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Phase transformations of siderite ore by the thermomagnetic analysis data

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ABSTRACT

Thermal decomposition of Bakal siderite ore (that consists of magnesium siderite and ankerite traces) was investigated by thermomagnetic analysis. Thermomagnetic analysis was carried-out using laboratory-built facility that allows automatic registration of sample magnetization with the temperature (heating/cooling rate was 65°/min, maximum temperature 650 °C) at low- and high-oxygen content. Curie temperature gradually decreases with each next cycles of heating/cooling at low-oxygen content. Curie temperature decrease after 2nd cycle of heating/cooling at high-oxygen content and do not change with next cycles. Final Curie temperature for both modes was ~320 °C. Saturation magnetization of obtained samples increases up to 20 Am^2/kg. The final product of phase transformation at both modes was magnesioferrite. It was shown that intermediate phase of thermal decomposition of Bakal siderite ore was magnesiowustite.

1. Introduction

Siderite is a mineral of calcite group with chemical formula $FeCO_3$. It is a widespread iron mineral which finds application in various industries (iron industry, mining, etc.). Natural samples of siderite often show a significant amount of substitution of iron in the lattice by magnesium, calcium, manganese [1]. The pure siderite is rarely found. Siderite is commonly found in hydrothermal veins. It may be also deposited by sedimentary processes.

Siderite crystallizes in the trigonal crystal system, and is rhombohedral in shape, typically with curved and striated faces. The color of siderite ranges from yellow to dark brown or black, the latter being due to the presence of manganese. This is an antiferromagnetic mineral with Neel temperature of 38 K, which is paramagnetic at ambient temperature [2,3]. Moreover, metamagnetism was reported to be magnetic property of siderite, namely, antiferromagnetic lattice gradually transforming into a ferromagnetic lattice when exposed to strong magnetic fields of 12–14 T.

Nowadays, the usage of weakly magnetic iron ores for iron production is of very importance, because the deposits of magnetite iron ores are becoming exhausted. The main problem that interferes the usage of weakly magnetic siderite ores for iron production is complexity of their beneficiation, i.e. separation of siderite from other admixtures in the ore. In this case, thermal decomposition of the mineral siderite is the topic of interest because of possibility of strongly magnetic phase formation without any reducing agents in contradistinction to goethite and hematite [4,5].

Thermal decomposition of siderite in different atmospheres (air, oxygen, nitrogen, etc.) is widely used for different applications. For example, thermal decomposition characteristics of siderite are utilized in paleomagnetic studies [6]. Interest for such investigation is caused by transformation of siderite into magnetite and maghemite which can potentially carry a chemical remanent magnetization. As far as roasting of siderite yields to high pore volume and high surface area species, the end products also could be used to capture the sulfur dioxide (SO_2) in a wide temperature range. The decomposition product of siderite is also used as a natural brown pigment in the paint industry [7]. Besides, magnetite is present in the ALH84001 Martian meteorite thought to be produced by thermal decomposition of siderite [8]. However, second possibility of magnetite presence in the ALH84001 is of biogenic origin [9,10].

The final products of thermal decomposition of mineral siderite are generally hematite in an oxidizing atmosphere [11,12], magnetite in a carbon dioxide atmosphere, and magnetite and wustite in an inert atmosphere or in vacuum [13,14]. Identification of decomposition products of natural siderite is difficult due to the significant amount of substitution of iron in the lattice by magnesium, calcium, manganese [15].

The aim of present work was to investigate the thermal decomposition of siderite ore of Bakal's deposits at low- and high-oxygen content by the method of thermomagnetic analysis.

2. Materials and methods

The samples of Bakal siderite ore (the western slope of the Southern Urals) that was grinded up to 0.07 mm were investigated.

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Thermomagnetic analysis was performed with laboratory-built facility that allows automatic registration of sample magnetization as a function of temperature. Phase transformations of siderite ore was carried out in quartz mini-reactor, at low- and high oxygen content under heating up to 650 °C. The rate of sample heating/cooling was 65°/minute.

Chemical composition of the samples was investigated using X-Ray Fluorescence analysis (XRF). X-Ray Fluorescence analysis of the samples was performed at Thermo ARL Optim'X spectrometer equipped with a Rh-anode X-ray tube of 50 W power, goniometer with three crystals (AX06, PET, LiF 200), and two detectors (FPC, SC). Preparation to XRF analysis included the samples milling to the powder and pellet pressing with boric acid. Measurements were done according to the requirements of OptiQuant software.

Magnetic characteristics of initial and obtained samples were determined using magnetometer with Hall sensor. An external magnetic field of magnetometer varied in the range of 0 to ± 0.45 T.

Mineral composition of siderite ore and products of its thermal decomposition were determined by the methods of X-Ray Diffraction (XRD) (X-Ray diffractometer DRON-4). The XRD phase diagnostics was performed using [16] by detected d-spacing.

Thermogravimetric analysis of siderite ore was carried out in air at a heating rate of 10°/min in the 20–1000 °C range using a Derivatograph Q-1500D (Paulik, Paulik and Erdey, MOM, Budapest) with TG-DTA (differential thermal analysis).

3. Results and discussion

Chemical composition of siderite ore determined by the method of XRF is shown in Table 1.

It was shown by the XRD-data that the initial sample of siderite ore was composed by siderite ($FeCO_3$) and ankerite ($Ca(Fe, Mg)(CO_3)_2$) (Fig. 1). Characteristic peaks (d-spacing) (Å) for siderite are shown in Table 2. However, siderite thought to be a complex of iron-magnesium carbonates solid solution series. Characteristic peaks: 2.889 Å and 2.539 Å are typical for both ankerite and dolomite. We attributed these peaks for the phase of ankerite according to the initial chemical composition of the sample.

Shift of characteristic peaks of siderite compared with the standard from Powder Diffraction File (PDF) database, probably, could be interpreted by isomorphic substitutions of iron in the structure of siderite by magnesium.

It was shown by the DTA method that by sample heating up to 1000 °C the weight loss was equivalent to 37% (Fig. 2). As the analyzed samples consist mainly of carbonate minerals, we could relate such weight change with the loss of CO_2. The moderate weight loss (about 2%) in the range 25 – 400 °C is attributed to the residual water loss.

The curve of differential thermogravimetric analysis (DTG) points up the most significant change of weight in the range from 460 to 670 °C due to decarbonization. It was observed that start decomposition temperature of investigated siderite (460 °C) is higher than that of pure siderite (350 °C), which is attributed to the presence of Mg impurities in siderite ore [7]. Obtained data correspond with literature data [7,17] for decomposition of natural siderite containing Mg impurities. It was shown that maximum peak at DTG-curve (640 °C) is shifted by almost 100 °C to the area of higher temperatures in comparison with literature data (550 °C) [17]. There is another small endothermic peak at a temperature ~750 °C which we refer to thermal decomposition of ankerite. It was shown on thermogravimetric (TG) curve that contribution of this peak to total weight loss is only 2%. Consequently, the remaining amount of weight loss (33%) can be attributed to siderite. We could suggest that the oxidation can also occur and is observed as exothermic effect on the DTA curve in the temperature range 650–900 °C.

Initial sample of siderite ore does not demonstrate magnetic properties and its saturation magnetization was ~0.3 Am^2/kg.

Phase transformations of siderite ore were studied by thermomagnetic analysis (up to 600 °C) at low-oxygen content (Fig. 3).

There is no peak on heating curve, while magnetization of the sample increases considerably after cooling. So, we could conclude that magnetic phase formation occurs at temperatures above Curie temperature of obtained sample. Authors [6] report that formation of magnetic phase is already observed at the thermomagnetic curves at 400 °C with Curie temperature approximately 580 °C. We haven't observed this in our experiments. Moreover, Curie temperature determined by differentiating the cooling curve is 508 °C. This value is slightly lower than Curie temperature of pure magnetite (580 °C). Measured Curie temperature is typical for series of solid solutions of magnetite – magnesioferrite (magnesiomagnetite) with ~9% MgO according to equation of Curie temperature dependence on magnesium content [18]:

$$a_{MgO} = 85 - 0,149 \cdot Q$$

where a_{MgO} is content of MgO, and Q is Curie temperature.

XRD pattern for obtained sample is shown at Fig. 4.

In comparison with initial sample, the intensity of siderite peaks with d-spacings (Å): 2.776; 2.134; 1.951; 1.717; 1.508 decreases after the first cycle of thermomagnetic analysis. Characteristic peak of ankerite with d-spacing 2.894 Å is also observed. At the same time, characteristic peaks of magnesiomagnetite (with d-spacings (Å): 2.978; 2.539; 2.103; 1.717; 1.618; 1.487) and magnesiowustite (with d-spacings (Å): 2.462; 2.134; 1.508) appeared. One could attribute peaks of magnesiowustite to mineral with the following composition: $(MgO)_{0,432}(FeO)_{0,568}$ (PDF 77-2368). At the study [13] it was also detected magnesiowustite as final product of thermal decomposition of natural siderite at high vacuum.

Thus, we could propose the model of phase transformation of siderite: at the first stage siderite decomposes with formation of phase $Mg_{1-x}Fe_xO$ ($0 < x < 1$) and carbon dioxide. At the second stage partial oxidation of Fe (II) occurs with formation of magnesiomagnetite $Mg_{1-x}Fe_xO{\cdot}Fe_2O_3$.

Further, thermomagnetic analyses of the sample were carried-out at low- and high-oxygen content (Fig. 5). The behavior of the samples depending on different oxygen content differs significantly.

During the second cycle of heating/cooling at low-oxygen content the magnetization of the sample continues to increase. Thus, the formation of a magnetic phase continues due to the partial oxidation of magnesiowustite and decomposition of the residual siderite. Curie temperature has not changed significantly compared to the first cycle (Fig. 3). During the second cycle of heating/cooling at high-oxygen content the magnetization of the sample decreases. Curie temperature (328 °C) significantly decreases compared to the first cycle. One could observe two peaks on cooling curve and, therefore, we could conclude formation of two phases in the sample.

Subsequent dynamics of change of Curie temperature and magnetization during all 20 cycles of heating/cooling are shown at Fig. 6.

During initial 7 cycles of heating/cooling at low-oxygen content the magnetization of the sample increases (Fig. 6a) due to partial oxidation of Fe (II) in magnesiowustite and thermal decomposition of siderite. So, one could conclude, that magnetic phase formation occurs. Obviously, the ratio of Fe (II)+Mg (II)/Fe (III) after 7 cycles is about

Table 1
Chemical composition of siderite ore.

Component	wt%
Fe_2O_3	27.6
MgO	13.5
SiO_2	2.1
Al_2O_3	1.3
CaO	1
others	< 1