

# ФІЗИКА ТВЕРДОГО ТІЛА, ЗБАГАЧЕННЯ КОРИСНИХ КОПАЛИН

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## ON FORMATION OF ELECTRICALLY CONDUCTIVE PHASES UNDER ELECTROTHERMAL ACTIVATION OF FERRUGINOUS CARBONATES

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## ПРО МЕХАНІЗМИ УТВОРЕННЯ ЕЛЕКТРОПРОВІДНИХ ФАЗ ПІД ЧАС ЕЛЕКТРОТЕРМОАКТИВАЦІЇ ЗАЛІЗОВМІСНИХ КАРБОНАТІВ

**Purpose.** Study of the formation of an electrically conductive phase in carbonates using siderite as an example and determination of the temperature dependence of its formation and silicon content during simultaneous heating and the action of a weak electric field.

**Methodology.** Analysis and generalization of the results of experimental studies. Physicochemical analytical studies have been performed using electron and optical microscopy, petrographic and X-ray phase analysis, thermogravimetric analysis and differential scanning calorimetry, and gas chromatography. Phase equilibria in the “iron oxides – carbon – carbon oxides” system have been evaluated using data on the standard change in the Gibbs energy Evaluation.

**Findings.** Formation of electrically conductive phases in siderite has been studied. The dependence of new phase formation on heating and the magnitude of the electric field strength have been determined. The regularities of the change in threshold temperatures of phase transitions in samples of siderite and calcite containing silicon impurities have been established.

**Originality.** Due to the thermally stimulated increase in the concentration of mobile charge carriers in intergranular space, the electric field of point charges takes the prominent part in the formation of the end product of chemical reactions. The additional effect of electric current on the increasing destabilization of chemical bonds between surface atoms leads to the formation and transport of ions, to a decrease in the energy barrier of nuclei formation of the electrically conductive phase near the active centres. The abrupt increase in electrical conductivity is due to the spontaneous formation of the nuclei of a new phase and the transition of ionic conductivity to a mixed one or an electronic one primarily. A composite semiconductor is formed as a result of electrothermal activation of siderite. This semiconductor consists of a matrix-semiconductor representing the initial mineral and is penetrated by parallel-oriented high-conductivity threads.

**Practical value.** Experimental results show that such processes occurring in rock are quite real under the conditions of the earth’s crust, and the physical values of thermodynamic quantities (factors of metamorphism) are sometimes overestimated significantly in the interpretation of various geological events.

**Keywords:** *siderite, electric field, phases, temperature, electrothermal activation, electrical conductivity, ions*

**Introduction.** The physicochemical processes occurring in the rock mass are mainly considered as a result of the action of temperature and mechanical effects (compression, extension, shear, etc.). These two factors are the main ones in determining the rock metamorphism. The effect of electric fields, especially weak ones, in this process is not taken into account. Perhaps this is due to the traditional ideas about the principle possibility of phase and structural transformations in condensed matter only under the influence of high value thermodynamic parameters.

Interpretation of the features of physical and chemical transformations in rock is often limited to the action of thermal field and pressure, taking into account the partial pressure of volatile components in the fluids. Probably, this approach is substantiated by the fact that the action of a weak electric field on solid phases does not cause noticeable changes. Simple estimates show that the energy of thermal motion of molecules exceeds the energy of weak electric fields by several orders of magnitude. So it is a convincing argument in favour of neglecting their effect. Such point of view has been formed due to experimental PT diagram of elements, property data of various chemical compounds, metals, alloys, minerals and rocks in a wide range of pressures and temperatures. Virtually all analyses of the obtained geological and mineralogical data, their interpretation and conclusions are based on the regularities deduced from physical experiments.

Modern petrophysics has a number of relevant tasks connected with the study of phenomena, mechanisms and regularities of electrification, radio-wave electromagnetic and acoustic emission of minerals and rocks under various types of excitation. Relevance is due to both the fundamental challenge of phenomena and mining problems. In particular, one of the tasks is to study the changes in electrical characteristics of minerals and rocks with the simultaneous action of several different factors. These factors are similar to natural physical and chemical ones – pressure, temperature, concentration, electric and magnetic fields.

Information on new phenomena, regularities, properties and characteristics of mineral systems is necessary for increasing the efficiency of electrical methods for minerals prospecting, developing new search criteria and methods for minerals enrichment, improving technological processes in the mining industry, creating energy-efficient processing of some raw materials to produce a marketable end product. The mechanism of iron ore formation (possibly as a result of siderite decomposition) and conditions for the formation of high-grade iron ore, the mechanisms of graphite formation (diamond growth in primary deposits) from calcite carbon, as the most probable source of atomic carbon, still remain undetermined. In nature, siderite is often found in clay-band and blackband ironstones, forms associations with ores of various metals, and is an integral part of Precambrian iron ores. Considerable reserves of siderite are high quality iron ore and have commercial value. Moreover, siderite is of academic interest when

studying the formation of texture and structure of ferruginous quartzites.

Considering the fact that several physical factors have an effect on mineral systems in the earth's crust, it is natural to assume that there is some "competition" between the types of impacts. The predominant role of any of the factors – pressure, temperature, electric or magnetic field strength, leads to the formation of different phases in the same physicochemical system. A mineral system consisting of atomic carbon can be an example. Deviation from equilibrium leads to the formation of diamond, graphite or other carbon phases in the system. In accordance with the principle of the displacement of the chemical equilibrium, the external action that leads the system out of thermodynamic equilibrium causes processes in it that tend to weaken the effect of the exerted influence. Thus, the increase in pressure stimulates processes leading to decrease in volume, and in some cases to the formation of the so-called high baric phases. An increase or decrease in temperature leads to chemical processes corresponding to the absorption or release of heat respectively. It can be assumed that this way corresponds to the development of physicochemical processes with a change in the electric field strength. In this case, the equilibrium position and processes in the system consisting of semiconductors will shift in the direction of weakening the effect of the acting field. Chemical reactions will occur in the system with the formation of a phase with a greater electrical conductivity.

Overall, experimental studies of the properties of minerals and rocks under the influence of a complex of physical parameters, along with geological and geophysical data, significantly expand the understanding of the physicochemical processes occurring in the earth's crust.

In particular, such studies were caused by the great need of various industries in creating new technically efficient and economically viable ways of producing superhard materials and composites based on them.

**Analysis of the recent research and unsolved aspects of the problem.** The high activity of scientific research on the physical properties of minerals of the carbonate group at various temperatures and pressures was in the period of the 60–80s of the last century. At this period there was a boom in mining and metallurgical industry, geophysics, and earth sciences. For the last three decades, a significant amount of scientific research has been directed to the search for conditions for obtaining atomic carbon and the mechanisms for the formation of new carbon and carbon-containing phases. In particular, such studies were caused by the great need of various branches of industries in creating new cost-effective ways of superhard materials manufacturing and their composites. There should also be highlighted key works in the study of the stability of thermally activated carbonates (siderite, calcite, etc.), the magnetic and electrical properties of newly formed components at different pressures and temperatures. These are the works of such authors as S.K. Grebnev & N.A. Vasiutinskii, V.I. Bagin, E.I. Parkhomenko, L.F. Vereshchagin,

Yu. A. Litvin, A. V. Bobrov, V. V. Sobolev, J. D. Bernal, M. Seguin, J. Janowski, J. M. Coey, J. L. Kulp, P. Kant and others.

Experimental results on the decarbonization process, which is typical for the metamorphism, are given in the paper by E. Parkhomenko & S. Mkrтчchan. Authors studied the change in the electrical conductivity of some carbonate minerals with heating up to 1170 K. In particular, it is established for siderite that the electrical conductivity increases abruptly by two orders of magnitude before the beginning of decomposition  $\text{FeCO}_3 \rightarrow \text{FeO} + \text{CO}_2$ . This effect is observed both in isobaric and isothermal conditions (this result highlights a problem and will be discussed below). The authors suggested that this effect can be manifested due to formation of a special activated state, in which the ionization energy decreases or the mobility of charge carriers increases before the decomposition reaction. Maurice Seguin believes that decomposition of siderite is accompanied by simultaneous reactions:

- 1)  $4\text{FeO} \rightarrow \text{Fe} + \text{Fe}_3\text{O}_4$ ;
- 2)  $3\text{Fe} + 2\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4$ ;
- 3)  $4\text{Fe}_3\text{O}_4 + \text{O}_2 \rightarrow 6(\alpha\text{-Fe}_2\text{O}_3)$ .

The reaction (1) develops only at a temperature higher than 840 K. E. Parkhomenko & S. Mkrтчchan assumed that there are Fe, FeO,  $\text{Fe}_2\text{O}_3$  and  $\text{FeCO}_3$  simultaneously in the temperature range of 780...900 K. The preferential formation of any of the iron oxides (wustite, magnetite, hematite, maghemite) corresponds to a certain field of thermodynamic values, at which this phase is formed with maximum probability.

According to the available experimental data wustite (300...670 K), magnetite (700...760 K), maghemite and hematite (760...1170 K) are formed sequentially when siderite is heated. These data confirm the results of the study of magnetic properties of intermediate phases in the thermal decomposition of siderite obtained by V. I. Bagin et al. So, the authors found that there are two phases in the temperature range 570...700 K, and one phase becomes predominant with temperature increasing. The magnetization of the main phase disappears at a temperature of up to 730 K (the magnetization arises at 570...670 K). Maghemite is converted to hematite at temperature of 730...740 K, however, maghemite continues to form almost to 820 K with a Curie point of 870 K. Maghemite is the main phase almost to the temperature of 970 K, but then goes into a stable phase – hematite in accordance with  $\text{FeCO}_3 \rightarrow \text{FeO} \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \gamma\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3$ . The authors of this work have established the features of the thermal decomposition of fine-crystalline and coarse-grained siderite.

Accessory minerals of graphite mineralization such as wollastonite, wustite, garnet, diopside, larnite and forsterite have been obtained for the first time from experiments in the mineral system siderite-calcite-silicon (V. Sobolev, R. Kamkov). These minerals are also present in calciphyres of the Zavalevskiy graphite deposit in Ukraine. It has been shown that the formation of this association of minerals occurs as a result of solid-phase

chemical reactions occurring under the action of an electric field, temperature up to 970 K, and pressure in the range  $(1.5...5) \times 10^5$  Pa. It has been established that an abrupt increase in electrical conductivity for solid samples of siderite was observed at temperatures corresponding to or close to the temperature of siderite dissociation when simple heated. Transformation degree of siderite to other phases in ground samples increased especially not only with an increase of holding time at a temperature exceeding 500 K, but also with a decrease in the heating rate.

Works in the field of phase transformations in coal as a result of electrical influences [1] and phase transformations in solids caused by complex treatment of physical fields [2] give new interpretation of certain ideas about the nature of physical and chemical phenomena in minerals and rocks [3]. This is particularly topical for those caused by the action of electric fields (E. I. Parkhomenko, A. A. Urusovskaia, A. S. Lizun and others).

**Objectives of the article.** The research aims at study of the formation of an electrically conductive phase in carbonates using siderite as an example and determination of the temperature dependence of its formation on silicon content during simultaneous heating and the action of a weak electric field.

**Materials and methods.** Samples of siderite and achromatic iceland spar were used in experiments. Samples were prepared in the form of a cube with an edge length of 1 cm. Micropowders of iceland spar, siderite and silicon were also used; size of grains were in the range of 40...20  $\mu\text{m}$ . The moisture content of samples was 0.1...1.5 %. The average composition of impurities in the initial samples of siderite ( $\text{FeCO}_3$ ) was CaO – 0.8;  $\gamma\text{-Fe}_2\text{O}_3$  – 4.5; MgO – 0.7; MnO – 0.3;  $\text{SiO}_2$ , etc. – <1.5 wt. %.

The investigations were carried out according to the methods described in [1]. Stimulation of chemical reactions was carried out simultaneously by thermal action with a given heating rate and an electric field strength up to  $3 \times 10^5$  V/m. Uniaxial compression of the test samples did not exceed  $(1.5...5) \times 10^5$  Pa. The stabilized voltage was applied to opposite faces of the sample and its value was from 5 to 300 V. The maximum value of the constant current was 0.29 A. Analysis of the experimental data involved already-present and the authors' results. Electronic and optical microscopy, petrographic and X-ray phase analysis, thermogravimetric analysis and differential scanning calorimetry, gas chromatography, experimental installation for electrophysical treatment of materials, etc. were used in the studies.

**Presentation of the main research and explanation of scientific results.** Experimental dependences of the electrical conductivity of solid samples of siderite on temperature for given values of the electric field strength (up to  $3 \times 10^5$  V/m) and pressure  $(4...5) \times 10^5$  Pa in air are shown in Fig. 1. Electrical conductivity  $\lg \sigma$ -vs- $1000/t$  curve ( $t$  – temperature, K) is generally expressed by straight lines inclined to the axis of abscissas. The activation energy is calculated according to the formula

Table

Values of the activation energy of ions at different temperatures

| $\lg \sigma = f(1/t)$ | Legend of the section in the Fig. 1 | Temperature, K | The energy of ion activation, $E$ , eV (Identified phases)                       |
|-----------------------|-------------------------------------|----------------|--|
| 11                    | o-b                                 | 300–480        | 0.020 (FeO)  |
|                       | b-c                                 | 480–570        | 0.064  |
|                       | c-k                                 | 570–935        | 0.28 ( $\gamma\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3$ ) |
| 2                     | o-b                                 | 300–480        | 0.01 (FeO)   |
|                       | b-c                                 | 480–570        | 0.054  |
|                       | c-d-g                               | 570–690        | 0.246  |
|                       | g-h                                 | 690–710        | 2.86 ( $\gamma\text{-Fe}_2\text{O}_3$ )  |
|                       | h-j                                 | 710-jump       |  |
|                       | j-f                                 | 710–725        | 0.07...0.180 ( $\gamma\text{-Fe}_2\text{O}_3$ )                                  |
| 3                     | o-b                                 | 300–480        | 0.014 (FeO)  |
|                       | b-c                                 | 480–570        | 0.050  |
|                       | c-d                                 | 570–625        | 0.80...2.03 ( $\gamma\text{-Fe}_2\text{O}_3$ )                                   |
|                       | d-e                                 | 625-jump       |  |
|                       | e-f                                 | 625–725        | 0.085 ( $\gamma\text{-Fe}_2\text{O}_3$ )   |

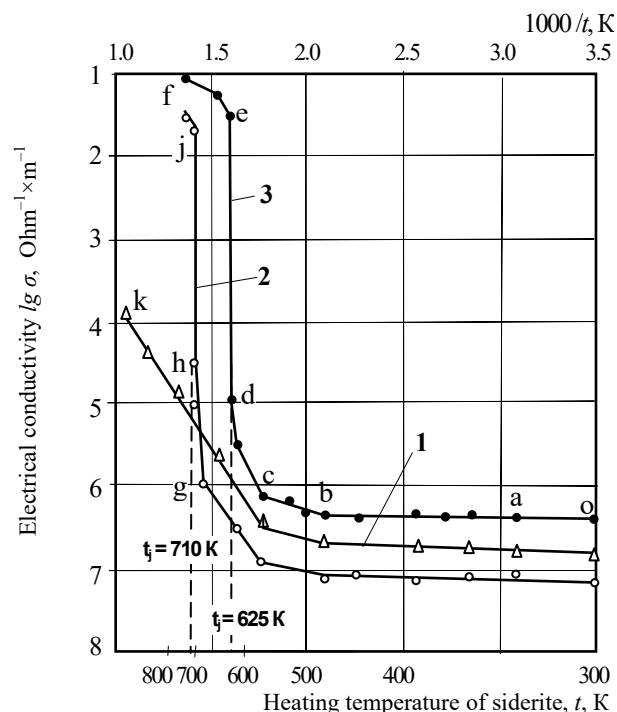


Fig. 1. Change in the electrical conductivity of siderite depending on the temperature at a value of the electric field strength  $E$ , V/cm:

1 – 0; 2 – 55; 3 – 290. Legends of the sections are given below in the Table

$E = 0.2 \text{ tg}$ . The inclination of a line is determined by the activation energy of carriers of the electric current: the greater this angle is, the greater the energy is required for ion activation (Table).

The value of the field strength  $E = 0$  refers to the sample of siderite, which was only heated. The number of kinks and the character of dependence  $\lg \sigma = f(1/t)$  indicate phase transformations in siderite. An abrupt increase in electrical conductivity for the test (solid) samples of siderite occurred at temperatures of 625 K (curve 3) and 710 K (curve 2). Differential thermal analysis of siderite samples testifies that the dissociation corresponds to temperatures of 660...680 K. The maximum heat absorption by heating the test sample corresponds to a temperature of 840 K, i.e. at 130...215 K higher than under the additional action of an electric field.

In all the experiments, the temperature jump ( $t_j$ ) differs little from the initial temperature of siderite dissociation when simple heated. The jump of electrical conductivity during a simple heating process is not observed. The effect is manifested only when the temperature and electric field are simultaneously affected. It is assumed that the reason for an abrupt decrease in electrical resistance is the spontaneous formation of a new phase with predominantly electronic or mixed type of conductivity. Such phase can be hematite, magnetite and the carbon phase. A sample of siderite after electrothermal activation is strongly magnetized. The surface of the fresh fracture contains a black ultra-dispersed phase like smoke-black and amorphous carbon.

The change in the electrical conductivity from temperature, shown in curves 2 and 3, is fundamentally different from curve 1 (pure heating). The regularity of the variation in the shape of curve 1 with simple heating of siderite consists in the presence of two sections: a straight line reflecting the dependence of the electrical conductivity to a heating temperature of 570 K (point c) and at temperatures above 570 K. The main charge carriers are impurity ions in the temperature range 300...570 K. In the temperature range of 570...725 K, the ions of basic elements of the siderite lattice are mostly charge carriers. It can be seen from the graphical dependencies that a change in the type of a charge carrier requires an increase in the activation energy of the ions. The inclination of line increases with temperature growth, and formation of the phase with a mixed type of conductivity (sections of straight lines h-j and d-f) makes this angle about 90°. In the latter case, the activation energy of charge carriers tends to infinity. This may indicate a kinetic mechanism for the formation of a new phase. Growth of the inclination angle indicates both an increase in the activation energy of charge carriers and a significant effect of the electric current on chemical processes in the reaction zone.

According to experimental conditions, the maximum value of the applied current and voltage are stabilized and in accordance with the technical data of the used power source can not exceed 0.29 A and 300 V. The current from several milliamperes jumps up to a stabi-

lized value at the moment of spontaneous formation of a new phase of high electrical conductivity (Fig. 1). The voltage drops from some initial value to several tens of volts simultaneously with the increase in current. Fig. 1 shows the behaviour of electrical parameters. This behaviour repeats itself again and again. In experiments with samples of siderite, differing in the amount of impurities, the marked character (e.g., the jump in electrical characteristics) does not change in principle. Only the initial temperature of the jump, the value of the current in the jump, and the finite value of electrical potential difference across the sample are changing during the abrupt increase in electrical conductivity at constant values of the heating rate, pressure, and the strength of the external electric field.

After the formation of conductive phases (without switching off the electric current), further sample heating sometimes leads to an increase in resistance, which is due to the melting of the electrically conductive phase and the formation of slags (O. V. Orlinska et al.). The process of reducing the electrical conductivity is characterized by a sharp transition to the almost initial values. The reason for the increase in local temperatures is external heating, heat produced by exothermic interactions between solid phases, and heat released as a result of the passage of electric current through the newly formed phases. According to our estimates, the maximum density of current passing through the newly formed phases could reach up to  $6 \times 10^7$  A/m<sup>2</sup>.

Study of phase transformations in ground samples of siderite, especially mixtures of siderite and silicon powders, arouses much interest. By varying the content of the addition of silicon powder (no more than 70 %) to siderite powder, the temperature of the jump in electrical conductivity with increasing silicon content decreased and the temperature was about 400 K at 70 % Si (Fig. 2). Additions of silicon make the temperature difference to 430 K.

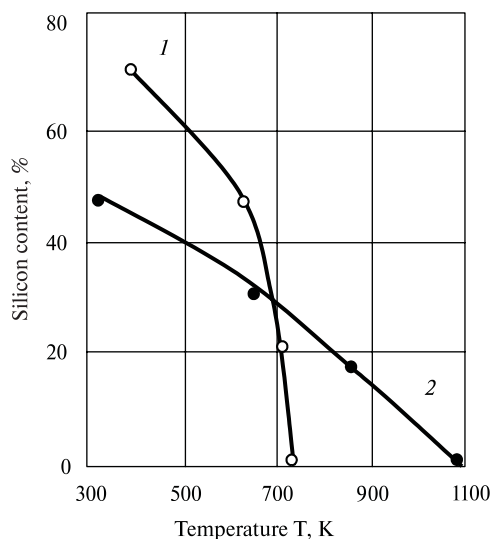


Fig. 2 Pattern of temperature drop during phase change depending on silicon content:  
1 – in siderite; 2 – in calcite

The temperature of an abrupt change in electrical conductivity depending on the silicon content ranges from 1100 K (Si = 0 %) to 325 K (Si = 45 %) under the electrothermal treatment of ground iceland spar in a mixture with silicon powder (Si content is up to 45 %, Fig. 3, curve 2). These results show that such processes occurring in rock are quite real under the conditions of the earth's crust, and the physical values of thermodynamic quantities (factors of metamorphism) are sometimes overestimated significantly in the interpretation of various geological events.

Maghemite is the main new phase of iron oxides to the temperature of 970 K, but then goes into a stable phase – hematite in accordance with  $\text{FeCO}_3 \rightarrow \text{FeO} \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \gamma\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3$ . X-ray phase analysis did not detect FeO in siderite treated at a temperature of 730 K. The main reliably identified phases are  $\text{Fe}_3\text{O}_4$ ;  $\gamma\text{-Fe}_2\text{O}_3$ ;  $\alpha\text{-Fe}_2\text{O}_3$ . Taking into account the presence of the gas phase (CO and CO<sub>2</sub>), the system of listed components will represent a typical four-phase, non-invariant system in which no state changes are possible without decreasing the number of phases. The stability of such system is easily calculated from the model proposed by G. G. Mikhailov et al.

X-ray patterns of siderite samples showed lines with very low intensities of 0.336, 0.203, 0.170 and 0.123 nm, which correspond to interlayer distances in graphite  $d_{002}$ ,  $d_{101}$ ,  $d_{004}$  and  $d_{110}$ . It is assumed that the observed low intensity of the main line (002) may be due to a large content of another carbon phase – graphene, which does not have these lines. The origin of the nucleus of the carbon phase is directly related to fluctuation phenomena in the intergranular space supersaturated by atomic carbon and formed as a result of the dissociation of carbon oxides. The final identification of the carbon phases will be carried out using Raman spectroscopy.

Analysis of the results of more than a hundred experiments indicates that the final product will always be at least one phase represented by a series of threads with

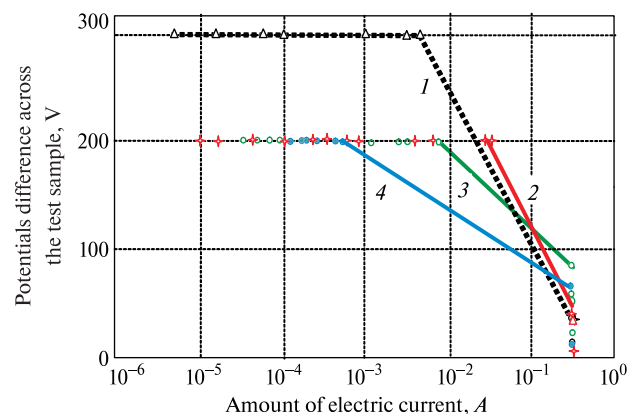


Fig. 3. Current voltage characteristic:

1 – ground siderite without additives; 2 – mixture of ground samples of siderite (85 %) and silicon (15 %); 3 – mixture of ground samples of siderite (55 %) and silicon (45 %); 4 – mixture of ground samples of siderite (30 %) and silicon (70 %)

higher electrical conductivity than the initial sample has before the additional action of the electric field on the chemical reaction. For example, the permittivity ( $\epsilon$ ) of the initial phase of siderite is 7 at a frequency of  $10^2$ , but newly formed maghemite and hematite has permittivity about 5–7, magnetite – 10.6, and graphite – 10–15. Magnetite and graphite are good conductors of electrons. Thus, a composite semiconductor is formed as a result of electrothermal activation of siderite. This semiconductor consists of a matrix representing the initial mineral and is penetrated by parallel-oriented high-conductivity threads.

The features of the effect of an abrupt increase in the electrical conductivity of siderite and its derivatives during the electrothermal activation of phase transformations were investigated by V.V. Sobolev et al. An abrupt change in electrical conductivity was reliably recorded in all experiments. The fundamental difference between the interpretation of the results obtained in this study from the conclusions of E. Parkhomenko & S. Mkrtchyan is that only with the additional electric stimulation of siderite (voltage in the range of 5...300 V) a new stable phase with a high electrical conductivity is formed abruptly. In the experiments of those authors, the measurement of the electrical resistance of siderite in each experiment was carried out continuously, i.e. a weak electric current passed through a thin sample of siderite at a potential difference across the sample of about 5...8 V.

The abrupt change in electrical conductivity of siderite does not occur during simple heating and the absence of an external electric field. It is known that FeO and CO<sub>2</sub> are formed as a result of the decomposition of siderite under heating. 48-hour observations have established that phase transformations in siderite did not occur under the influence of an electric field of weak intensity and temperatures from room temperature to 295 K. The energy of a weak electric field is much less than the thermal energy of molecules. In this connection, questions arise as to what effect the electric field can have, as well as what reasons and mechanism stimulate the formation of electrically conductive phases in the case of an additional action of a weak electric field on thermally activated siderite. Perhaps it is appropriate to recall the famous Le Chatelier's principle, which states that "when any system at equilibrium is disturbed the system will adjust itself in such a way that the effect of the change will be nullified". This principle can be used when describing the change in the state of a thermally activated system affected by an external electric field.

The advantages of electrothermal action in comparison with the action of either a thermal or an electric field are evident from the experimental results. But the regularities of nuclei formation and their further growth, from the point of view of physical mechanisms, are the same. The main difference consists in shifting the temperature thresholds towards a significant decrease according to experimental data obtained only by heat treatment.

Disorder caused by temperature increase is accompanied by the appearance of vacant anionic and cationic

sites. In the absence of an electric field, ion transition from the lattice sites to interstitial positions and vacant lattice points run disorderly, preserving the electroneutrality condition. Due to the thermally stimulated increase in the concentration of mobile charge carriers in intergranular space, the electric current affects the organized displacement of these carriers and the formation of the end product of chemical reactions. The additional effect of electric current on the increasing destabilization of chemical bonds between atoms of surfaces leads to the formation and directional transfer of ions, to a decrease in the energy barrier of nucleation of the electrically conductive phase, and to a decrease in their critical size. A.A. Chernov & L. I. Trusov, M. I. Molotskiy showed that the probability of the formation of a critical nucleus near a charge (for example, near an edge dislocation) increases by a factor of  $10^{22}$  in comparison with a defect-free surface. The probability of formation of ions, potential reaction catalysts, increases substantially as a result of bond breaking under the influence of an electric field. Quantum-mechanical estimates of the stability of the chemical bonding of small molecules in the ion field indicate the catalytic function of the ion field strength in an elementary chemical act. The estimates were calculated for the system "chemical bond of a small molecule – Coulomb centre" in the temperature range of 0...1000 K.

The formation of a new electrically conductive phase can be illustrated by a scheme for the development of the reaction zone using the example of the interface of two grains, Fig. 4. Destabilization of the siderite lattice as a whole increases with the temperature growth. Bonds on the surfaces of grains become unstable, which activates the breaking of chemical bonds and increases the concentration of mobile components in the intergranular space, respectively. Electric current stimulates the formation of electrically charged particles. The reaction zone is localized at the interface between the grains and phases of the reactants and products.

Chemical processes in solid-phase reactions begin from the formation of individual molecules on internal surfaces (in the volume of the phase) (Fig. 4, *a*). Then, the individual nuclei of the new phase begin to form on the surfaces (Fig. 4, *b*) and, accordingly, new boundaries appear between the initial grain of the crystal and the new phase. At the next stage (Fig. 4, *c*), the reaction rate reaches a maximum, begins to decrease when the growing nuclei begin to fuse, forming a continuous layer (Fig. 4, *d*), the boundaries of which gradually move deep into the siderite grains.

Another result that should be noted is directly related to the formation of a "current thread" (Fig. 4, *d*). It is a phase that is likely to have a mixed or predominantly electronic type of conductivity. The formation of threads consisting mainly of maghemite, magnetite, and possibly nanocrystals of graphite (graphene) is a natural direction of the process, "arranging" the directional displacement of charge carriers. In nature, a similar mineral composition was detected during the study of ore mineralization in zones of carbonatization

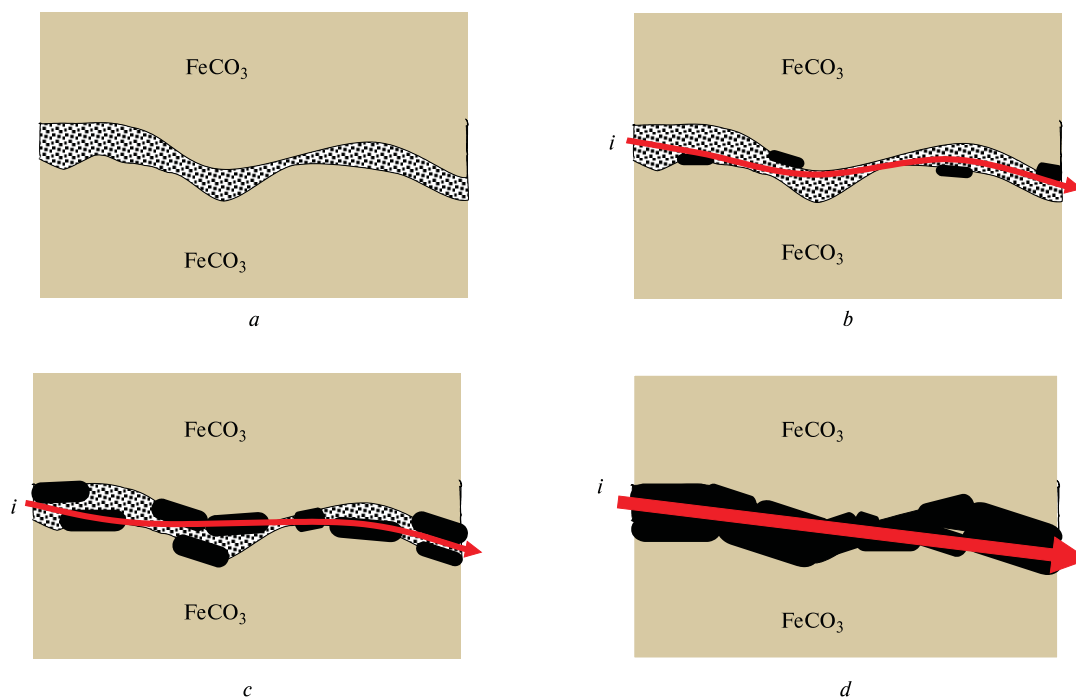


Fig. 4. Development pattern of the reaction zone and the formation of new phases in the space between the surfaces of siderite grains:

the red curve shows the possible path of electric current, and the straight line shows the path formed by the passing current; a – formation of individual molecules in the volume of the phase; b – formation of new phase nuclei on interfaces; c – formation of new boundaries between the initial grain of a crystal and a new phase; d – formation of a continuous layer of the new phase as a result of nuclei fusion

within the Bilozerska green-stone structure in the Ukrainian shield [4]. The electric current initiates the formation of threads (the shortest path with the least resistance), reducing in such a way the degree of influence of an external disturbance (the action of an electric field).

Why is the decomposition of siderite under simple heating efficient to electrically neutral products? Does the probability of the release of ions increase dramatically in the case of the passage of an electric current? P. Yu. Butiagin investigated the kinetics and nature of mechanochemical reactions and the role of active centres. He showed that electrically neutral products of decomposition are formed with maximum probability (in terms of the thermodynamics) in the “ideal case of breaking in a vacuum” of ionic bonds.  $\text{FeO}$  and  $\text{CO}_2$  are such products under the thermal effect to siderite. It is sufficient to expend energy equal to the strength of the  $\text{Fe}-\text{CO}_3$  bond to obtain electrically neutral products. In order to have iron ions and carbonate ions as the products of chemical decomposition reaction, it is necessary to expend additional energy, taking into account the fact that the difference in the ionization potential of the iron atom and the electron affinity for the  $\text{CO}_3$  molecule would have a negative value. As a rule, this difference, even in the limiting case of ionic bond ( $\text{NaCl}$ ), is positive (1.33 eV), which indicates a more advantageous production of electrically neutral atoms than ions.

Molotskyi M. I. showed by numerical simulation that “the interaction of the electrons of the surface zone

with dislocation leads to the localization of the free carrier in the places where the edge dislocation leaves the surface”. It is known that the dislocation charge is very weak in semiconductors, and, as a rule, it is neglected in estimating calculations. However, the exit point of a dislocation that has captured a free charge can be a singularly charged centre characterized by a local electric field. In comparison with the growth rate on an ideal surface, such an active centre can significantly increase the rate of heterogeneous reactions (in  $10 \dots 10^3$  times). Two- and three-charged centres are capable to increase the speed in  $10^4 \dots 10^{27}$  times depending on the heating temperature. The experimental values of the diameter of an active centre were given by Yu. L. Krasulin. Average diameters are equal to  $3 \mu\text{m}$ . The area of such centre is  $10^7$  times larger than the average size of the critical nucleus of the new phase. Thus, as the concentration of active centres increases, the appearance of new phase nuclei, their growth and fusion to a continuous layer will proceed as a single chemical reaction. Intensification of this process can be caused by additional effect of an external electric field.

**Conclusions.** Experiments on electrothermal activation of siderite samples proved that temperatures corresponding to the start of the formation of a new phase shift to a range of values of 130...215 K that is less than under simple heating.

The value of the jump temperature in the electrical conductivity increases with decreasing electric field strength, and in the absence of a field, a jump in the electrical conductivity is not detected.

As a result of electrothermal activation of siderite, a composite semiconductor is formed which consists of a matrix representing the initial mineral and saturated by parallel-oriented high-conductivity threads.

A physical and mathematical model for the numerical evaluation of the stability of the chemical bond of small molecules in the field of singly charged and multiply charged ions was used in this work. The established regularities of the behaviour of the chemical bond in the ion field were taken into account in discussing the possible mechanism of the influence of the electric field on the kinetics of chemical processes.

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**Мета.** Дослідити механізм утворення електропровідної фази в карбонатах на прикладі сидериту, і встановити залежність температури її утворення від вмісту кремнію під час нагрівання та одночасному впливі слабого електричного поля.

**Методика.** Аналіз і узагальнення результатів експериментальних досліджень. Фізико-хімічні аналітичні дослідження з використанням електронної та оптичної мікроскопії, петрографічного й рентгенофазового аналізу, термогравіметричного аналізу та диференціальної скануючої калориметрії, газової хроматографії. Оцінка стану фазової рівноваги в системі „оксиди заліза – вуглець – оксиди вуглецю“ з використанням даних про стандартні зміни енергії Гіббса.

**Результати.** Досліджено механізм утворення електропровідних фаз у сидериті. Встановлена залежність утворення нових фаз від температури нагріву й величини напруженості електричного поля, закономірності зміни порогових температур фазових переходів у пробах сидериту й кальциту, що містять домішки кремнію.

**Наукова новизна.** За рахунок термостимульованого збільшення концентрації рухливих носіїв електричних зарядів у міжзерновому просторі сидериту зростає роль електричного поля точкових

зарядів у формуванні кінцевого продукту хімічних реакцій. Додатковий вплив електричного струму на зростаючий ступінь дестабілізації хімічних зв'язків між поверхневими атомами приводить до утворення й переносу іонів, зниження енергетичного бар'єру утворення „зародків“ електропровідної фази поблизу активних центрів. Стрибкоподібне збільшення електропровідності обумовлено спонтанним характером утворення „зародків“ нової фази й переходом іонної електропровідності на змішаний або переважно електронний тип. У результаті електротермоактивації сидериту формується композитний напівпровідник, що складається з матриці-напівпровідника, представленої вихідним мінералом і насиченою паралельно орієнтованими струмовими нитками високої електропровідності.

**Практична значимість.** Експериментальні результати свідчать про те, що в умовах земної кори подібні процеси, які протікають у досліджуваних гірських породах, цілком реальні, а фізичні значення термодинамічних величин (чинників метаморфізму) під час інтерпретації тих чи інших геологічних подій іноді виявляються значно завищеними.

**Ключові слова:** сидерит, електричне поле, фази, температура, електротермоактивація, електропровідність, іони

**Цель.** Исследовать механизм образования электропроводной фазы в карбонатах на примере сидерита, и установить зависимость температуры ее образования от содержания кремния при нагреве и одновременном воздействии слабого электрического поля.

**Методика.** Анализ и обобщение результатов экспериментальных исследований. Физико-химические аналитические исследования с использованием электронной и оптической микроскопии, петрографического и рентгенофазового анализа, термогравиметрического анализа и дифференциальной сканирующей калориметрии, газовой хроматографии. Оценка состояния фазовых равновесий в системе „оксиды железа – углерод – оксиды углерода“ с использованием данных о стандартном изменении энергии Гиббса.

**Результаты.** Исследован механизм образования электропроводных фаз в сидерите. Установлены зависимости образования новых фаз от температуры нагрева и величины напряженности электрического поля, закономерности изменения пороговых температур фазовых переходов в пробах сидерита и кальцита, содержащих примеси кремния.

**Научная новизна.** За счет термостимулированного увеличения концентрации подвижных носителей электрических зарядов в межзерновом пространстве сидерита возрастает роль электрического поля точечных зарядов в формировании конечного продукта химических реакций. Дополнительное воздействие электрического тока на возрастающую



степень дестабилизации химических связей между поверхностными атомами приводит к образованию и переносу ионов, снижению энергетического барьера образования вблизи активных центров „зародышей“ электропроводной фазы. Скачкообразное увеличение электропроводности обусловлено спонтанным характером образования „зародышей“ новой фазы и переходом ионной электропроводности на смешанный или преимущественно электронный тип. В результате электротермоактивации сидерита формируется композитный полупроводник, состоящий из матрицы-полупроводника, представляющей исходный минерал и насыщенной параллельно ориентированными токовыми нитями высокой электропроводности.

**Практическая значимость.** Экспериментальные результаты свидетельствуют о том, что в условиях земной коры подобные процессы, протекающие в горных породах, вполне реальны, а физические значения термодинамических величин (факторов метаморфизма) при интерпретации тех или иных геологических событий иногда оказываются значительно завышенными.

**Ключевые слова:** сидерит, электрическое поле, фазы, температура, электротермоактивация, электропроводность, ионы

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## ANALYSIS OF THE ERROR OBTAINING WHILE DETERMINING CHARACTERISTICS OF ROTOR SYSTEM WITHIN THE RUN-DOWN

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## АНАЛІЗ ОТРИМАННЯ ПОХИБОК ПРИ ВИЗНАЧЕННІ ХАРАКТЕРИСТИК РОТОРНОЇ СИСТЕМИ НА ВИБІГУ

**Purpose.** The objective of the paper is to determine reasons of origin and conditions of reducing errors while obtaining combined geometrical (axial moment of inertia, mass centre location), mass (rotor weight), frictional (relative radii of bearings) characteristics of rotor system within the run-down. This is required to determine constant (gravitational moment), linear (being proportional to rotational velocity), and quadratic (ventilator moment) components of complete moment of rotor rotation resistance with the following balance problem solving with the help of peak method.

**Methodology.** Theoretical research of rotating rotors relies upon basic theoretical provisions (dynamics) of machines and mechanisms, pre-developed algorithm of 1.2... of N-planar balancing of rigid rotors using peak method as well as analysis of calculation error obtaining.

**Findings.** A statement concerning the necessity of equality of initial errors while measuring experimental values (i.e. time, turning angle, rotational velocity) of run-down has been developed. The statement results in minimization of an error while determining required characteristics of a rotor. The developed algorithm of serial computations identifies definitely geometrical, mass, and frictional characteristics of balanced rotor system in the case of negative discriminant of total moment of rotational resistance. In the context of another, arbitrary relation of rotor system parameters (not negative discriminant), both methodology and order of rotor characteristics determination remain similar. It is planned to use the algorithm as one of the potential alternatives to obtain values of the rotor characteristics with the following substantiated selection of sets of characteristics using the least square method and to come to the balancing problem.

**Originality.** The basic reason or a source to form the error while determining geometrical, mass, and frictional characteristics of rotor systems within the run-down has been identified – difference in measuring errors of certain run-down parameters: time and rotational velocity of rotor turning angle. Theoretically, in terms of any measuring errors being similar in value within the run-down (for example, its time) we obtain true value of target characteristics in the process of each experiment.

**Practical value** is in potential use of permanent stoppages of rotor systems to monitor basic total rotor characteristics – wear and tear of operating devices, block bearings, changes in a value of a process moment, redistribution of bulk weight of a rotor, and the following moment balancing problem solving with the help of a peak method. The proposed solution technique involving the least square method will make it possible to select reasonably the most adequate set of characteristics from the solution set for zero (two possible solutions), non-zero (generalized case), and positive discriminant of a rotor rotational resistance moment.

**Keywords:** *rotor system, permanent stoppages, run-down, axial inertia moment, block bearings, frictional characteristics, rotor weight, mass centre location*