Experience with Weld Overlay and Solid Alloy Tubing Materials in Waste to Energy Plants

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1.0 Introduction

Corrosive conditions in waste to energy boilers produce rapid wastage rates of traditional boiler tube materials. It is not unusual to see corrosion rates in the range of 1 to 3 mm/y (40-120 mpy) on carbon steel boiler tubes and occasionally corrosion occurs at even higher rates. In the mid1980’s there were several boilers that experienced corrosion failures of carbon steel waterwall tubes in less than 6 months of service (1,2). Because of this experience, it has become accepted that some type of corrosion protection is required for boiler tubes in refuse-to-energy boilers. Over the years, many different alloys have been evaluated to improve tube life in waste-to-energy boilers. The most successful materials used for corrosion protection are nickel alloys.

Waterwall tubes are generally attacked by molten chloride salts (3) and superheat tubes appear to be attacked by a combination of molten chloride/sulfate salts as well as gaseous chloride constituents (primarily HCl) (4-7). Figure 1 shows the corrosion rates of carbon steel as a function of temperature for various corrosion mechanisms. The corrosion due to gaseous chloride atmospheres increases steadily with temperature. Corrosion produced by chloride rich deposits or salts increases rapidly once the melting point of the salts is reached; corrosion rates continue to increase with temperature until the chloride salt becomes hot enough to vaporize, after which corrosion decreases. Likewise for sulfate rich deposits or salts: the onset of melting sharply increases corrosion rates and vaporization of the sulfates at even higher temperatures results in a decrease of corrosion. These various corrosion mechanisms give rise to somewhat different alloy requirements, depending on the temperature of the metal in the refuse-fired boiler.

The main corrosion mechanism which occurs on water wall tubes, which typically operate in the 200-315°C (400-600°F) range, is corrosion by molten chloride salts. The most successful alloys used for waterwall tubes are generally high in nickel and molybdenum with moderate amounts of chromium, such as Alloy 625 and Alloy 50 (a recently introduced alloy from ThyssenKrupp VDM). These alloys are applied to waterwall tubes as a weld overlay.

Because of the mixed corrosion modes in the superheater region, the selection of alloys is more complicated. Figure 2 shows a photomicrograph of a Fe-Ni-Co-Cr alloy that was exposed in a refuse boiler at approximately 900°C (1650°F) (8). Figure 2 shows that multiple corrosion mechanisms are active at this temperature; both sulfidation (evidenced by the chromium rich sulfides) and chloride attack (evidenced by the internal voids caused by volatile metal chlorides) are observed. In this case, a material not only requires a high nickel content to resist chloride attack (both gaseous and molten salts), but also requires...
a high chromium content to resist sulfidation. Solid Alloy 825 and weld overlay Alloy 625 are perhaps the most common materials now used in superheater tubes in waste-to-energy boilers. Another high chromium material was recently introduced in Europe for this application with good success: Alloy 45TM.

While Alloy 825 solid tubes and Alloy 625 weld overlay have a proven track record in many boilers, there are also many boilers where corrosion continues to be a problem. Alloy 825 also has been unsatisfactory in many superheater applications. Alloy 625 weld overlay also does not always give the desired superheater tube life. It is fair to say that most of the chronic corrosion problems are in superheater applications.

The corrosion problems in waste-to-energy boilers vary with unit design, geographical region, time of year, and other factors. One clear trend that has been observed is that the increased use of plastics has led to an increase in the chloride content of the household waste. This increase in chloride content of the fuel corresponds to an increase in the corrosivity of the boiler environment.

Because of the variability among waste-to-energy boilers, site specific testing is always recommended. ThyssenKrupp VDM continues to work with operators and applicators to test new overlay materials in the field.

2.0 Material Options

There are many materials that have been evaluated in refuse-to-energy boilers. The most successful of these materials include Alloys 625, 50, 59, 825, and 45TM. The chemistry of these alloys is given in Table 1.

Alloys 625, 50, and 59 are applied as a weld overlay onto carbon steel boiler tubes and Alloy 825 and 45TM are used as solid tubing only for superheater applications.

Alternate methods of applying corrosion resistant alloys have been tried. Spray coatings have not historically worked well in waste-to-energy boilers (9, 10). Flame spray coatings all have some degree of porosity. This allows corrosive gases to permeate beneath the protective coating and corrode the carbon steel substrate. The extremely corrosive nature of the waste-to-energy boiler is severe enough to cause disbonding of spray coatings from the carbon steel base metal. Diffusion coatings and other coating systems have also been tried in refuse-to-energy boilers with mixed success. Generally all of these coating systems have some degree of porosity or have inherent defects in the coating system, which leads to unacceptable localized corrosion. Therefore, weld overlays and solid tubing are the most reliable options for deploying corrosion resistant alloys.

For waterwall tubing, weld overlays are exclusively used. Since these tubes are water wetted on the inside surface, the use of solid austenitic materials is generally not allowed by the ASME boiler code. Therefore, application of nickel alloys to waterwall tubes will be as a clad or coating; weld overlays have proven to be the most reliable process for economically applying this corrosion barrier.

For superheater applications, both solid and weld overlay tubing are both used. The decision on whether to use a solid or weld overlay tube for a superheater application will depend on economics and delivery schedules. The relative costs of various superheater tube options are given in Table 2. Solid Alloy 825 tubes are the least expensive option and are used in the first few rows in the superheater tube banks, where gas temperatures are highest. Alloy 625 weld overlay tubes are the closest option, relative to cost, to solid Alloy 825 tubes. Alloy 625 overlay tubes have given good tube life in numerous applications and also have the advantage in that they usually can be provided more quickly than solid tubing.

A solid tube material that has been used in Europe is Alloy 45TM. The relative costs of solid Alloy 45TM tubing is also shown in Table 2. While the relative cost is somewhat higher than other options, the increased corrosion performance of Alloy 45TM has justified its use in several applications.
When comparing the prices of solid tubes to weld overlay tubes, it is noted that the price differential increases with tube size. This trend is a result of the increasing differential between the amounts of nickel alloy used in weld overlay versus solid tubing as the tube diameter increases. Another factor when considering solid versus weld overlay tubes is the life of the tube. The corrosion rates of weld overlay tubes will increase rapidly after the cladding has been corroded away. Cladding thickness of weld overlay tubes are generally in the range of 1.5-2mm (0.060-0.080”). Corrosion rates on solid tubes will not change as the result of tube wall thinning. Therefore, solid tubes may last longer than weld overlay tubes at the same corrosion rate. Solid tubes have a greater thickness of corrosion resistant material. The relative life of solid tubes versus weld overlay tubes increases as the minimum wall requirement of the superheater tube decreases (i.e. solid tubes are more economical as more wall loss can be tolerated).

3.0 Corrosion Testing

3.1 Waterwall tubes

Alloy 50 is a Nb-free welding product that is being considered as a replacement for Alloy 625 in numerous applications. Figure 3 shows the mass loss of single pass GMAW weld overlay specimens when exposed to a simulated refuse boiler combustion atmosphere. The mass loss of the specimens corresponds to the amount of corrosion. While this laboratory test does not exactly duplicate the temperatures and environment that the waterwall tubes might see, it does give a direct comparison of Alloys 50 and 625 in a corrosive high chloride environment. These laboratory data show that Alloy 50 has excellent corrosion resistance as a weld overlay material and is capable of providing corrosion resistance better than Alloy 625 weld overlays in environments applicable to refuse-to-energy plants.

Figure 4 shows an example of corrosion attack of an Alloy 625 weld overlay removed from a coal fired boiler after an extended exposure time (11). The corrosion attack occurs more rapidly on the dendrite cores of the weld, which are depleted in Mo and Nb due to segregation. Alloy 50 is a Nb free material and so does not exhibit segregation of Nb; however, some segregation of Mo is unavoidable. Alloy 50 does have a fairly fine uniform microstructure with less segregation than observed for Alloy 625 in the welded condition. These features help avoid preferential attack of the Alloy 50 weld overlay, which in turn reduces the overall corrosion rate.

3.1 Superheater tubes

Corrosion of superheater tube materials was measured in the laboratory using a high temperature simulated refuse-boiler combustion gas consisting of 2.5 g/m³ HCl + 1.3 g/m³ SO₂ + 9% O₂ + balance N₂. Results of tests in this environment are shown in Figure 5. In this laboratory test, the Alloy 45TM corrodes at lower rates than Alloy 625 and the other alloys at all temperatures tested. Alloy 625 was the second best material and was much better than Alloys 800H and AC66. Alloy 45TM can be used only as solid tubing and Alloy 625 can only be used as a weld overlay (due to current ASME code regulations).

4.0 Field Testing

4.1 Waterwall tubes

Several field tests of Alloy 50 are still ongoing in Europe. These tests have been in progress for nearly 2 years. Most of the information so far is based on visual inspection; so far the Alloy 50 is performing very well. One customer removed the weld overlay samples and showed that Alloy 50 indeed performed better than Alloy 625. Based on these tests, approximately 50,000 pounds of Alloy 50 will be installed onto waterwall tubes in the spring of 2004 in this European waste-to-energy boiler. Testing of Alloy 50 weld overlays is also on-going in North America, after 1½ years in a refuse-fired boiler, a weld overlay of Alloy 50 visually shows little sign of attack.

Figure 6 compares several alloys in the so-called Varistrant test. This test measures the tendency of a material to exhibit hot
cracking and form micro-fissures during welding. Figure 6 shows that Alloy 50 will be less likely to form fissures and cracks during welding than Alloy 625.

4.2 Superheater tubes

Testing in the late 1970’s at the refuse-to-energy plant in Saugus, MA lead to use of Alloy 825 solid tubes (5), this material was subsequently adopted by several boiler designers as a standard material and is still used today in some boilers. Another common superheater material being used is Alloy 625 weld overlay onto standard carbon steel boiler tube materials. However, as steam temperatures increase and the corrosiveness of the environment increases (such as by the increasing amount of plastic in the municipal waste being burned), these standard tube materials are not always adequate.

One alloy recently introduced by ThyssenKrupp VDM is Alloy 45TM. This alloy was specifically designed to have a high corrosion resistance in highly contaminated high temperature environments, such as are found in refuse-fired boilers. Figure 7 shows test data that compares the corrosion behavior of Alloy 45TM with traditional carbon steel superheater tubes (13). This figure shows tube wall thickness measurements of the superheater tubes from an operating refuse-fired boiler in Bielefeld, Germany; the tube wall thickness was measured periodically using ultrasonic thickness (UT) sensors. The corrosion rates of each material are calculated from the average wall loss versus time. Figure 7 shows that the Alloy 45TM was able to improve the service life by a factor of over 6 times, when compared to standard boiler tube materials.

Since the mid 1990’s, there have been several installations of Alloy 45TM into refuse-fired boilers. The performance of the Alloy 45TM as a superheater material has been quite good. As with any new material, field trials are suggested to demonstrate the performance under actual operating conditions. This is especially true for refuse-fired boilers, where the conditions are known to vary widely between units.

Discussion

The use of Alloy 625 in the refuse-to-energy market has a long and mostly successful history. Waterwall tubes that have been covered with Alloy 625 weld overlay have generally shown few problems; most of the observed problems were attributed to application issues (such as pin-holes in the weld). Recently, ThyssenKrupp VDM introduced Alloy 50 as an alternative to Alloy 625 for weld overlay applications in refuse-to-energy plants. Alloy 50 exhibits better corrosion resistance in the laboratory and has also show excellent results in field tests. Alloy 50 is also less likely to form micro-cracks and fissures than Alloy 625, making it a more forgiving alloy for weld applications. Lastly, the Alloy 50 has a more uniform microstructure and exhibits less segregation than Alloy 625; this helps improve corrosion resistance by reducing the degree of selective corrosion attack.

Alloy 45TM has been successfully used in several superheater applications in refuse-to-energy boilers. Alloy 45TM is only available as solid tubing. While Alloy 45TM can be readily joint welded with selected filler metals (typically FM28 or Alloy 625), it cannot be directly used as a weld overlay, due to the higher Si content in this material. Alloy 45TM can give excellent corrosion resistance and has improved the tube life in several boilers with chronic superheater tube wastage issues.

Conclusions

Based on the information from laboratory and field tests, the following conclusions on materials for refuse-fired boilers can be made:

1) Alloy 625, applied as a weld overlay, has demonstrated that it is quite resistant to corrosion under most boiler operating conditions.
2) Alloy 50, a new Ni-Cr-Mo-Fe Alloy, exhibits lower corrosion rates in laboratory tests and also has given excellent corrosion resistance in field tests.
3) Alloy 50 exhibits less tendency to form micro-cracks and fissures than
Alloy 625 during weld trials in the Varistrant test.

4) Alloy 50 has a more uniform microstructure and shows less segregation in the welded condition than Alloy 625.

5) Solid alloy superheater tubing can be a viable alternative to weld overlay tubing; smaller tube sizes and a thinner allowable minimum tube wall thickness make solid tubing more attractive.

6) Solid Alloy 45TM shows excellent corrosion resistance in most refuse-to-energy superheater applications.

References


2. Private communication with personnel involved with tube failures at the Lawrence, MA waste-to-Energy facility.


10. Private communication with personnel involved with testing at the refuse-fired boiler operating in Columbus, OH.


Table 1. Chemistries of common alloys used in waste-to-energy boilers

<table>
<thead>
<tr>
<th>ThyssenKrupp VDM Designation</th>
<th>Alloy</th>
<th>UNS No.</th>
<th>Ni %</th>
<th>Cr %</th>
<th>Mo %</th>
<th>Fe %</th>
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<tr>
<td>Nicrofer® S6020</td>
<td>FM625</td>
<td>N06625</td>
<td>63</td>
<td>22</td>
<td>9</td>
<td>&lt;1</td>
<td>3.4Nb</td>
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<tr>
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<td>FM59</td>
<td>N06059</td>
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<td>23</td>
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<td>1</td>
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<td>11</td>
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<tr>
<td>Nicrofer® 45TM</td>
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<td>N06045</td>
<td>46</td>
<td>27</td>
<td>-</td>
<td>23</td>
<td>2.75Si 0.1RE</td>
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Table 2. Relative pricing of Alloy 625 weld overlay compared to solid tubing.

<table>
<thead>
<tr>
<th>Tube Size</th>
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<th>825 Solid Tube Relative Price*</th>
<th>45TM Solid Tube Relative Price*</th>
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<tr>
<td>1.5” x 0.150” MW</td>
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<td>0.75</td>
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<td>2.0” x 0.150” MW</td>
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<td>3.0” x 0.150” MW</td>
<td>1</td>
<td>0.80</td>
<td>1.64</td>
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* Relative Price Compared to Alloy 625 Overlay (i.e. Alloy 625 Overlay = 1)

Figure 1. Schematic of the influence of temperature upon various corrosion mechanisms.
Figure 2. Photomicrograph of a Fe-Ni-Co-Cr alloy from a refuse-fired boiler. Operating temperature was about 900°C (1650°F). Note the presence of chromium sulfides and internal voids that indicate that both sulfidation and chloride attack are occurring simultaneously.

Figure 3. Comparison of the corrosion resistance of Alloy 50 compared to Alloy 625 in a simulated refuse boiler combustion environment at various temperatures after 1050 hours of exposure. Atmosphere is 2.5 g/m³ HCl + 1.3 g/m³ SO₂ + 9% O₂ + balance N₂.
Figure 4. Examples of corrosion attack associated with segregation of Nb and Mo in Alloy 50.

Figure 5. Mass change after 1050 hours for selected alloys in a high temperature simulated refuse-boiler combustion gas consisting of 2.5 g/m³ HCl + 1.3 g/m³ SO₂ + 9% O₂ + balance N₂.
Figure 6. Varistrant testing of various weld overlay materials. Alloy 50 is much less prone to fissuring and hot cracking than Alloy 625. Alloy 59 is the most resistant material to cracking in this Varistrant test.

Figure 7. Corrosion rates of Alloy 45TM in a superheater application in a European waste to energy facility. The 45TM showed much lower overall corrosion rates than the traditional boiler tube material 15Mo3.