig. 11 Arc sprayed patented Castolin Eutectic alloy for boiler tubes and waterwalls

Figure 11 shows the microstructure of this patented alloy deposited by arc spray, BTW 66. The very high density of this coating (porosity less than 1%) and the very limited oxide content is exceptional for an arc sprayed coating.

New alloys with even better corrosion resistance are currently in our development program and initial tests in commercial boilers has started recently.

3.4 High quality coatings

The processing parameters must be optimized for each process/alloy couple in order to get the best properties from all these coatings. This is achieved using our own specialist on-site equipment and consumables that are manufactured internally under tight specifications. Our automated systems help to reduce the operational costs while keeping the coating quality to the highest level.

4. PRACTICAL RESULTS AND EXPERIENCE IN BOILERS

The Castolin Eutectic Group has been involved in the development of S&F alloys for high temperature erosion/corrosion prevention since the early 1970s with the launch of the 14112 alloy which subsequently was licensed by the then Combustion Engineering. This was originally used successfully in BOF-Fume hood applications but has also had success at Tennessee Valley Authority (TVA) in the AFBC pilot plant in the USA. New S&F alloys have been developed since 1989 specifically for severe erosion/corrosion applications in a range of boiler types (PF, CFB, AFBC, PFBC) including waste incineration (municipal and hazardous). A suite of arc wire sprayed boiler coatings have been developed in the 1990s for boilers and some are still in use today. These have been added to recently with even more wear resistant alloy systems.

4.1 Severe erosion case:

In MVA, nickel based coatings are used extensively for corrosion protection. If there is also strong erosive or abrasive wear, then the necessary hard phases that are required in the coating are not possible to bring into a solid wire for Welding overlay cladding. However, the spray and fuse method is ideal and the nickel based matrix can take up to 65% of the hardest phase used for protection (Wolfram Karbid). Sucha solution has recently been installed in a French MVA (BTC ????) and all the coating work (XX M) was performed in a specialist Boiler Coating workshop. Numerous specialist Boiler coating workshops exist in Europe, and recently over 46km of tubes and elbow were coated with arc wire spraying for erosion in superheater tubes (Figure 12).

Fig. 12 Arc sprayed boiler tubes (left) and Castolin Eutectic arc spray booth (right)

4.2 Severe corrosion case:

A major French waste company tested the patented 53606 spray & fuse alloy in their laboratory accelerated corrosion reactor which simulates the typical corrosion mechanism observed on their superheater tubes used in their waste to energy boiler plants. Many different alloys and coating systems were tested including Inconel 625 weld overlay. It has been proven that Castolin Eutectic's 53606 alloy outperformed all the other alloys and deposition systems, even the traditional weld overlay 625.

4.3 Mixed erosion-corrosion case: waste-to-energy boiler

In many biomass and waste boiler, there is a mixed erosion/corrosion attack of the boiler tubes, which is the most severe form of attack, as the usual protective oxide by-products of the corrosion are removed by erosion. An Italian Waste-to-Energy company encountered a severe corrosion problem when they have started to add about 10% of waste to the coal usually burned in their boiler. A field test has been done with two different arc sprayed Ni-based arc wire sprayed coatings on waterwalls in-situ. One was produced with our patented wire BTW 66 (erosion-corrosion) and the other with our BTW 65 (corrosion and softer) wire. Both in-situ arc sprayed coatings subsequently went through the proprietary "densification" process. The coating made with the BTW 66 wire had out-performed the BTW 65 and the customer consequently ordered this coating for the protection of a much larger surface (Figure 11).

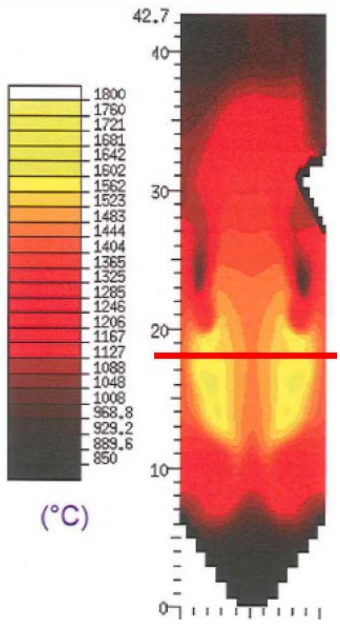


Fig. 11 Field test with BTW 66 (left) and position of the field test in the combustion chamber (right)

6. CONCLUSIONS

- The thinning of boiler heat transfer tube cross-sections is an expensive and complex process that reduces the availability, unplanned outages and efficiency of modern MVA power plants, the severity varies for waste type, operations and MVA design.

- The main causes of boiler tube thinning are erosion from particulates derived from the combustion process or fuel impurities. Corrosion is the other cause, derived from low grade fuel, unsorted fuel, high chlorine or sulphur levels and sub stoichiometric operations.

- The rate of cross section thinning will increase in the future with greater demands for higher temperature combustion, lower cost fuels (high impurities), mixed fuels, longer operation cycles, etc. In addition, solutions to this erosion/corrosion need to be more effective under these severe environments, with improved reliability and lower costs.

- To combat this problem requires a range of protective alloys and specific coating deposition techniques that can be tailored to the corrosion/erosion performance, cost, application demands of the plant. Today, reliable solutions have been developed over decades and include weld overlay with nickel alloys.

- For the future, new alloys, processes and coatings have had to be developed under the pressure of making these technologies cost effective and practical for workshop and onsite. These new technologies include: arc wire spray, HVOF, laser cladding with the use of densification technology together with patented nickel-based alloys, high chrome alloys and the integration of ceramic particles.

- There are now several years of positive experience in a range of boilers including circulating fluidised bed, traditional coal fired boilers, waste incineration and biomass, where these new protection coatings have extended the lifetime of critical boiler tubes around the world.

- This coating range has been applied to new single tubes and panels, and also on worn components in situ.

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