State of the Art of Thermal Spray Technology in the International Waste To Energy Industry

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ABSTRACT
International Waste to Energy and Incineration markets are likely to continue to grow in capacity over the next 5 to 6 years. With this comes a greater need to burn more corrosive materials combust at higher temperatures and extract more energy. The reliability burden that this places on operators of plants will re-open opportunities for thermal spray solutions. Where maintenance costs, opportunity costs and access restrictions may preclude alternative in-situ technologies, thermal spray technology may fill a gap in providing new reliable and flexible process and materials technologies for at least the mid-term protection of water wall and superheater tubes. The state of the art of the technology is such that coating performance in WTE corrosive environments now approach the performance of corrosion resistant wrought materials. This is verified through accurate laboratory modeling and scale tests and trials conducted by OEM’s and plants.

BACKGROUND
The need for incineration capacity for waste materials, whether from municipal solid waste or from industrial waste requirements is increasing internationally as a result of zero landfill and aggressive recycling policies. For many European and Japanese markets waste incineration is the only viable alternative to previous methods of waste disposal. The European Union Landfill Directive (1999/31/EC) specifically precludes certain materials such as hospital waste, tires, and certain reactive and flammable materials from land filling, [1]

Increased demand for combined heat and power (CHP) plants and the use of renewable resources for fuel is set to double. The electricity market share will increase from 9% to 18% by 2010 demanding an increase from 6% to 12% in the use of renewable fuel sources. As a consequence, new plants have to be built and existing plants need to be modified and made more efficient [2].

The presence of highly corrosive elements in these waste fuels such as Cl, S, Na, Zn, Pb, Al when taken in combination with free H2O and oxidizing conditions can lead to rapid corrosion of boiler tube waterwalls and superheater tubes. In order to minimize the extent of this wastage, and in doing so increase plant reliability, plant operators will conservatively maintain maximum steam conditions at 400°C (752°F) and 40bar(580psi.). Increased demands for energy efficiency and emission regulations [3] requiring a 2 second maintained temperature of 850°C, or 1100°C in the case of halogenated organic substances, further exacerbate tube wastage conditions.

One of the primary methods of increasing reliability and the operational window of waste to energy (WTE) plants is application of corrosion resistant surface engineering technologies. Principle techniques employed are refractory lining, replacement of tubes with Ni alloys, weld overlay and thermal spray coatings.

WELD OVERLAY
The use of refractory lining reduces the effectiveness of heat transfer surfaces and as such, has limited scope. Weld overlay technologies have been applied extensively with Alloy 625
being the most commonly specified material. Exhaustive testing of this material under high temperature gaseous and ash covered corrosion conditions has yielded positive results for the wrought alloy [4].

Field applications, although largely successful, have not always been as reliable because of high iron dilution with slow weld pool cooling. This results in the formation of dendritic structures that extend this iron rich region. This, in combination with carbon absorption from the carbon steel tube material, forms corrosion sensitive carbides, which render the material sensitive to localized corrosion (Figure 1) under the influence of salt melts [5],[6],[7]. Further limitations for the weld overlay process are the relatively slow and expensive deposition rate as well as the difficulty of automation on ceilings and in corners. It is also not well suited for in-situ application on single superheater tubes.

Thermal spray coatings are increasingly employed in WTE units as they overcome some of these problems. The technology is well suited to in-situ out of position application, with faster coverage rates reducing both material and opportunity costs. [2] As thermal spray is a metallurgically cold process, no dilution of the base metal occurs and little to no distortion takes place.

THERMAL SPRAY COATINGS IN WTE UNITS

Historical Experience

Thermal spray as a technology in highly corrosive applications, such as WTE, has had a checkered history. The reasons for this are as a result of a.) material and process, and b.) application technique. Problems arising from the latter are common to both overlay and thermal spray, e.g. inadequate surface preparation. Analysis of early failures has shown the primary cause to be substrate corrosion and subsequent spalling.

Figure 2, below, is illustrative in gaining an understanding of the mechanisms driving corrosive attack in this application [8].

It can be seen that the primary corrosion mechanisms are the Chlorination/Oxidation or Sulfdation of Fe with Cl or S provided by salts in the ash. Although this tube may be operating at 400°C, it is possible, given the thermal gradient through the deposit, for the surface temperatures to be significantly higher. This enables the formation of any number of salt smelt eutectics, having low melting points, in the deposit. Some of these are listed below in Table 1.
### Table 1 – Salt Eutectics melting temperature

<table>
<thead>
<tr>
<th>Eutectic [Weight %]</th>
<th>Melting Point [°C]</th>
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<tbody>
<tr>
<td>ZnCl₂</td>
<td>318</td>
</tr>
<tr>
<td>PbCl₂</td>
<td>498</td>
</tr>
<tr>
<td>48 ZnCl₂ – 52 KCl</td>
<td>250</td>
</tr>
<tr>
<td>82 ZnCl₂ – 18 KCl</td>
<td>262</td>
</tr>
<tr>
<td>84 ZnCl₂ – 16 KCl</td>
<td>262</td>
</tr>
<tr>
<td>73 ZnCl₂ – 27 PbCl₂</td>
<td>300</td>
</tr>
<tr>
<td>31 NaCl – 69 PbCl₂</td>
<td>410</td>
</tr>
<tr>
<td>21 KCl – 79 PbCl₂</td>
<td>411</td>
</tr>
<tr>
<td>17 NaCl – 83 PbCl₂</td>
<td>415</td>
</tr>
<tr>
<td>39 ZnCl₂ – 50 KCl – 11 PbCl₂</td>
<td>275</td>
</tr>
<tr>
<td>35 ZnCl₂ – 48 NaCl – 17 PbCl₂</td>
<td>350</td>
</tr>
<tr>
<td>16 NaCl – 40 KCl – 44 PbCl₂</td>
<td>400</td>
</tr>
<tr>
<td>K₂SO₄ – Na₂SO₄ – ZnSO₄</td>
<td>384</td>
</tr>
<tr>
<td>KCl – ZnCl₂ – K₂SO₄ – ZnSO₄</td>
<td>292</td>
</tr>
<tr>
<td>K₂SO₄ – Na₂SO₄ – CaSO₄</td>
<td>776</td>
</tr>
</tbody>
</table>

In high sulfur environments Sulfur permeation with Iron Sulfidation can be seen to occur, however it is generally found that both mechanisms are mutually exclusive.

No coating failure has been determined from wastage of the coating material itself, inevitably porous coating materials have been susceptible to permeation and substrate attack.

### Coating Development

Initial coating applications in the US were largely unsuccessful as early arc-spray coatings failed rapidly through substrate attack and coating spalls. Having determined that the primary mode of failure experienced in prior WTE coating applications resulted from permeation, attention was directed to the development of process and materials used in a thermal spray system. Alloy 625 is known to present sufficient corrosion resistance to the process and as such has been selected as the bench mark material for optimization.

Two systems are most widely used for in-situ thermal spray applications:

1.) The **HVOF** process whereby metal powder feedstock is fed into a High Velocity Oxy-Fuel gun. Internal combustion of the gases generates high temperature combustion products. Powder is continuously injected into this area from the rear of the gun and is heated to a plastic condition. The combustion product gas stream exits the nozzle and propels the powder particles out of the gun. On impact with the substrate, the particles form flat "splat"s and freeze instantaneously. Subsequent particles are deposited similarly and the coating thickness is built up until it meets a specified thickness.

The **Wire Arc-Spray** process, whereby metal wire, typically 0.063mils in diameter, wound on two spools, is fed from two spools by a wire drive system into a gun. A DC Voltage potential is created across these two wires and as they intersect, an arc is struck between them, which melts the wire tips. A stream of air directed across this intersection point strips molten metal droplets from the wire tips, these fly towards the substrate, impact, form a splat and freeze. The Arc Spray processes are further differentiated into High Velocity arc processes and standard or Low Velocity arc process. See Figures 3 and 4 below for micrographs of Alloy 625 coatings sprayed with different systems.

![Micrograph of Low Velocity Arc Process](image1)

![Micrograph of High Velocity Arc Process](image2)

Coating System Corrosion Resistance

As has been shown, within a given system having a single material feedstock, there may be great variability in the structure of a coating. In order to determine the effectiveness of a given coating against a permeable corrosive species,
electro-chemical testing was undertaken as a way of quantifying the corrosion rate of one material relative to another. To calibrate the test equipment for these experiments the potentiostat was tested using the standard reference test method designated in the ASTM G5 standard.

Tafel analysis was used for determining corrosion rate measurements from the potentiodynamic test set. This technique was used to obtain a corrosion rate value for the various coatings in an aqueous solution of 0.1N HCl. The cell current was measured during a slow sweep of the potential from -200mV to +200mV relative to EOC (open circuit potential). The scan rate used was 1mV/sec with a sample period of 2 seconds. A fit of the data to a standard model obtained an estimate of ICORR (corrosion current density) which was used to calculate a corrosion rate. All of the calculations used a density of 7.87 g/cm³ and an equivalent weight of 27.92. The test cell measures the activity of the substrate material through the coating. As all materials evaluated in this test sequence were Alloy 625 type materials, a representative sample of Alloy 625 plate was also evaluated to determine the degree of activity of the material itself. It is important to note that the corrosion rate values are sensitive, and comparable with each other, but do not represent the actual corrosion rates expected in a boiler, due to differing electrolyte concentration and temperature.

Corrosion Rate Range

A grit blasted 1018 CS plate was used as the most active material, and the Alloy 625 plate as the least. The data are given in Table 2 below.

Table 2 – Corrosion rates for unprotected plate and Alloy 625

<table>
<thead>
<tr>
<th>Material</th>
<th>Corrosion Rate (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grit Blasted Substrate</td>
<td>1237</td>
</tr>
<tr>
<td>Alloy 625 plate</td>
<td>0.37</td>
</tr>
</tbody>
</table>

The LV arc and HV arc coatings were evaluated for varying thicknesses. Wire spray systems generally form coatings with thin interlaminar bands of oxide material. This interlaminar oxide forms as a result of inflight oxidation of the particle. As the particles need to be fully molten in order to separate from the wire and are heated in the arc on separation, they have a high oxidation potential. Measurement of the oxide film composition by EDS shows them to be predominantly Chrome Oxide. These oxide bands are occasionally spongy and fractured and as such represent a potential conduit for corrosive media. This also leaves Chrome depleted Nickel rich, areas adjacent to the oxide films, which are susceptible to sulfidation. Figure 6 shows the corrosion rate dependence on coating thickness for the high and low velocity end of the range. The scatter apparent for the low velocity readings is likely due to the large splat size and statistical likelihood of interconnected porosity through to substrate, as well as thicker oxide structures which are more conducive to ion transport. It should be noted that this curve represents the coating qualities that were commonly applied 10 to 15 years ago. It is apparent, from the high corrosion rates that little to no protection is offered. The high velocity system is better behaved as the finer splat size and greater number of particles between the
coating surface and substrate reduce the degree of interconnected porosity. This trend can be seen more clearly in Figure 7, where the corrosion rate for a fixed thickness of coating is charted against splat size.

**Figure 6 - Corrosion rate vs coating thickness for high and low velocity systems**

The mechanism driving splat refinement can be seen in Figure 8, where the total air power (not velocity) available to strip molten material from the wire tip is seen to reduce the corrosion rate. Nozzle velocity is constant for a choked nozzle condition.

**Figure 7 - Corrosion rate vs splat size for a given coating thickness**

The mechanism driving splat refinement can be seen in Figure 8, where the total air power (not velocity) available to strip molten material from the wire tip is seen to reduce the corrosion rate. Nozzle velocity is constant for a choked nozzle condition.

**Wire system summation**

Improvements in air flow control through wire spray units have given rise to an approximately four fold decrease in permeability. Of greater significance is the fact that the behavior of the coating in a corrosive environment is more predictable, and less susceptible to the anomalies present in traditional arc systems. This improvement is corroborated by the good performance of this material in less corrosive areas of WTE units.

**Material Development**

Optimization of HVOF systems is conducted routinely by adjusting and calibrating new gas flow parameters to ensure optimum deposit efficiency. This is broadly indicative of good coating quality. However, the biggest advances in corrosion performance with these materials has come about as a result of the flexibility that exists with powders for tweaking the composition of standard alloys to define better microstructure, bond strength, and in some cases, erosion properties as well. This development can happen at a faster pace due to the shorter lead times and batch sizes required in the supply of new powder materials.

Figure 9 represents the corrosion data from two Alloy 625 coatings. These have been modified by a few percentage points in terms of nominal composition, but as can be seen for the UTEx 2-025 material, the difference in performance is remarkable. At a thickness of 12 to 15 mils UTEx 2-025 yields a corrosion rate of 1.5 mpy, which is almost negligible when compared to the corrosion rate in excess of 600 mpy for originally applied arc spray materials. UTEx 2-100CB is a material that has already seen substantial service in tire burning and electronics copper recycling incinerators. UTEx 2-025 is a newer material, also in the Alloy 625 family.
To simulate high temperature corrosive conditions, several sections of coating were inserted into an autoclave with NaCl, KCl and ash mixed into a wet paste and applied to the coupon. After a period at elevated temperature (550°C), the coupons were allowed to cool before being sectioned for microscopic evaluation. Figure 11 is a section of the coating after the test, point 5 is a small surface pore with traces of Fe, Ca, and Cl visible in the EDS analysis given in Figure 12 below.

![Figure 9 - Corrosion resistance of HVOF Alloy 625 type materials.](image)

![Figure 10 - Traditional HVOF Alloy 625 coating (note faint appearance of oxide structures).](image)

![Figure 11 - HVOF UTEx 2-025 coating (after High Temperature Corrosion Tests).](image)

**Table 3 - Data from simulated WTE high temp corrosion tests**

<table>
<thead>
<tr>
<th>Material</th>
<th>Corrosion Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>UTEX 2-025</td>
<td>16 um</td>
</tr>
<tr>
<td>UTEX 2-1027</td>
<td>60 um</td>
</tr>
<tr>
<td>Alloy 625</td>
<td>27 um</td>
</tr>
<tr>
<td>2.25Cr1Mo</td>
<td>586 um</td>
</tr>
</tbody>
</table>

**Sealants**

Several tests were performed with surface sealants baked at 550°C. To ensure that no skin effect was taking place, the sealer was removed from the top surface of the coating prior to the electrochemical test procedure. This was done to evaluate the true sealing ability of the coating. The best HVOF materials showed no discernable difference in corrosion rate between sealed and unsealed coupons. The bonding tenacity of some of the non-organic sealers to the as-sprayed surface...
suggests that even if the coatings are so dense that sealing is not required, the treatment might still provide some benefit as insurance against a random defect or surface irregularity.

CONCLUSIONS

As increasing demand for waste incineration capacity and higher emission control legislation comes into play on European and Japanese markets, there is an escalating need for a medium term, low opportunity cost solution to improve plant reliability.

• Thermal spray solutions have progressed considerably from earlier days when the technology was insufficiently developed to provide a reliable solution. Developments in modern materials and process understanding have led to the development of alloys tailored for thermal spray application that can now produce corrosion resistances matching those of the wrought alloy.

• These results have been verified through extensive in-house testing, independent OEM test bed qualification, and good results from recent inspections of installed systems in several European and Japanese WTE units.

REFERENCES