ZINC LAYER REMOVAL AT THE STEEL APPLIANCES SCRAPS

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ABSTRACT

All appliances contain an important quantity of steel and iron. These can be further recycled at the end of product usefulness. A component of the appliances is the bodies. These are made from galvanized steel. A study for the zinc coated layer removal from the surface of the galvanized steel, prior to recycling the steel scrap by melting in the steelmaking process is presented.

KEYWORDS: appliances, zinc removal, galvanized steel, air and chlorine atmosphere

1. Introduction

Appliances include washing machines, dryers, dishwashers, ranges, air conditioners, refrigerators, freezers and water heaters. A most part of the appliances components is made from steel. By weight, the typical appliance consists of about 65 % steel. Appliances are, in fact, systems of mechanical and electrical components encased in steel shells or bodies. This steel, and the iron components, is recyclable. All appliances contain a minimum of 25 % recycled steel that can be further recycled at the end of product usefulness. To extend the life of landfills and encourage appliance recycling, several states have enacted landfill bans for large appliances (known as „white goods”) thereby forcing the contained steel into the post consumer scrap stream.

The use of coated sheet with zinc from old appliances as raw material increases the amount of zinc in dust. The zinc is a volatile metal, which concentrates in the fumes of the steelmaking reactors and ends up in the dust, or in the sludge, if wet collection is used. Zinc oxide, either zincite or more complex spinels, is the chemical form of zinc found in the dust. If can be sent back to the zinc smelters, but the concentration is usually too low (typically less than 5 % in the oxygen steelmaking dust, or more than 25 % in the EAF dust) to qualify as a substitute for ore concentrate, which has a grade of 60 %. [1]

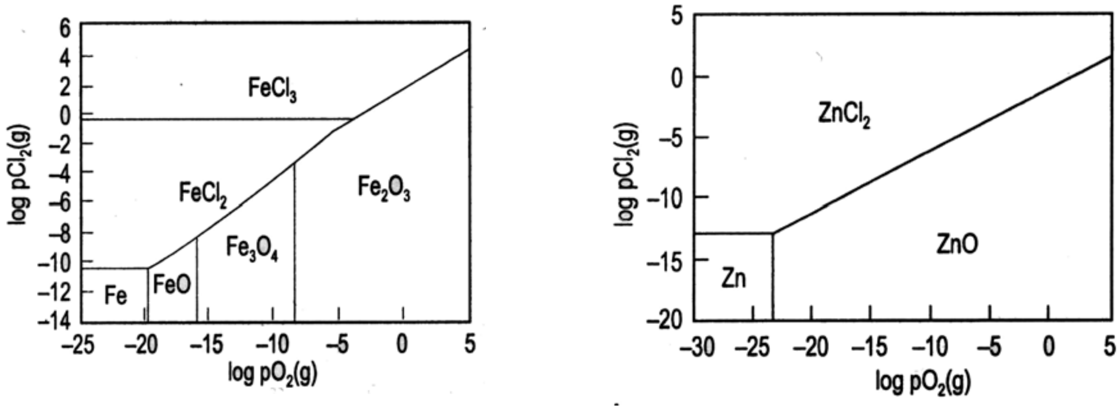
When the concentration of zinc in materials for recycling is comparatively low (less than ~ 35 %) it may not be economically viable. Therefore, a process must be carried to increase its zinc content to at least 55-60 % at which concentration zinc recovery becomes economically viable.

For this reason, the best method for separate and recover both the original metals, iron and zinc is the removed of the zinc coated layer from the surface of the galvanized steel, prior to recycling the steel scrap by melting in the steelmaking process. This work present the laboratory studies for converting galvanized scrap into clean scrap for new steel making by the air and chlorine mixture in the dezincing process. Also, the recovery of the zinc is easily.

2. Thermodynamically data

The experimental conditions can be established if the thermodynamically parameters are analyzed. Figure 1 shows the equilibrium specification of Zn and Fe in a system air and chlorine mixture. Thermodynamics data shows that zinc chloride is more stable than its oxide, and the reverse is true for iron. [2].

The possible reactions together with their respective standard free energy changes (ΔG^0) are given in the table 1.



a

b

Figure 1. *Phase stability diagrams at 800 ^{0}C for the*
(a) Fe-O_2 –Cl_2;
(b) Zn-O_2 – Cl_2 system [1]

Table 1. *Standard free energy changes, ΔG^0*

Eq.no.	**Reactions**	**ΔG^0, kJ/mol (at 800 ^{0}C)**
1	$Zn(l) + Cl_2(g) \rightarrow ZnCl_2(g)$	- 272.430
2	$Zn(l) + 1/2\ O_2(g) \rightarrow ZnO$	- 240.160
3	$ZnO + Cl_2(g) \rightarrow ZnCl_2(g) + 1/2\ O_2(g)$	- 32.270
4	$Fe + 1/2\ O_2(g) \rightarrow FeO$	- 202.347
5	$3\ FeO + 1/2\ O_2(g) \rightarrow Fe_3O_4$	- 163.111
6	$2\ Fe_3O_4 + 1/2\ O_2(g) \rightarrow 3\ Fe_2O_3$	- 86.371
7	$Fe_3O_4 + 9/2\ Cl_2(g) \rightarrow 3\ FeCl_3(g) + 2\ O_2(g)$	+ 73.550
8	$Fe_2O_3 + 3\ Cl_2(g) \rightarrow 2\ FeCl_3(g) + 3/2\ O_2(g)$	+ 77.831

The thermodynamically data show that at the typical operation temperature of 800 ^{0}C and under reducing conditions only volatile zinc is thermodynamically stable, whereas under oxidizing conditions solid ZnO and volatile $ZnCl_2$ are present in about equivalent amounts.

After the removal of the zinc coating, iron is oxidized to form mostly Fe_2O_3 with a small amount of Fe_3O_4. This iron oxide is a protective layer that resists attack from chlorine. [2, 3]

3. Experimental

Materials. Samples of the galvanized steel, obtained by dipping in the melting zinc are utilized. An iron-zinc alloy coating with excellent adhesion and variable zinc content on the depth layer is present on the sheet sides. The structure phases and the microhardness variation on the depth layer are shown in figures 2 and 3. [4, 5, 6]

The zinc layer thicknesses on the two sheet sides can be modified precisely in a range between 60 and more than 750 grams per square meter, by adjustments of bath analysis, bath temperatures and dipping time in consequence of changing sheet surface properties and steel grades. The zinc layer thicknesses of the hot galvanized samples utilized in the experiments was uniformly, about 72 grams per square meter.

Experimental equipment. Tests were conducted on the laboratory scale. A precinct containing the sample is placed in the heating furnace (figure 4).

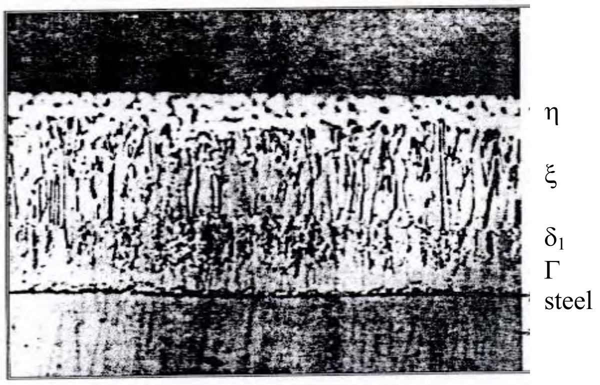


Figure 2. *Structural phases in the galvanized layer formed at the bath temperature 460 ^{0}C*

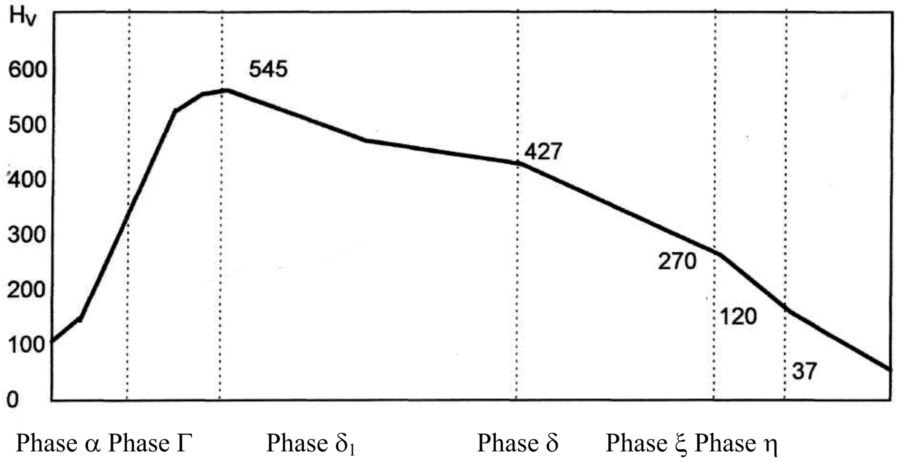


Figure 3. *The microhardness on the depth layer on the sheet sides.*

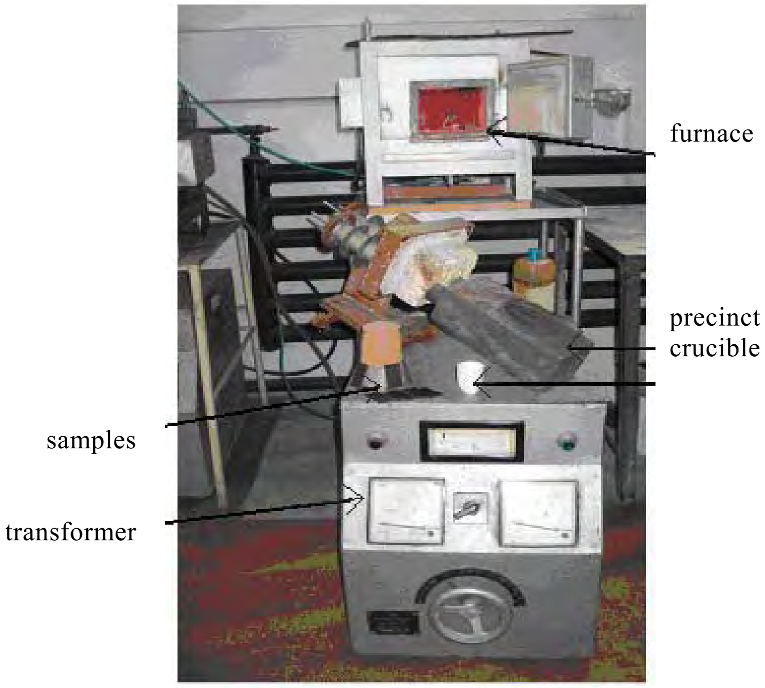


Figure 4. *Experimental installation for the galvanized steel treatment.*

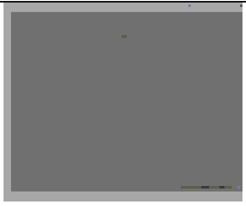
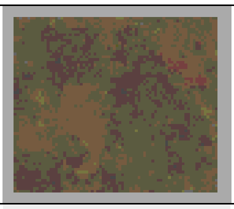
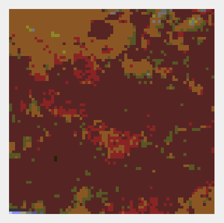
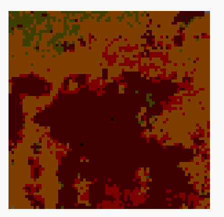
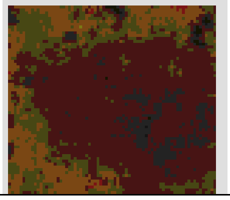
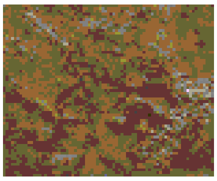
Experimental conditions. The samples were heating in the air and chlorine mixture. Air and chlorine are readily available, by the chloric acid oxidation. An excess chlorine was using, for the complete chloric acid oxidation, more than the literature ratio air/chlorine. Depending of the zinc content in the sheet layers, chloric acid between 9 and 15 cm^3 is utilized for an experimental precinct with a volume of 0,003 m^3.

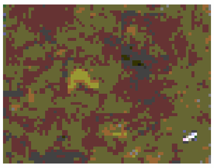
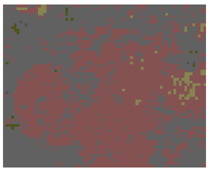
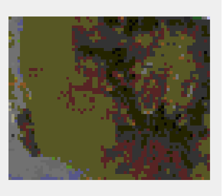
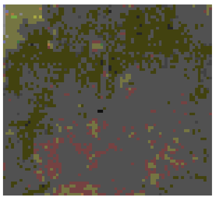
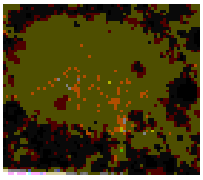
The heating is developed at the variable temperatures, from 570 to 860 ^{0}C. Each sample was maintained then minutes to the constant temperature and then was slowly cooled.

4. Results and discussion

During chlorination at the varied heating temperatures, the appearance of the galvanized steel samples is modified. Theirs comparable evolution and remarks are given in table 2

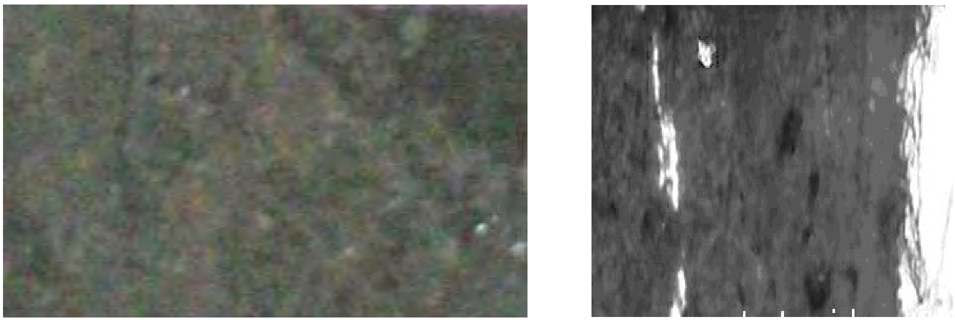
Table 2. *The samples, after chlorination at the varied heating temperatures*

No. sample	The heating temperature, (^{0}C)	The surface of the sample	Remark
1.	before heating		Normal surface of the galvanized steel sheet before chlorination
2.	570		Small areas of the nonconsumed zinc coating (grey areas), and zinc free-zone composed by the ferric oxide (red areas)
3.	630		Punctiform areas of nonconsumed zinc coating (grey areas), and extensive ferric oxide areas (homogeneous red areas)
4.	650		Ferric oxide is present nearby of the all area (homogeneous red areas); the nonuniform surface given the varied colors shades.
5.	680		Ferric oxide is greatly extended of the all area (homogeneous red areas); small oxide areas are detached from the surface sample
6.	710		Ferric oxide areas is present; great oxide areas are detached from the surface sample

7.	760		Ferric oxide areas; the oxide areas detached from the surface sample is enlarged
8.	790		Ferric oxide areas (red colour) alternated with ferroferric oxide areas (black colour)
9.	820		Ferroferric oxide areas (black colour) and small ferric oxide areas (red colour)
10.	840		Ferroferric oxide areas (black colour) and greatly reduced ferric oxide areas (red colour)
11.	860		Ferroferric oxide areas (black colour) and punctiform ferric oxide areas (red colour)

Results from researches show a zinc removal variation with the temperatures. At the temperature increase, the great iron oxide areas early appear: firstly the ferric oxide and then the ferroferric oxide. This iron oxide coating has replaced the zinc coating.

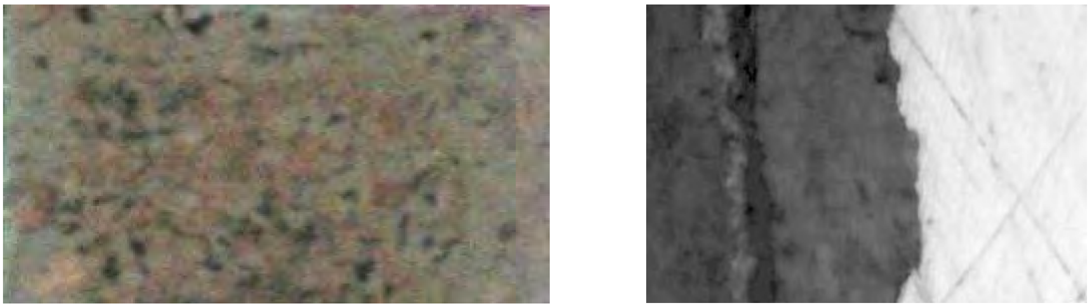
The microstructural analysis cross section of the some samples (No. 2, 4 and 11), heated at 570, 650 and 860 ^{0}C respectively, is presented in figure 5. For the different zones of the same sample, a variable rate of removal is observed. In these cases the nonuniform consistence of the zinc layer is possible to be the cause. For the maximum heating temperature, an acceptable rate of removal was obtained.



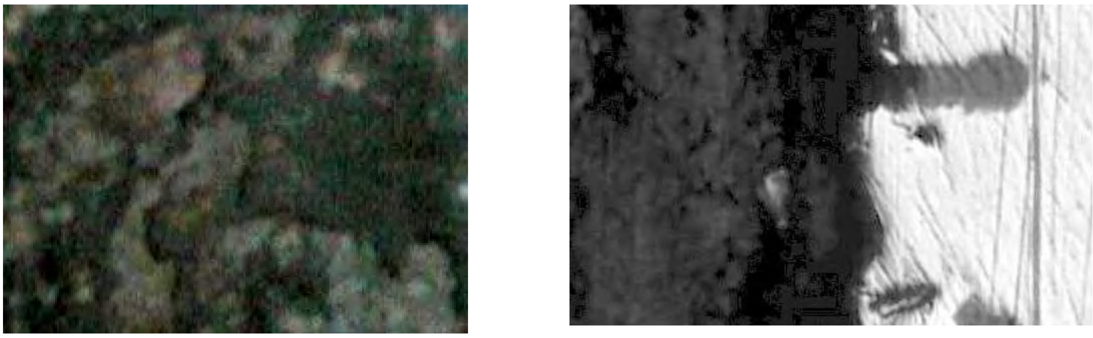
The ferric oxide zone and the small nonconsumed zinc marks

The ferric oxide zone and the extended nonconsumed zinc areas

(a)



The ferric oxide layer and the intergranular and intragranular oxidation
on the all length sample
(b)



The great iron oxidation is observed; the ferric and ferroferric oxide are formed
(c)

Figure 5. *The microstructural analysis cross section for the different zones of the same sample, heated at 570 (a), 650 (b) and 860 ^{0}C (c) respectively (500 x).*

In accord with thermodynamically data, the depth of the oxide layer ranges with heating temperature. The correlation between these two parameters is given in figure 6.

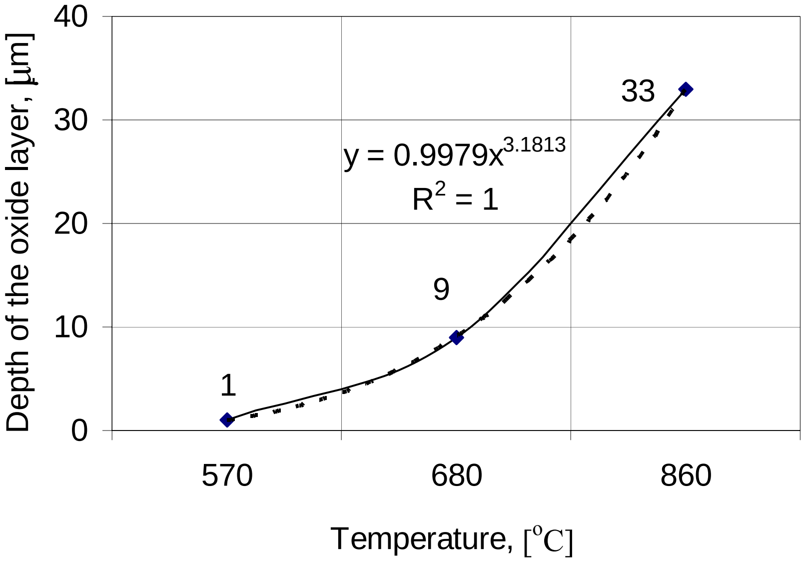


Figure 6. *The variation of the iron oxide layer depth during heating.*

4. Conclusion

This method is technically possible to the cleaning of the galvanized steel scraps before the utilization for new steel making. Also, the recovery of the zinc from volatile chlorides is easy to realize. For an efficient zinc removal rate, the process parameters (heating temperature and time, concentration air/chloride mixture), established in correlation with the nature galvanized scrap (steel grade, properties of the zinc layer and the steel sheet), must be check very accurately.

References

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[3]. J.K.S. Tee, *„Recycling of galvanized steel scrap. A feasibility study”* R’99 Congress, 1999
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