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OXIDATION KINETICS OF COPPER SLAG

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Abstract: *The study presents kinetics of oxidation of copper pyro-metallurgical waste (fayalite), by the TG-DTA analysis method. This is necessary due to the application of a developed method for oxidation of the waste mass, by means of a constructed and developed a suitable laboratory system operating using the "fluidized bed" method, type ProCell System.*

For this purpose, oxidation kinetics are investigated with different (relatively high 10 to 40^o/min) heating rates and a different amount of synthetic air at 20 to 40 mL/ min. The values of the kinetic parameters, the activation energy and the pre-exponential factor, have been determined based on data DTA and clasical Johnson-Mehl-Avrami-Yerofeev-Kolmogorov (JMAYK) equation. The obtained data can optimize the process of thermal decomposition of the pyrometallurgical copper slag by oxidation in synthetic air.

Keywords: *Copper slag, oxidation, kinetics, fayalite, decomposition, Arrhenius parameters.*

INTRODUCTION

This report examines issues related to the investigation of the kinetics of the decomposition of waste iron-silicate powder - fayalite, obtained at the Aurubis Bulgaria AD, after flotation of copper slags. This is about development of waste product recovery technology, as a major step in the technology is to decompose the fayalite at a temperature of 800-1000^{o}C in the "fluidized bed" mode. For this purpose, a pilot reactor is developed in which a fluidized bed "fluidized bed" is generated in a specially adapted fire chamber to provide the dynamic mode required for degradation of the wound and separation of the binding components. As a fluid, a pre-heated mixture (about 900 °C) of air and gas is used. This enables the required thermal degradation effect to be achieved at a relatively lower temperature.

Thermal decomposition of pyrometallurgical copper scrap by oxidation in oxidizing gas is studied.

MATRIALS AND METHODS

Nonisothermal oxidation kinetics are studied in the temperature range of 373 to 1273 K using thermogravimetric analysis data and the classical Johnson–Mehl–Avrami–Yerofeev–Kolmogorov (JMAYK) equation.

Fayalite slag obtained during the matte smelting and refiningof copper in Aurubis Bulgaria AD, sifted through a100-mesh sieve. The oxidizing of the slag samples (with initialweight 200 mg) was carried out in a thermogravimetric analyser (TG, DTG, DSC; SETARAM 2400) at atmospheric pressurein a flow of air (100 %), with a 20 and 40 mL.min^{-1} rate of air delivery. The air was used as an oxidant to provide constantpartial pressure of oxygen during all experiments.

The experimental TGA curves were analysed to evaluate rate constants, activation energies and the most probable reaction mechanisms. Solistate reactions can be successfully described with the Johnson-Mehl-Avrami (JMA) (Johnson, W.A., Mehl, R.F. 1939)equation:

$$X=1-\exp[-(kt)^n] \quad (1)$$

Following logarithm and rearrangement of equation (1),(Avrami, M. 1940) there is obtained:

$$\ln(1-X) = n\ln k + n\ln t \quad (2)$$

where:

X - the amount of crystalline fraction formed after time t;

n - parameter Avrami, depending on the mechanism of crystal growth;

k - velocity constant [s^{-1}], whose temperature dependence is expressed by the equation of Arrhenius:

$$k=V\exp(-E_a/RT) \quad (3)$$

where:

V - frequency factor [s^{-1}],

Ea - activating energy of crystallization [J.mol^{-1}],

R - gas constant and T - temperature [K].

The Avrami (Avrami, M. 1939) parameter n can be calculated from the DTA results and the values obtained for the activating energy Ea:

$$n=\frac{2.5}{\Delta T}\frac{T_p^2}{(E_a/R)} \quad (4)$$

where: ΔT is the width of the straight line passing half the maximum intensity of the exothermic peak, Tp is Tmax, as measured by the DT analysis (Figure 1). The value of the activating energy of crystallization is determined using a method based on the JMA equation, which was first used by Kissenger and subsequently modified.

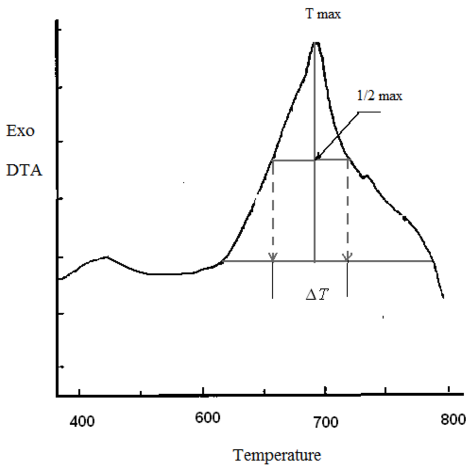

Fig. 1. Example DTA curve for calculating ΔT

This method is based on the temperature dependence of the formation of a new phase corresponding to the peak of the exothermic peak (Tp), the heating rate (β).

$$\ln\frac{T_p^2}{\beta} = \ln\frac{E_a}{R} - \ln V_a + \frac{E_a}{RT_p} \qquad (5)$$

where: Ea is the corresponding activation energy, Tp - peak temperature and Va - frequency factor in the formation of the new phase.

When plotting in coordinates ln (Tp^2 / β) / (1 / Tp) linear relationships with Ea / R slopes and ln (Ea / R) - lnVa are obtained.

RESULTS AND DISCUSSION

Through TGA, an experimental series of decomposition of copper waste with different heating rates of 10, 20, 30 and 40 °C/min was investigated. Oxidation of the copper samples was carried out at two feed rates of air in the thermogravimetric apparatus of 20 and 40 mL. min^{-1}. It is thus possible to trace the influence of the different amount of lyxide during the experiment.

In Fig. 3 shows DTA curves of copper slag oxidized at different heating rates of 10, 20, 30 and 40 °C/min, air - 20 mL.min^{-1}. Observe the last two exo-peaks with oxidation of the fayalite ($2FeO.SiO_2$) and the formation of Hematite and Magnetite (Gyurov, S., Y. Kostova, G. Klitcheva, A. Ilinkova, 2011). in the schematic reaction:

$2FeO.SiO_2 + ½\ O_2 = αFe_2O_3$ (Hematite) + SiO_2 (amorphious silica)

$2FeO.SiO_2 + ½\ O_2 = 2/3\ Fe_3O_4$ (Magnetite) + SiO_2 (amorphious silica)

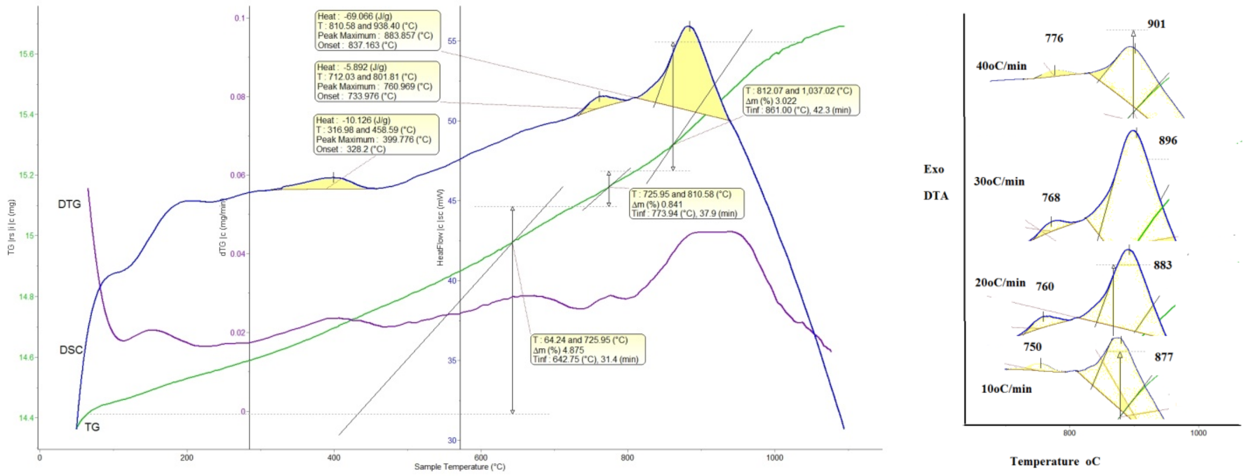

Fig.2. (a)- DTA of copper slag oxidized heating rates 20 °C/min, air - 20 mL.min^{-1} ; (b) -DTA curves of copper slag oxidized at different heating rates of 10, 20, 30 and 40 °C/min, air - 20 mL.min^{-1} (exo-peaks II, III).

The obtained TG–DTA curves are similar in shape to the one shown in Fig. 2 (a). It shows endothermic effect within the temperature range 323 to about 500 K and a broad exothermal effect in the temperature interval 593–1273 K, where three peaks could be distinguished. The general view of the exothermic effect revealed the simultaneous run of several (oxidation or phase transition) processes. The endo- effect is characterized by a minimum decrease of mass and is due to the released residual moisture in the slag. The exo-effect is characterized by gradual increase of mass and is due to the oxidation processes in the slag. It can be observed that the sample mass increases continuously between 973 and 1273 K and is associated with the oxidation processes of the slag (exo-peaks II, III). The process of slag oxidation isaccompanied by structural transformation and formation ofstructure of ordered platelike crystals of hematite, magnetite, amorphous silicate phase, and residual fayalite (Gyurov, S., D. Rabadjieva, D. Kovagheva, Y. Kostova, 2014).

In Fig. 3 shows coordinates ln (Tp^2 / β) / (1 / Tp) for last two exo-peaks (II, III).

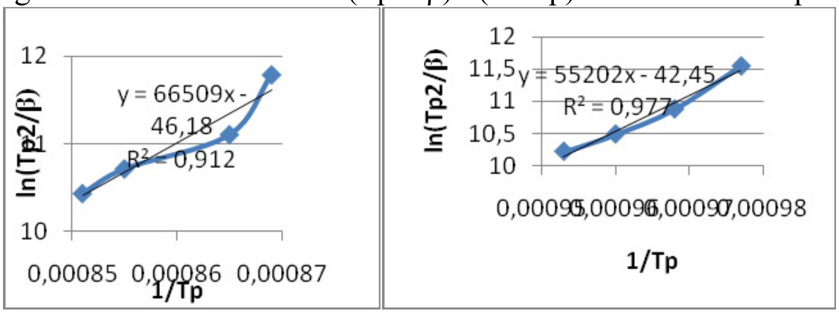

Fig. 3. Arrenius plots of copper slag in oxidizing heating rates of 10, 20, 30 and 40 °C/min, air - 20 mL.min^{-1}(exo-peaks II, III).

In Fig. 4 shows DTA curves of copper slag oxidized at different heating rates of 10, 20, 30 and 40 °C/min, air - 40 mL.min^{-1}.

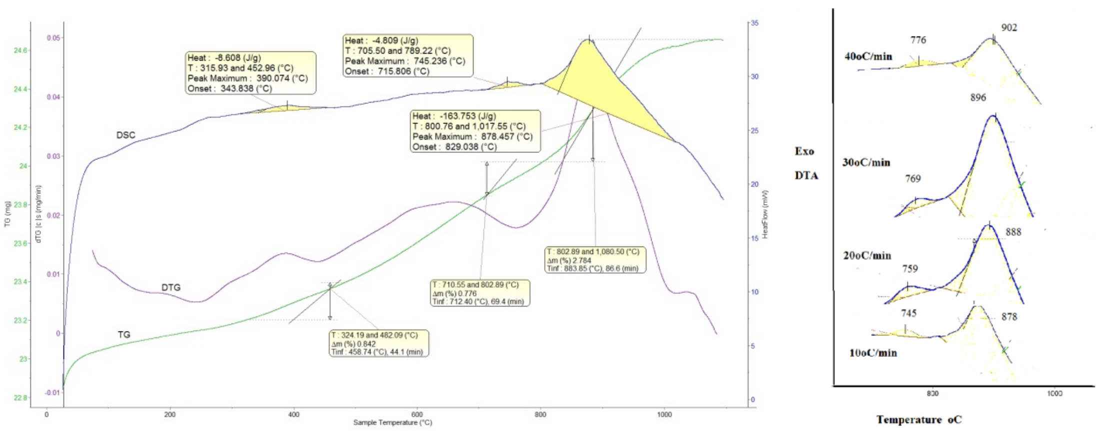

Fig.4. (a)- DTA of copper slag oxidized heating rates 10 °C/min, air - 40 mL.min^{-1} ; (b) -DTA curves of copper slag oxidized at different heating rates of 10, 20, 30 and 40 °C/min, air - 40 mL.min^{-1} (exo-peaks II, III).

From the coordinates ln (Tp^2 / β) / (1 / Tp), for two exo-peaks (II, III) calculated activation energies (Ea, kJ/mol), which has the same values for the different quantities of oxidizing gas treatment (20 and 40 mL.min^{-1}) in the oxidation process - from exo-peaks II - Ea 458 kJ/mol , from exo-peaks III - Ea 485 kJ/mol.

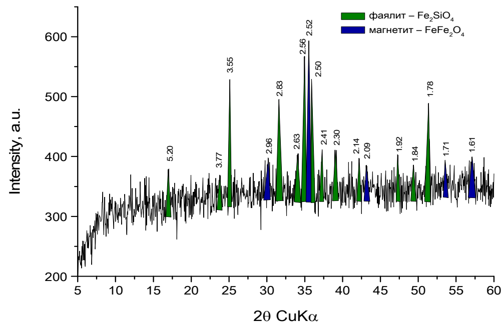

Fig.5. XRD of initial copper slag

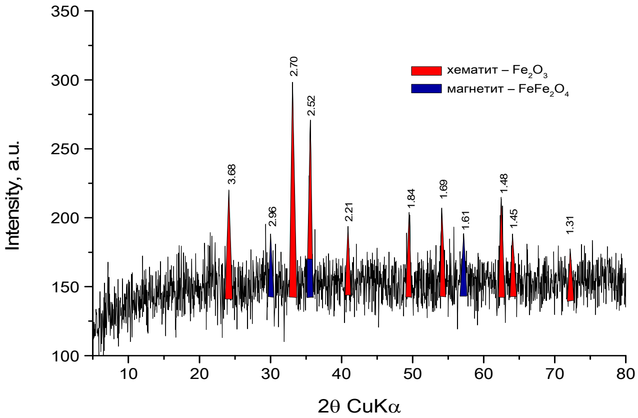

Fig. 6. XRD pattern of oxidet at 1273K copper slag

Fig. 5 and fig. 6 shows the results of XRD of initial copper slag, and XRD pattern of oxidet at 1273K copper slag. It is clear that after the heat treatment at 1273K there are formed two main crystalline phases of Hematite and Magnetite.

CONCLUSION

The simultaneously performed thermal (TG/DTA) and XRD of air oxidizedslag prove that the process is complex. The obtained TG–DTA shows endothermic effect within the temperature range 323 to about 500 K and a broad exothermal effect in the temperature interval 593–1273 K, where three peaks could be distinguished. The exothermic effect revealed the simultaneous run of several (oxidation or phase transition) processes. The endo- effect is characterized by a minimum decrease of mass and is due to the released residual moisture in the slag. The exo-effect is characterized by gradual increase of mass and is due to the complex oxidation processes in the slag. It can be observed that the sample mass increases continuously between 973 and 1273 K and is associated with the oxidation processes of the slag (exo-peaks II, III).

The tests carried out for oxidation of copper slag at relatively high heating rates of 10 to 40 °C/min, at 20 and 40 mL /min of oxidising gas, have made it possible to calculate the energy of activation of the processes at the final oxidation step of the material (exo-peaks II, III). The results obtained show that the amount of oxidizing gas in the oxidation does not cause a substantial degradation of the oxidation processes.

The process of slag oxidation isaccompanied by structural transformation and formation ofstructure of ordered platelike crystals of hematite, magnetite, amorphous silicate phase, and residual fayalite.

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