

EFFECT OF OXYGEN CONTENT ON THE NON-ISOTHERMAL OXIDATION OF WASTE SLAG FROM COPPER PRODUCTION

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Abstract

Oxidation of waste slag from copper production was studied in oxygen-nitrogen gaseous mixtures (21, 43, 63 and 100 vol.% of O₂) under non-isothermal conditions using DTA-TG analysis at constant gas flow rate of 30 ml min⁻¹ and varying heating rate. The results revealed that the mechanism of slag oxidation does not change with changing the oxygen content but intensification of the process occurs. Kinetic analysis was performed and a decrease in the values of the activation energy was observed with increasing of the oxygen partial pressure.

Key words: copper slag oxidation, thermal analysis, DTA-TG, kinetic analysis, activation energy

1. INTRODUCTION

Chalcopyrite (CuFeS₂), bornite (Cu₅FeS₄), chalcocite (Cu₂S), enargite (Cu₃AsS₄), etc. (Ayres *et al.*, 2002) are the ores usually used for copper production by the pyrometallurgical method. During the process, large amounts of copper slag are generated (Byung-Su Kim *et al.*, 2013). The chemical composition of the slag varies with the type of furnace or process of treatment, but it generally consists of FeO (35-49 %), SiO₂ (28-40%), CaO (1-10%), MgO (1-3%), Al₂O₃ (2-15%), Cu (about 1%), as well as Mn, Ni, Zn, Co below 1 % (Gorai *et al.*, 2003). Deposition of this slag causes loss of valuable elements and creates environmental issues owing to the occupation of large areas of land for its disposal (Gonzalez *et al.*, 2005).

Various hydrometallurgical methods using different leaching agents such as acids (H₂SO₄), bases (NaOH, NH₄OH) or salts (FeSO₄, (NH₄)₂SO₄) have been developed for extraction of metals from slags. For example, Aydogan *et al.*, (2000) reported more than 90% Cu extraction from Hafik–Madentepe copper slag containing 2.62% of Cu by sulfuric and ammonia leaching at 95 °C. Anand *et al.*, (1983) extracted more than 90% of Cu, Co and Ni from Ghatsila smelter copper slag by pressure leaching at 130 °C. However, the authors did not give information on iron coextraction and silica gel formation. The formation of silica gel prevents metal extraction, filtration of the pulp and also causes the formation of trash during solvent extraction. Besides, no significant reduction in the slag volume was achieved due to the silicate components remaining untapped.

A new approach has been proposed for copper slag recycling to iron oxide concentrate, alkali metal silicate or a solution of silicon in alkali metal hydroxide which can be used for production of water glass and silica gel (Gyurov *et al.*, 2012 EU patent No. 2 331 717 B1, Gyurov *et al.*, 2017). The proposed method consists of thermal decomposition of the main mineral component of the copper slag - fayalite (2FeO.SiO₂) through oxidation in air atmosphere and subsequent hydrothermal treatment with alkali hydroxides or carbonates.

A limited number of studies on the oxidation of fayalite as a chemical compound, but not as a slag component (Mackwell, 1992; Gorai *et al.*, 2003) have been reported. Gyurov *et al.*, (2011, 2014) studied the oxidation of copper slag in air atmosphere. They proved that the process is complex and takes place in four stages: (i) oxidation of magnetite and formation of metastable spinel (γ-Fe₂O₃); (ii) transformation of γ-Fe₂O₃ into the stable α-Fe₂O₃; (iii) oxidation and decomposition of fayalite

($2\text{FeO} \cdot \text{SiO}_2$); (iv) decomposition of the residual fayalite and polymorphic transformations in the silicate and iron phases. The complexity of the process also affects the calculated values of kinetic parameters that are differing from those of the pure single-phase components of the slag.

The aim of this study is to investigate the oxidation of waste slag from pyrometallurgical copper production at different oxygen contents in oxygen-nitrogen gas mixtures and to obtain kinetic data characterizing the ongoing process. These data could be used in process optimization and estimation of real-time material performance.

2. EXPERIMENTS AND METHODS

2.1. Materials

The copper slag used in the experiments is a waste product from the pyrometallurgical production of copper in Aurubis Bulgaria AD Company. The slag was sifted through a 100-mesh sieve and the fraction with particle size below 100-mesh was used in the experiments.

2.2. Non-isothermal oxidation

The non-isothermal oxidation of copper slag was carried out using the computerized combined apparatus for differential thermal and thermogravimetric analyses (DTA-TG) LABSYS Evo, SETARAM Company, France. The experiments were carried out in the temperature range of 25 – 1000°C using a gas flow of oxygen-nitrogen mixtures with oxygen content of 18, 43, 63 and 100 vol.% at a constant gas flow rate of 30 ml min⁻¹ and a heating rate of 5, 10, 15, and 20 °C min⁻¹. Corundum crucibles with a volume of 100 µl were used. The sample weight in all tests was 80±1 mg. The oxidized samples were subjected to XRD analysis.

2.3. XRD analysis

The XRD analyses were performed using an automatic Bruker D8 Advance powder X-ray diffractometer with Ni filtered CuK α radiation and registration by LynxEye solid-state position-sensitive detector. The X-ray spectra were recorded in the range from 5.3 to 80° 2 θ with a step of 0.02° 2 θ . The qualitative phase analysis was made using the PDF-2(2009) database of the International Center for Diffraction Data (ICDD) by means of the DiffracPlusEVA software package. Powder diffraction patterns were evaluated with the Topas-4.2 software package for line broadening interpretation. The mean crystallite size was determined by whole powder XRD pattern fitting using the fundamental parameters for peak shape description and including appropriate corrections for the instrumental line broadening and diffractometer geometry (Bruker 2007). The integral line width approach for the generalized treatment of the domain size broadening - $\beta_i = \lambda/L_{\text{vol}}\cos\theta$ was employed, where β_i is the integral broadening of the diffraction line i and L_{vol} is the volume weighed mean column height.

2.4. Elemental analysis

Elemental analysis was performed on a JEOL-JSM-6390 scanning electron microscope equipped with an energy dispersive X-ray microanalysis (EDXMA) device.

2.5. Kinetic analysis

The data from the TG-DTA and TG-DSC analyses were used to calculate the activation energy of the oxidation process using the general kinetic equation:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) = A \exp\left(\frac{-E_a}{RT}\right) \cdot f(\alpha) \quad (1)$$

where: $\alpha = \frac{G_{in} - G_T}{G_{in} - G_f}$ is the degree of conversion (G_{in} is the initial weight, G_T is the (current) weight for a given temperature (or time) and G_f is the final sample weight); t – time, $k(T)$ - rate constant; $f(\alpha)$

- reaction model; A - pre-exponential factor; E_a – activation energy; R – universal gas constant and T – absolute temperature.

According to the isoconversional methods for non-isothermal studies, the general kinetic equation is transformed into:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E_a}{RT}\right) \cdot f(\alpha) \quad (2)$$

where: $\beta = dT/dt$ is the heating rate.

We used computation procedures called Kissinger-Akahira-Sunose (KAS) (Kissinger 1957; Akahira & Sunose 1971). The authors have assumed that for a given DTA curve, maximum reaction rate occurs at the maximum temperature of the peak. At a given heating rate (β) and a first-order reaction, the proposed equation is:

$$\ln(\beta/T_p^2) = \ln(A R/E_a) - E_a/(R T_p) \quad (3)$$

where T_p – temperature of the peak. Plots of the function $\ln(\beta/T_p^2) = f(1/T_p)$ at $\beta = \text{constant}$ are straight lines by whose cuttings and slopes the values of A and E_a can be calculated.

3. RESULTS AND DISCUSSION

The copper slag used in the experiments is a waste product from the pyrometallurgical production of copper in Aurubis Bulgaria AD Company. The main raw material of Aurubis Bulgaria are copper concentrates produced from the mining industry in Bulgaria and imports mainly from the countries of the Black Sea region, North and South America. Table 1 shows the elemental composition of the waste slag, determined by X-ray microanalysis of different grains. With respect to the macro composition (Si, Fe, O), the slag is relatively homogeneous, while trace components (Cu, Zn, Na, Mg, Al, Ca, Ti, S) are not present in all grains analyzed. The small variation in the content of silicon and iron is due to the variation of aluminum and calcium included in fayalite. An exception is the sample denoted as 1.2 in Table 1, whose macro and micro composition does not match the others.

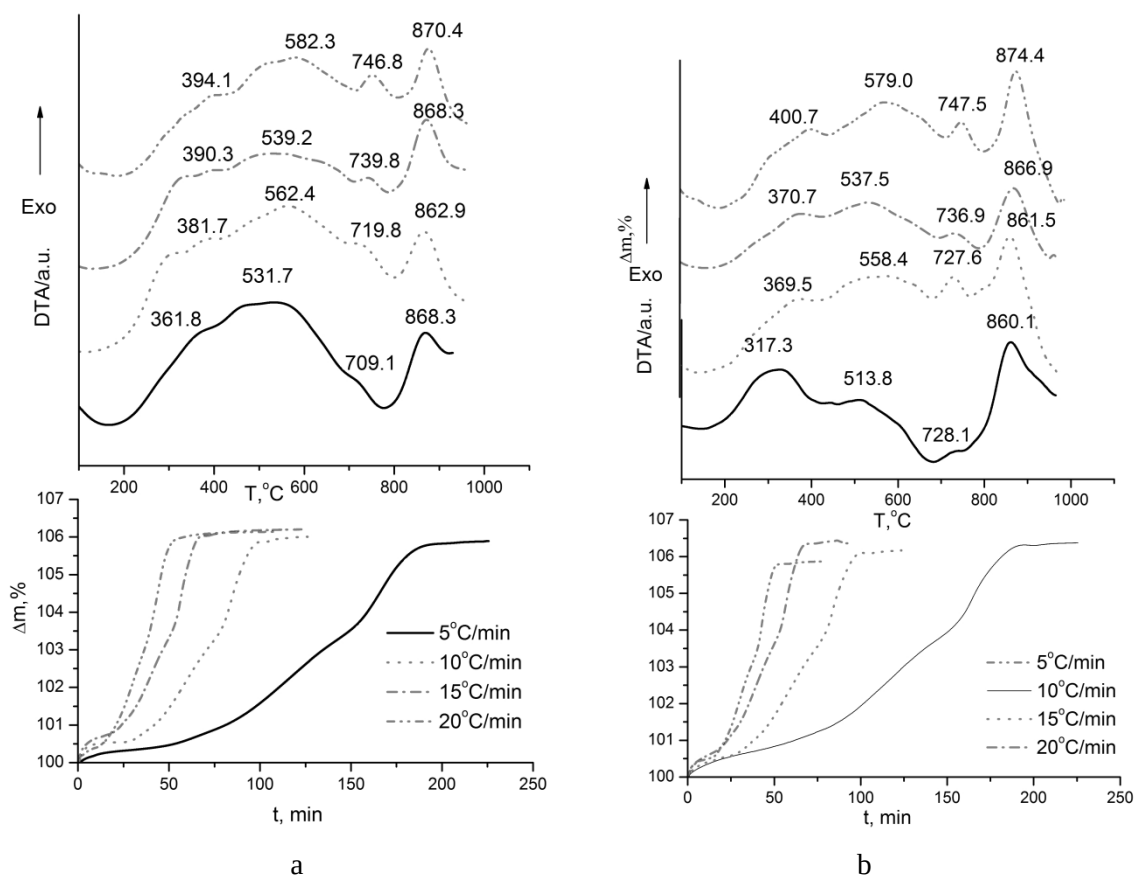
Table 1. Composition of the copper slag, mass. %

Sample №	O	Si	Fe	Cu	Zn	Na	Mg	Al	Ca	Ti	S
1.1	18.8	17.42	60.06	-	2.2	-	0.83	-	0.69	-	-
1.2	7.76	0.5	11.92	56.19	-	-	-	-	-	-	23.63
1.3	21.57	15.92	50.19	0.78	1.41	0.93	-	3.12	3.18	0.41	-
1.4	24.37	11.46	54.71	0.95	2.12	1.08	-	2.57	1.74	-	-
1.5	16.47	18.26	61.51		2.34	-	0.99	-	0.42	-	-
1.6	27.13	15.85	49.07	0.65	1.69	-	0.45	1.95	1.72	-	0.34
1.7	28.5	11.01	53.29	-	1.17	-	0.61	1.39	2.32	-	1.01

DTA-TG curves recorded during the experiments are shown in Fig. 1. All TG curves show an increase in sample mass on raising the temperature, up to the maximum weight of the sample. This weight gain is accompanied by the registration of a broad exothermic effect in the DTA curves in the temperature range of 100 - 980°C. The nature of this broad peak, where four maxima can be differentiated, indicates the complexity of the processes. The separate $T_{\max}$ followed, with minor exceptions, the

general pattern of the shift toward higher temperature values at higher heating rates. The discrepancies can be explained with the non-homogeneous chemical composition of the slag. No clear trend in the changes of the temperature maxima with increasing O₂ content at the same rate of heating are noticed.

The analogous nature of the DTA-TG curves in all series of experiments is a proof of the uniform mechanism of oxidation of the copper slag, regardless of the oxidizing gas used.



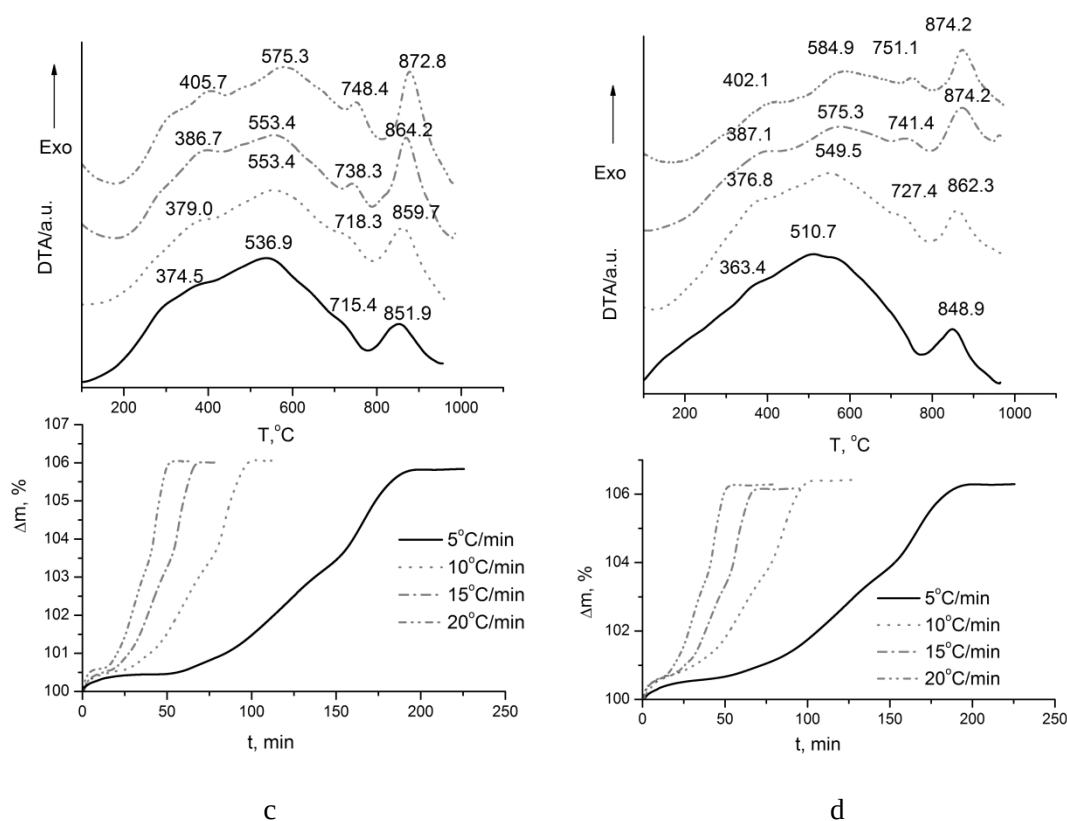


Fig. 1. DTA – TG curves of copper slag oxidation: (a) 21 vol% O₂; (b) 43 vol% O₂; (c) 63 vol% O₂; (d) 100 vol % O₂

The powder diffraction patterns of the oxidized slags are similar as well. The XRD diffraction patterns of the starting and the oxidized slag are shown in Fig. 2. The main crystalline phases in the starting slag are fayalite and magnetite. Small amounts of other silicate phases of calcium, magnesium and iron can also be detected. The oxidized sample primarily contains hematite and magnetite as crystal components. Cristobalite impurities and traces of other silicate phases can also be found. Most silicate phases are present in an amorphous state in the oxidized sample.

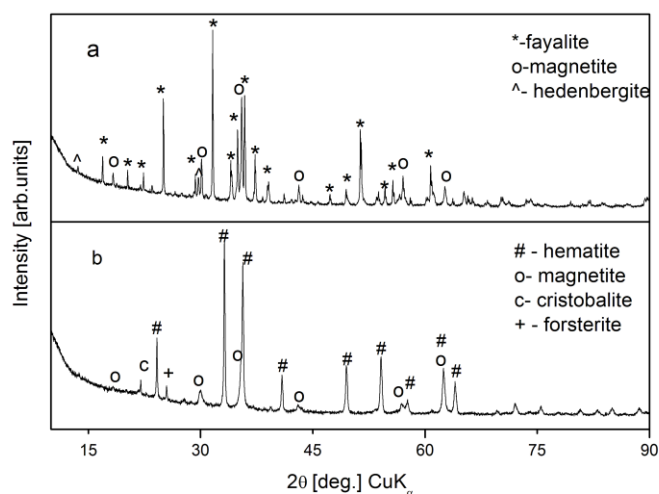


Fig. 2. XRD patterns of starting (a) and oxidized (b) slag

Our studies revealed that the heating rate has no significant influence on the average size of the crystallites of the obtained phases - hematite and magnetite (Fig. 3).

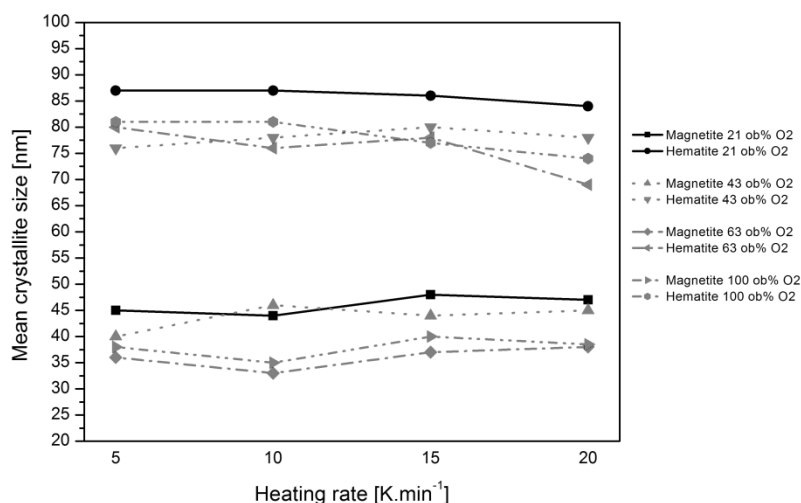


Fig. 3. Dependence of the mean crystallite size on the heating rate

The influence of the atmosphere during the heating of the slag on the final phase composition and on the particle size of the products is shown in Figure 4. The increase in the concentration of oxygen in the oxidizing gas mixtures leads to a slight tendency of increasing the amount of iron oxides (magnetite and hematite) and reducing the amount of silicate phase in the crystalline component of the sample (Fig 4a), which is an indication of more complete amorphization of the silicate phases by treating in an oxygen environment. A significant influence on the average size was observed by changing the oxygen concentration in the atmosphere of the thermal treatment. By increasing the amount of oxygen in the atmosphere, the average size of the magnetite and hematite particles decreases and reaches its minimum at 63% O₂. The subsequent increase in the size of the particles by oxidizing with 100 vol % O₂ is negligible.

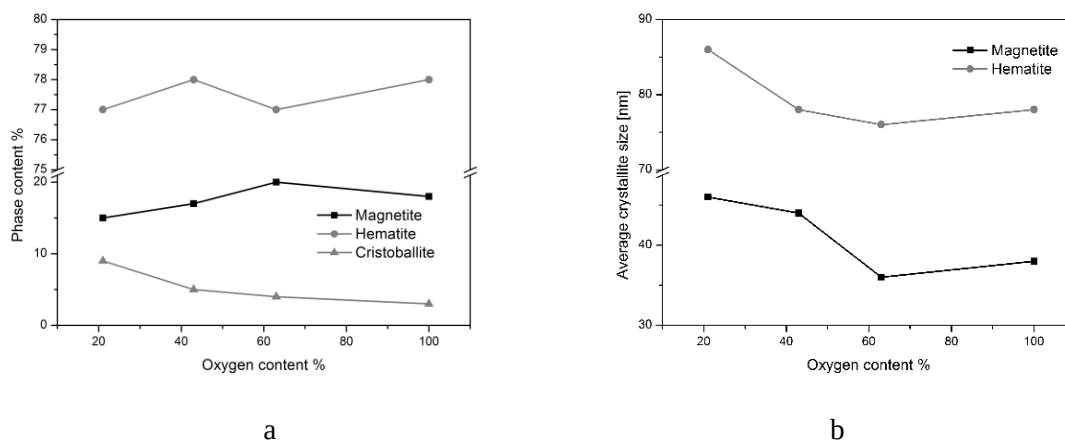


Fig. 4. Dependence of the phase composition (a) and average crystallite size (b) of the oxidized slag on the O₂ content

The registered $T_{\max}$ in the DTA curves (Fig. 1) were used to determine the kinetic parameters (activation energy and pre-exponential factor) of the oxidation process. The plots of the functions $\ln(\beta/T_p^2) = f(1/T_p)$ are presented in Fig. 5 and the calculated values of activation energy and pre-exponential factor – in Table 2.

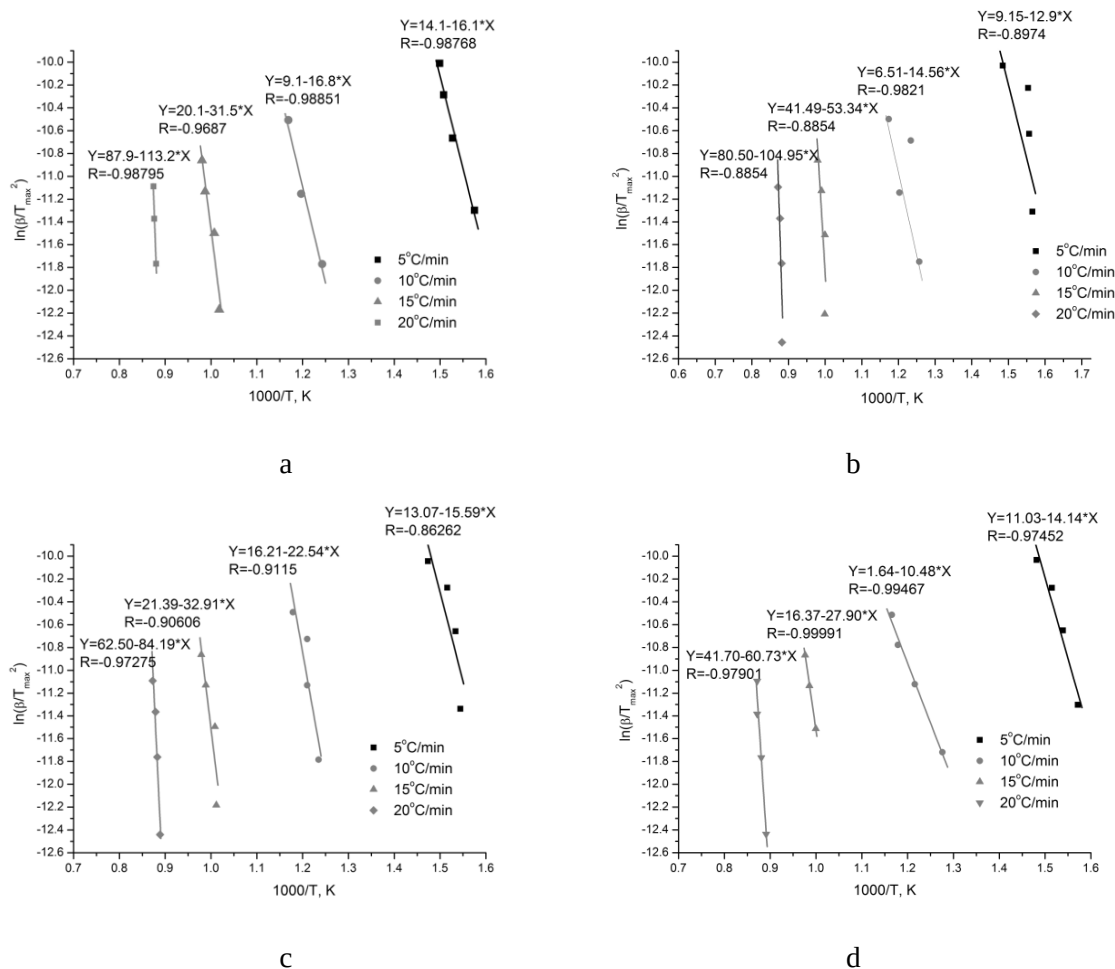


Fig. 5. Kissinger plot of the values of $\ln(\beta/T_{\max}^2)$ as a function of $10^3/T_{\max}$ calculated from the $T_{\max}$ registered in the DTA curves: (a) 21 vol% O₂; (b) 43 vol% O₂; (c) 63 vol% O₂; (d) 100 vol % O₂

Table 2. Kinetic parameters calculated by thermal analysis

Parameters	Gas mixtures			
	21 vol% O ₂	43 vol% O ₂	63 vol% O ₂	100 vol% O ₂
I Peak				
<i>E</i> , kJ.mol ⁻¹	134	139	262	941
ln <i>A</i> , s ⁻¹	16.8	11.9	23.5	92.6
R	-0.9876	-0.9885	-0.9687	-0.9879
II Peak				
<i>E</i> , kJ.mol ⁻¹	107	118	443	872
ln <i>A</i> , s ⁻¹	11.7	8.77	45.5	85.1
R	-0.8974	-0.9477	-0.8854	-0.8854
III Peak				
<i>E</i> , kJ.mol ⁻¹	129	187	273	699
ln <i>A</i> , s ⁻¹	15.8	19.3	24.9	66.9
R	-0.8626	-0.9115	-9061	-0.9727
IV Peak				
<i>E</i> , kJ.mol ⁻¹	117	87	231	504
ln <i>A</i> , s ⁻¹	13.6	3.9	19.7	45.8
R	-0.9876	-0.9946	-0.9999	-0.979

R = Correlation coefficient

There is a trend of increasing the values of the activation energy at each peak on increasing the heating rate. The values of the activation energy, calculated by the first and second peaks, are relatively close. They are also close to the average values reported by Sanders and Gallagher (2003) (about 120 kJ mol⁻¹) for the oxidation of magnetite. The third maximum of the DTA curves is associated with fayalite oxidation and decomposition to iron oxides and amorphous silicate mass. The values of the activation energy, calculated by the third maximum, are in the range of 231 - 443 kJ mol⁻¹, which are different from those reported by Gabbalah *et al.*, (1978) for the oxidation of single crystal synthetic fayalite. The nature of the fourth maximum is not completely clear. It may be due to some structural transitions of the silicate mass, as supposed by Gabbalah *et al.*, (1978) or to some effects due to the grain size distribution.

As our XRD studies show (Fig. 2), except fayalite, the initial slag also contains small quantities of other phases, which also undergo changes during the heat treatment. Moreover, the process is rather complex. Strict separation of the different stages is impossible. Each subsequent stage begins before the previous is fully completed. This is the reason for the differences between the kinetic parameters calculated by us and those of pure single phases reported in the literature.

Reduction in the values of the activation energy was observed with increasing content of oxygen in the oxidizing gas mixture (Fig. 6). The strongest reduction (almost two-fold) is observed in the final stage of the process. This intensification of the process is consistent with the decrease in the average size of the crystallites of magnetite and hematite in the final phases established by us (Fig. 4).

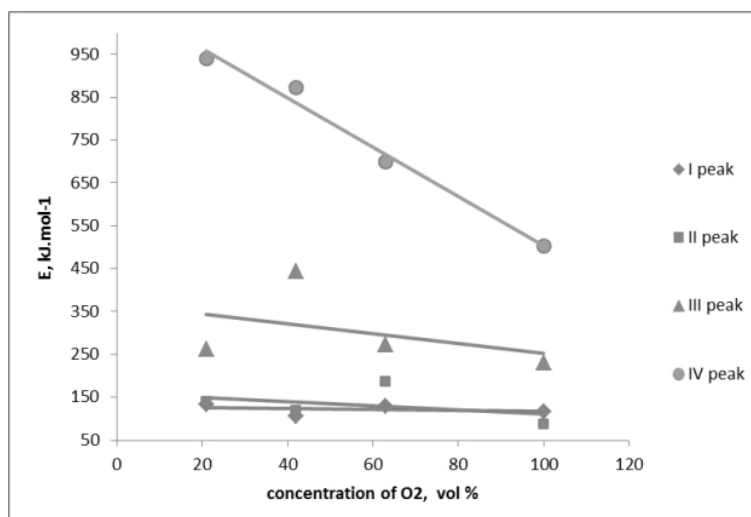


Fig. 6. Dependence of the activation energy on the oxygen content in the gas mixtures.

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