REDUCTION OF ZINC FERRITE CONTAINED IN STEELMAKING DUSTS BY CO - CO2 GAS MIXTURES[1]

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Abstract
In this work the reaction between an equimolar synthetic zinc ferrite sample and a mixture of CO - CO2 gases was studied to evaluate the effects of temperature and CO content.. The temperature ranged from 1073 to 1373K, and the gas mixtures from 50% to 100% of CO. These tests were supported by physical, chemical, structural and microscopic characterizations of both, initial zinc ferrite generated in laboratory and the remained after reaction. It was observed that the temperature and CO content were the main factors affecting the zinc ferrite reduction. The maximum reductions indexes obtained in these experiments were 95%, for 100% CO at 1373K, in 105 min, and 52%, for 50% CO at 1373K, elapsed 105 min. The Apparent Activation Energies obtained in this study were 55.60 and 91.71 kJ/mol, for 100%CO and 50% CO-50% CO2, respectively.
Key words: Zinc ferrite; Steelmaking dusts; Reduction.

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1 INTRODUCTION

Several residues generated in the reduction and refining sectors of a steelwork plant, bears expressive quantities of zinc in their compositions, mainly in the form of oxide and ferrite.compounds. Nowadays, these particulates, regarded as ambientally deleterious materials, are being the main focus of several stocking procedures and studies to reclaim its zinc content. Further, the zinc content in these residues could be as high as 25% to 40 % of their composition, being commonly distributed as 70% in the form of zinc ferrite and the rest as zinc oxide and metallic one (minor part).[1] Moreover, its quantity increases the particulates content in the generated fumes, as the recycling of galvanized steel scrap increases as burden in the steelmaking processes Therefore, the presence of zinc ferrite in steelmaking dusts is a hard reality, and, on top of that the reduction of this substance is still not well understood. According to Jyh-Jen et al.[2] in the temperature range of 1073 to 1473K the carbothermic reduction of zinc ferrite has an apparent activation energy of circa 92,91 kJ/mol. They also proposed a reduction phenomenology involving basically two steps: firstly, the initial decomposition of zinc ferrite, $ZnFe_2O_4$, to ZnO and Fe_2O_3, and secondly, a simultaneous and competitive final reduction of these oxides. Additionally, depending on the reduction temperature, their proposal is that the metallic zinc released should evolve as vapor, generating a degree of porosity in the solid which increases the specific surface of the remained reacting material and consequently, its volume. This increase in volume, accompanying the reduction of the iron oxides in the final stage of the process, should also be followed by the iron sinterization, thus producing a decreasing of the pores diameter and the particles volume.
This work is a part of a broader project which major purpose is to establish a complete kinetic and morphological phenomenology, aiming a better understanding of the reduction process of the zinc ferrite present in the steelmaking dusts , by gaseous mixtures of CO and CO2..

2 METHODOLOGY

Inicially, synthetic zinc ferrite samples were made in laboratory from Fe_2O_3 / ZnO : 1 / 1 mixtures following the technique developed by Hsi-Kuei Chen and Ching-Yi Yang;[1] Bid and Pradhan[3] and Gómez and D'Abreu.[4,5] In continuing it was agglomerated into the shape of cylindrical briquettes according to Özbayoğlu.(6) Firstly, the zinc ferrite was structurally characterized through X-Ray diffraction, using a difractometer Siemens, model D5000 and the following operational conditions: I=30 A, V=40 kV and copper anode (λ=1,5406 Å, CuK–α).. The analytical software applied was the Diffract Plus, Topas, version 2.1 from Bruker AXS for quantitative analysis by the Rietveld method.
The samples of zinc ferrite were also characterized morphologically using a Scan Electron Microscope – SEM (DSM 960 Zeiss West Germany, V = 20 kV) and a Transmission Electron Microscope – TEM (Model JEOL 2010 V = 200 kV).
The physical characterization of the zinc ferrite was made employing:
A Multipychnometer quanta crome V=120V and P=18psi, for the specific gravity measurements;
A Mastersize μ, Version 2.12 from Malvern Instruments, for the size distribution and specific surface determination.

After those essays, portions of zinc ferrite powder weighting 7 g were agglomerated in cylindrical briquettes with a diameter of 2.54 cm.
The reduction runs were performed in a tubular electric furnace, linked to a gas line with mixtures of CO, CO2 and N2. The experiment temperatures were 1073, 1173, 1273 and 1373K and the reaction times 8, 56.5 and 105 minutes. The gaseous compositions utilized were 100% CO and 50% CO – 50% CO2.

3 RESULTS AND DISCUSSION

3.1 Structural Characterization

In Figure 1 a Rietveld adjusted difractogram of a zinc ferrite synthetic sample is presented, showing the phases and their corresponding percentages: zinc ferrite (ZnFe2O4) – 94.82%, Iron (III) Oxide (Fe2O3) – 3.48%, Zinc Oxide (ZnO) – 1.70%.

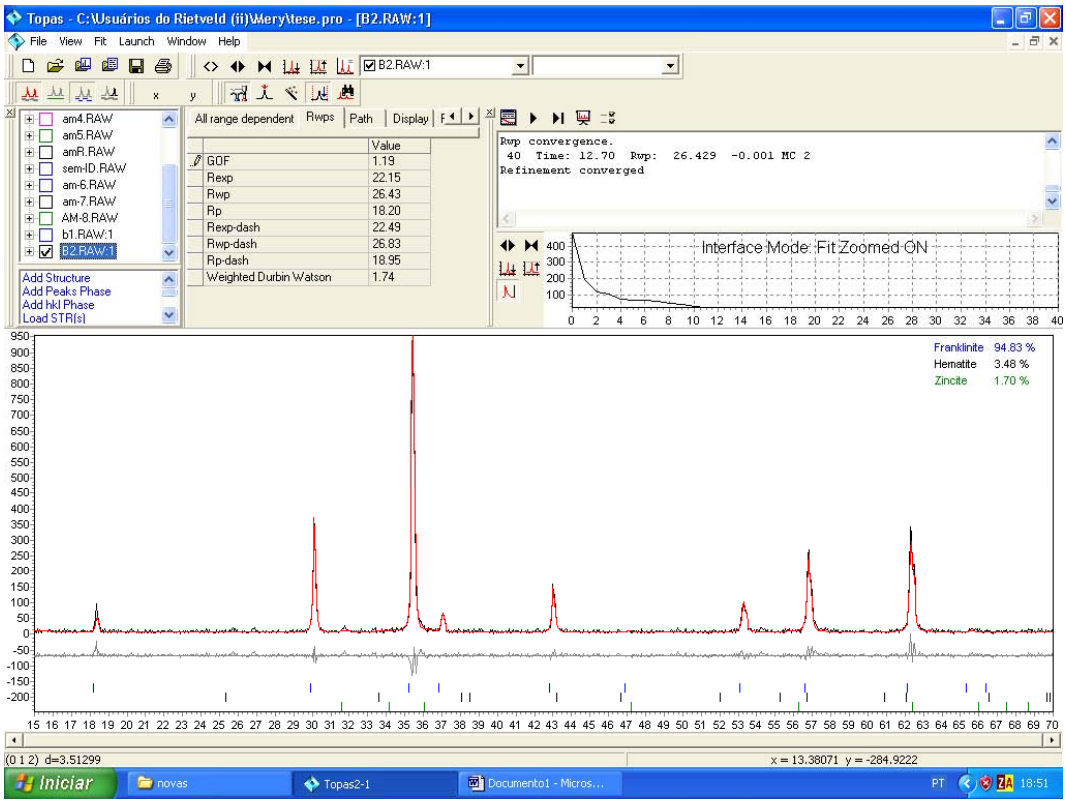

Figure 1 – Adjustment by Rietveld's method of XRD patterns of equimolar zinc ferrite.

3.2 Microscopic Characterization

Completing the identification and characterization of the phases present in the zinc ferrite samples, the SEM and TEM analysis were made.
In Figure 2 a SEM image of the zinc ferrite, as produced in the laboratory, is presented. In it is clear the major presence of zinc ferrite white globulae, besides of some pores. As for the TEM image, in Figure 3, one can observe the presence of tiny zinc ferrite particles having sizes on the range of 100 to 200 nm

3.3 Physical Characterization

In this aspect the samples particles average size, specific surface, specific gravity and porosity were measured. The results were:
Particle (clusters) average diameter : 37 μm
Specific surface: 0.1347 m2/g
Specific gravity: 5.71 g/cm3
Sample's briquette porosity: 0.45
One must observe that the specific gravity was significantly similar to the one presented in the Tong[7] work (the theoretical zinc ferrite specific gravity is circa 5.34 g/cm3).

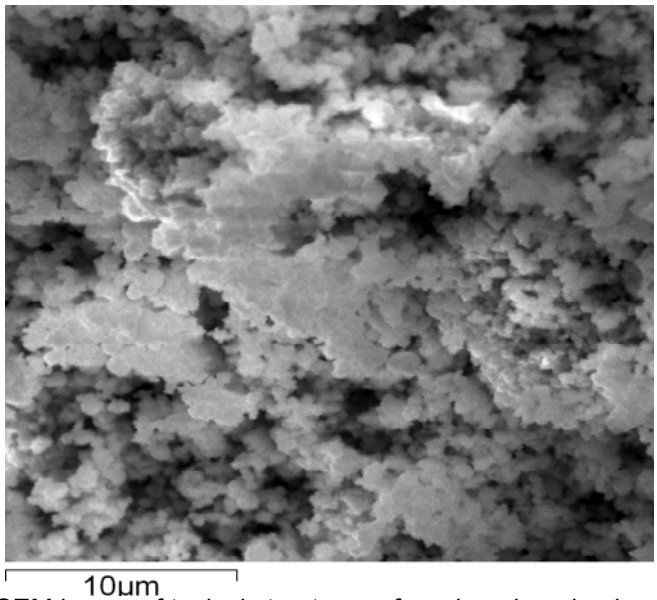

Figure 2 – SEM image of typical structures of produced equimolar zinc ferrite.

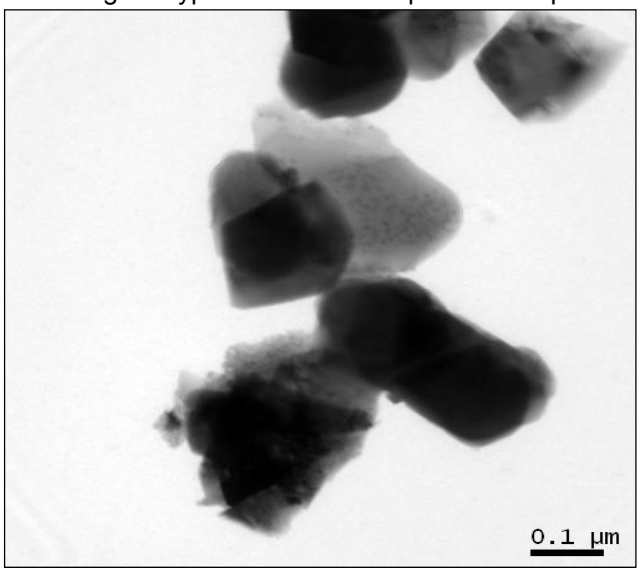

Figure 3 – TEM image of typical structures of produced equimolar zinc ferrite.

3.4 Reduction

The gas compositions and temperatures, elected for the tests, were chosen taking into account the phase predominance operational diagram – PPOD for the Zn-Fe-C-O system, determined by the authors.[8]

In Figure 4 the PPOD for Zn-Fe-C-O is depicted. In it the equilibria ZnO-Zn and Fe2O3-Fe3O4-FeO-Fe, with a CO-CO2 atmosphere, and the predominance area for various species, are signaled The reduction mechanism was the reaction occurring via gaseous intermediaties (equimolar zinc ferrite reduction by CO together with the Boudouard reaction):

$ZnO.Fe_2O_3(s) + 4CO(g) = Zn(g) + 2Fe(s) + 4CO_2(g)$

$CO_2(g) + C(s) = 2CO(g)$

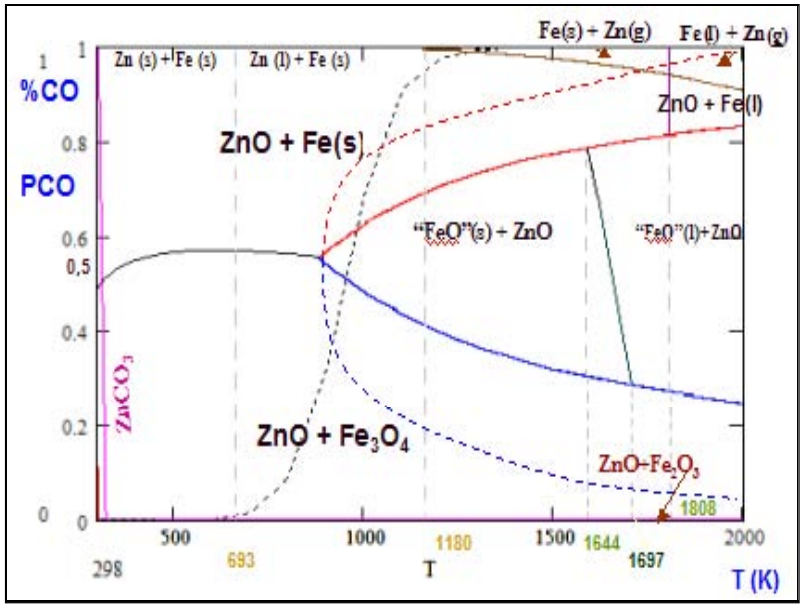

Figure 4 – Phase predominance operational diagram –PPOD, for the Zn-Fe-C-O system.

The obtained kinetic curves for the zinc ferrite reduction, for different temperatures, are presented in Figures 5 (50%CO–50%CO2 mixtures) and in Figure 6 (100% CO).

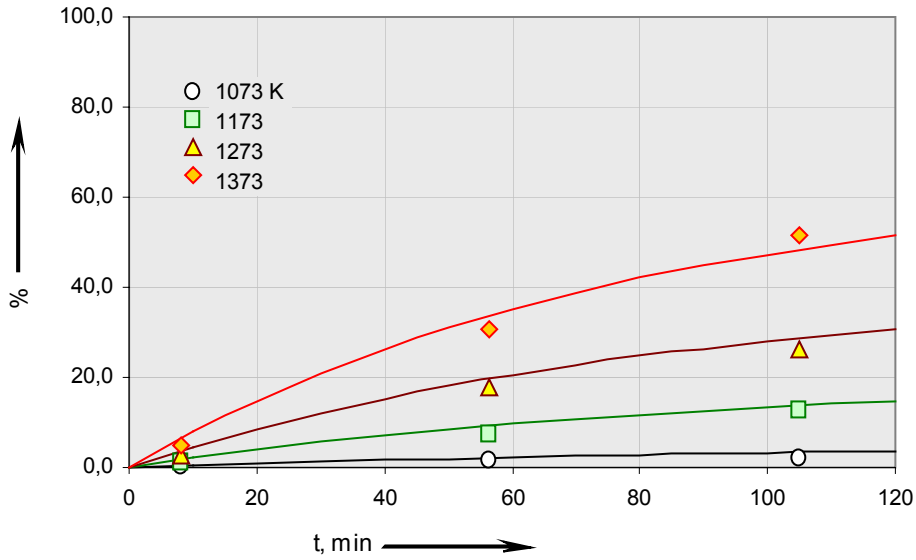

Figure 5 - Reduction of zinc ferrite at different temperatures by 50%CO - 50%CO2 gas mixtures.

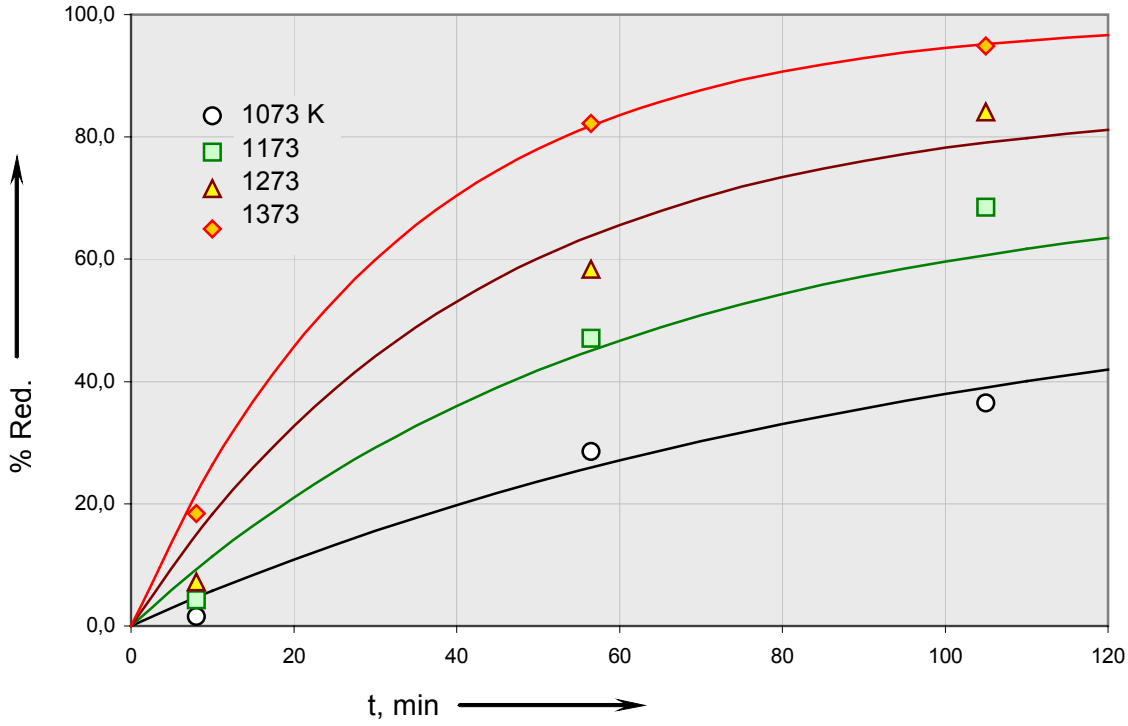

Figure 6 - Reduction of zinc ferrite at different temperatures by 100% CO.

Using those kinetic data, it was calculated the following Arrhenius parameters:
For the 50% CO-50% CO2: gas mixture: Apparent Activation energy, 91.71 kJmol-1;
Frequency Factor, 160 mHz.

For the 100% CO atmosphere: Apparent Activation Energy, 55.60 kJmol-1;
Frequency factor, 8.83 mHz

4 CONCLUSIONS

The phase predominance operational diagram – PPOD, furnished the key information for temperatures and %CO values utilized in the reducing kinetic experiments;
The microscopic characterization of the zinc ferrite powders, permitted the observation of clusters formed by the individual particles, which had the average size ranging from 100 to 200 nm;.
From the zinc ferrite and gaseous CO mixtures reducing curves, the following conclusions are drawn:
Increases in temperatures, reaction time and CO percentage produced, as expected, higher zinc ferrite conversions ;
For the pure CO atmosphere: Ea= 55.60 kJ/mol
For the 50% CO-50% CO atmosphere: Ea= 91,71 kJ/mol
The observed differences between the Activation Energy values, hints changing in overall reaction mechanism toward a less temperature sensitive process.

To determinate a comprehensive kinetic equation for the reduction process of zinc ferrite by CO, the study under other gaseous compositions is being carried out. The results will permit a better decision making actions aiming at the reclaim of the zinc element from steelmaking dusts.

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