

*Materials Solutions in
Waste-To-Energy (WTE) Systems*

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Technical Paper
No. 3 (rev. 1)

December 2008

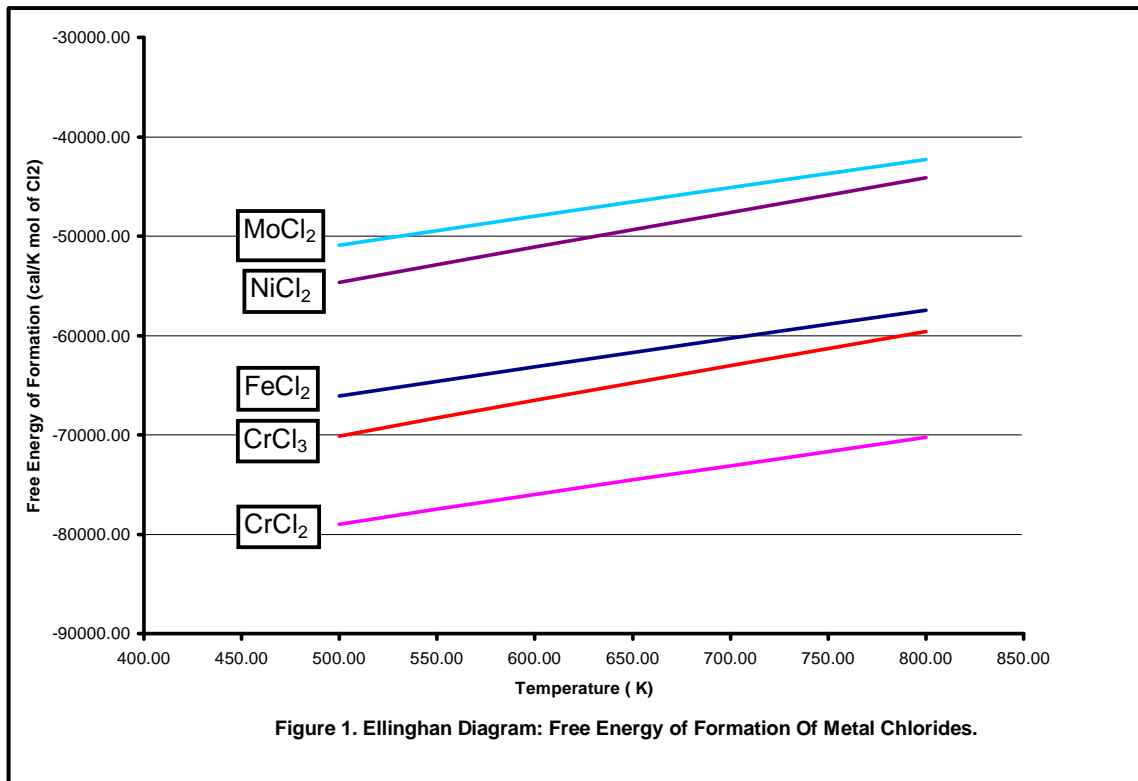
The wide spread implementation of Waste-To-Energy (WTE) systems has been limited in principle by the lower efficiency of current system designs ¹. Higher efficiencies can be achieved by operating at higher temperatures which in turn translates into lower emissions and in a more effective combustion of Municipal Solid Wastes (MSW). However, the major limitation to higher operating temperatures is the corrosion rates experienced by the heat transfer surfaces in the furnace cavity and in recovery convective paths ¹.

High-temperature chloridation and hot-corrosion are the primary modes of component degradation in WTE systems ¹⁻⁴. Chlorine containing compounds in chlorinated plastics and in paper, cardboard, and wood products generates relatively high HCl(g) contents in the flue gas. The poor combustion characteristics of the MSW fuel result in incomplete combustion, that leads to the condensation on heat transfer surfaces of aggressive deposits rich in alkali metals (Na, K), and in heavy metals such as lead tin, and zinc. The alkali and heavy metals are condensed primarily in the form of sulfates and chlorides that melt at relatively low temperatures causing hot-corrosion attack.

Low alloy steels are the preferred choice for heat transfer components in Waste-to-Energy boilers because of their affordability, excellent heat transfer capabilities, and adequate mechanical properties within the operating temperature range of the steam generating unit. However, these Fe-base alloys are highly susceptible to high-temperature chloridation by flue gases containing HCl(g), that result in the formation of low vapor pressure chlorides of Fe (i.e. FeCl₂ and FeCl₃), with vapor pressures in the order of 1×10^{-4} torr at temperatures as low as 300 °C (578 °F), resulting in the volatilization of the reaction product. The Fe-chloride vapor is then oxidized to Fe-oxide, and free chlorine is pushed back to the metal surface due to thermophoresis, a transport mechanism by which gases are delivered to the metal surface under heat flux conditions, i.e. a hot gas and a cooler heat transfer surface. This oxidation mechanism is known as “active oxidation” ³, a self-supported oxidation process where the Fe-base low alloy steel is rapidly wasted away due to the continuous reaction of chlorine with the metal surface.

Surface modification technologies including thermal spray coatings, weld overlays and diffusion layers represent an option to plant operators to manage the accelerated wastage of low alloy steels due to high-temperature chloridation attack. In particular, thermal spray coatings represent a reliable and cost effective approach to upgrade the metal component surface by adding effective alloying elements like Cr at concentrations not practical in wrought or cast alloys. Of these surface technologies, Twin Wire Arc Spray (TWAS) is the fastest application method that under well-defined quality controls, can generate protective surface layers with reasonable life spans. ArcMelt™ Company, through its patent pending consumable manufacturing process, is capable of producing any possible alloy composition by the use of powder core wire technology. ArcMelt™ core wire consumables can be sprayed significantly faster when using a slightly modified spray gun and wire delivery system. This results in well adhered coated layers with porosity levels below 5% and finely distributed oxides that impart lower build-up stresses. Improved surface coverage translates into shorter application times meeting the most stringent outage schedules.

ArcMelt™ produces a composition marketed as AMC 3201 with 42 % Cr- 8 % Fe- Ni- balance. This chemical composition is similar to the alloy type 45CT. To understand the merits of this composition in waste-to-energy applications we need to understand the fundamental process of alloy protection in high-temperature chloridating environments. Figure 1 shows the relative stability of metal chlorides in the temperature range from 200 to 550 °C (400 to 1000 °F). The Ellingham diagram reveals that the most stable chlorides are those of Cr. However, in high-temperature chloridation what matters is the volatility of the metal chlorides, and in this scenario, the important parameter is the vapor pressure of the chloride phase as a function of temperature. High vapor pressure compounds are usually those with the low melting points. Fe-chlorides are metal chlorides with lowest melting points, i.e. 282 °C (539 °F) and 350 °C (662 °F) for FeCl₂ and FeCl₃, respectively. The stable chlorides of Cr and Ni, CrCl₂ and NiCl₂, have higher melting points, 540 °C (1000 °F) and 728 °C (1342 °F), respectively, with vapor pressures in excess of 1 x 10⁻⁴ torrs at temperatures higher than 450 °C (842 °F), conferring a tremendous advantage as compared with Fe-based alloys.

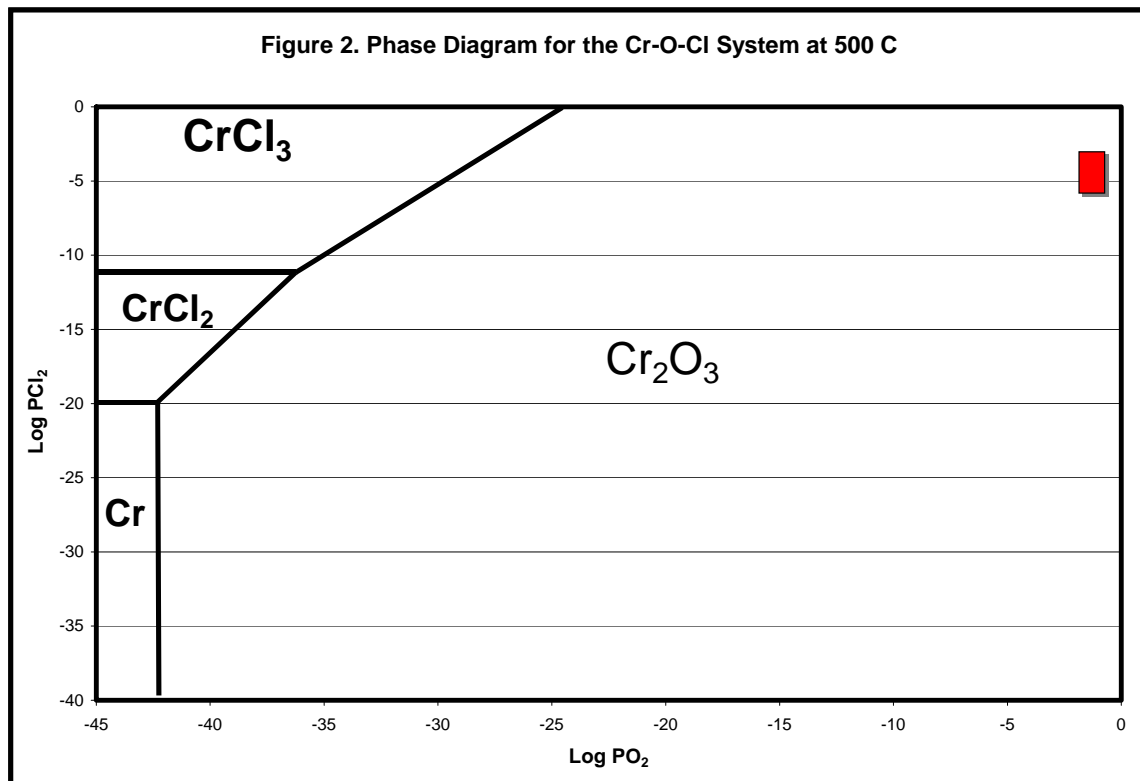


The environments generated during the incineration of waste are not only potentially chloridating but also oxidizing. Table 1 lists the typical flue gas composition in WTE units as reported in the literature^{1,4}.

Gas Constituent	Concentration
CO ₂	7.5 - 10 v%
H ₂ O	13 - 20 v%
O ₂	7 - 10 v%
HCl	1,000 - 1,500 ppm
SO ₂	300 - 500 ppm
N ₂	bal

Table 1. Flue gas compositions in WTE steam generators according to references 1 and 4.

The flue gases generated during the combustion of MWS are also oxidizing with SO₂(g) concentrations varying from 300 to 600 ppm in the presence of excess air, in the order of 7 v%. Thermodynamic calculations using the chlorine and oxygen indicators, log PCl₂ and log PO₂, respectively, for the gas compositions listed in Table 1 indicate that the formation of protective Cr-rich oxides is most likely to happen as illustrated in Figure 2.



The thermodynamic tendency to form this stable Cr-oxide is what provides resistance to this high-temperature resistant AMC 3201 alloy against most of the high-temperature oxidation phenomena, including high-temperature chloridation attack.

Figure 3 illustrates the ability of the coating AMC 3201 to form continuous and uniform surface Chromia scales in oxidizing environments.

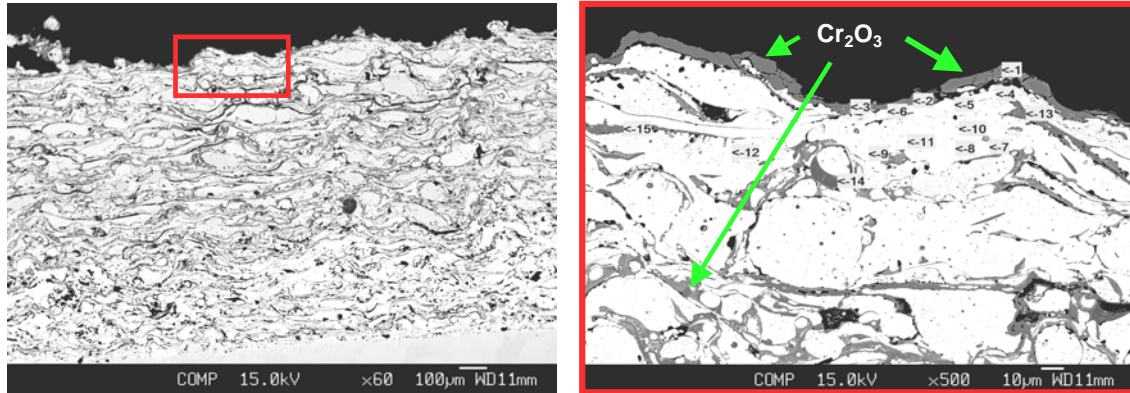


Figure 3. Oxidation resistance of ACM 3201 in still air at 816 °C (1,500 °F).

Upon exposure to the flue gases typical of WTE environments, the relatively low porosity of the coating structure will most likely be sealed by the formation of Cr-rich oxides as indicated by the thermodynamic analyses in Figure 2 and demonstrated in the Scanning Electron micrograph shown in Figure 3.

Additionally, the presence of SO₂ (g) in the flue gas can also react with (Na,K)-chlorides leading to the formation of (Na,K)-sulfates. The formation of alkali sulfates exacerbates the wastage rates because of their tendency to react with residual alkali and heavy metals chlorides to form a low melting eutectic phase. This eutectic phase is highly ionic and it dissolves most of the protective oxides including Chromia, Cr₂O₃. However, the dissolution of chromia in sulfatic melts neutralizes the ionic character of the flux by the formation of alkali chromates arresting the wastage process.

Any material designed for long-term resistance to all possible scenarios of high-temperature oxidation in waste-to-energy applications needs to be such that long-term protection relies on the formation of protective Cr-rich oxides. Alloy formulation AMC 3201 has been designed with this purpose by understanding all plausible environments generated during the incineration of municipal waste.

References

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