Recycling of Zinc-coated Steel Sheets

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Introduction

In the automotive industry, the trend for the car body goes more and more to coated steel sheets, as well as in home appliances and for panelling in civil engineering. In the EU, in 2000, about 50% of sheet production is coated, all together nearly 7 Mio. ton. Therefore, also in the scrap, rising amounts of coated material has to be expected. The amount of zinc on these sheets depends on the coating process; typical figures gives Table 1. So, depending on the percentage of coated sheets in the charge, the amount of zinc in the charge may go up to over 30 kg/t [2, 3].

Tab.1. Typical amount of zinc with coated sheets [1]

<table>
<thead>
<tr>
<th>Process</th>
<th>Coating</th>
<th>Zinc content (sheet 1mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolytic</td>
<td>7.5 µm one side</td>
<td>0.8 %</td>
</tr>
<tr>
<td>Electrolytic</td>
<td>7.5 µm both sides</td>
<td>1.6 %</td>
</tr>
<tr>
<td>Hot galvanizing</td>
<td>10.5 µm both sides</td>
<td>2.3 %</td>
</tr>
</tbody>
</table>

1. The Behaviour of Zinc During the Melting Procedure

To understand what happens with zinc during heating up the charge material, we should refer to the following diagrams:

Fig. 1. Vapour pressure of zinc (and some zinc compounds) depending on the temperature. Boiling point of zinc: 911°C.

Fig. 2. Reduction equilibrium of ZnO in an atmosphere of CO and CO₂, depending of the content CO₂.

Fig. 2 shows, that in pure CO, ZnO is reduced already at about 1000°C; at 1450°C is still reduced in a atmosphere containing 50% CO₂. What happens with zinc during the melting process, depends on the furnace: Whether the heating of the charge material is effected in a gaseous environment (of CO + CO₂), as in cupolas and (partly also) arc furnaces, or, whether likely a bigger part of solid material (with still zinc on it’s surface) can plunge into liquid metal, as with induction furnaces.

2. Cupolas and Arc Furnaces.

In a cupola, at the boiling point of zinc (911°C), the steel sheets are still solid and will not react immediately with zinc. Since the atmosfere is reducing (CO with some amount of CO₂), zinc will volatilize and be sucked away with the exhaust gases. Since the Zn is draw off continuously, the
partial pressure \( P_{Zn} \) will stay far below 1 bar: So, the reduction equilibrium temperature will be still lowered (see Fig.2). Going up in the cupola, the gases become cooler, the zinc vapour will be oxidized to \( \text{ZnO} \) (Fig.2). Part of the \( \text{ZnO} \) can cake to colder parts of the charge of to the walls, but the biggest part goes with the off-gas stream, from where it can be precipitated in the dust control unit, together with the normal dust of the cupola. So, almost no zinc will go to molten metal.

Melting steel in arc furnace: The steel temperature are quite high (1550–1750°C). Since at these temperatures are quite high (Fig.1), all of the zinc and it’s Compounds will evaporate.

The zinc oxide precipitated (together with the normal dust) from the gas, can be transferred to zinc recyclers, if the content surpasses 30%.

With lower zinc contents, the dust may be re-injected, together with coke-breeze, e.g. with a cupola, thrugh the tuyeres. The normal oxides, as \( \text{SiO}_2 \), \( \text{Al}_2\text{O}_3 \) and \( \text{CaO} \), are going to slag, whereas iron oxide and zinc oxide are reduced and go to the melt (iron) and the off-gas (zinc vapour). So, zinc content of the dust can be brought up as to 60% (Fig.3).

With higher amounts of dust, that injection may have a drawback: Due to the energy needet to smelt the dust and to reduce the oxides, the flame temperature goes down. To counterbalance that, the blast can be enriched with oxygen or, with high amounts of dust, also by a combination of natural gas and oxygen (Fig.4) [6, 7].

3. Induction Furnace

During melting in a coreless induction furnace, bundles may, at least party, plunge into liquid iron before zinc could evaporate. Under these circumstance, zinc can alloy into the melt (from where it may evaporate then).

But: there remains a problem: whereas the biggest part of zinc evaporates out of the melt, there may remain up to 0.15–0.2% of zinc in the melt [2, 8]. That isn’t detrimental to the mechanical quality of the iron (strength and structure) [2]; for nodular iron, the amount of Mg for nodulizing should be a little bit increased [8].

But: with zinc contents higher that 0.05%
there can be still some evaporation (e.g. from open ladles). Zinc vapour oxidizes in air, the zinc oxide smoke is very severely irritating. With zinc contents lower that 0.025%, no visible evaporation at all has been observed [9].

The zinc content in the can be lowered either by vacuum treatment or by intermediate overheating.

Vacuum treatment: Tissier et al. Found [9, 10], that already with moderate underpresure of e. g. 500 mbar the zinc content in a 50 kg-furnace could be lowered from initially 0.27% to about 0.01% (Fig.5) in not more that one minute. But, the furnace has to be fit for vacuum application.

Intermediate overheating: If only part of the charge material is contaminated with zinc, procedure with intermediate superheating may work (Fig.6) [2]: at the beginning (into the empty furnace) shold be cherged the zinc-bearing material. After liquefaction the melt should be superheated, to reduce the zinc content of that part of the melt (Fig.6). Then only the (zinc-free) rest should be charged.

In an inverter-fed coreless furnace, the superheating can be done with reduced frequency (to have high stirring, also with reduced power; power reduction for longer time for superheating). That cutting in half of the frequency, very simply can be effected by changing the condensed arrangement (Fig.7).

Lining life: lining will not be shortened with zinc in the melt, on the condition that sintering of the crucible will be executed with material free of zinc [2, 8].

Dust collection: For induction furnaces also, a very effective dust collection system is necessary. The dust may be high in zinc content (due to the modest amount of normal dust from an induction furnace), so it may be sold directly to zinc smelters.
4. Recycling of Zinc

There are in Germany two common ways for recycling zinc from ZnO-dust:
- The Waelz-Process (of Berzelius Umwelttechnik), that effects an enrichment of zinc up to
  about 60% (the “Waelz-oxide”). That product is accepted by zinc smelters;
- The “Imperial Semting Process” [1, 12], that produces metallic zinc.

The Waelz-process (Fig.8) is well established. The main aggregate is a rotary kil, fed
by ZnO-bearing dust, together with coke breeze. ZnO is reduced to metallic zinc, that
vaporizes. The zinc-containing gases are cleaned from solid dust particles; on it’s
further way (during cooling down), zinc vapour oxidises again. Zinc oxidise is won
by a dust control (hot gas electrostatic filter) as “Waelz-oxide” with at least 60% Zn.

The Imperial Smelting Process of MHD (Melting Hüttenwerke Duisburg) allows
the direct production of metallic zinc [1, 12]. It’s main unit is the Imperial Smelter, a shaft
furnace, connected to a special condenser (Fig.9). Dust, mixed with coal fines, is
injected together with hot blast: ZnO and also PbO are reduced to metal, the slag is
liquefied. Slag and

Fig. 8: The “Waelz – process”

Fig. 9: The Imperial Smelter Process (ISP).
lead bullion go to a forehearth; zinc volatilizes, the zinc vapour is condensed by injection of very fine droplets of liquid lead. The zinc-lead mixture is separated by liquration (separation of two metals, that don’t alloy, due to different densities): Zinc is won as “furnace zinc, lead is recycled to the condenser.

Conclusions

Recycling of zinc coated sheets in cupolas and arc furnaces makes no bigger troubles: Zinc vaporizes and is collected as ZnO in the waste gas dust control, liquid iron resp. steel are practically free of zinc.

During melting coated sheets in induction furnaces, the biggest part of zinc vaporizes also (and has to be sucked ff and collected as ZnO in a dust control). But: Residuals up to 0.2% Zn may stay in the melt. In that case, also from transport vessels zinc can continue to vaporate, generating severely irritating ZnO-dust.

The zinc content in the melt can be lowered by a two-stage melting procedure with intermediate superheating.

Collected ZnO-dust can be recycled as metallic zinc via the waelz-process and a zinc smelter, or directly via the Imperial Smelter Process.

References


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