# THERMOCHEMICAL AND ELECTROCHEMICAL DESCRIPTION OF THE Fe-C CATALYTIC SYSTEM

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The processes of the catalytic Fe-C system are investigated with thermogravimetric analysis and electrochemical impedance spectroscopy. It is shown that the presence of oxygen changes the electrochemical data of the system due to the formation of an oxide barrier layer on the metal surfaces. Thermochemical and electrochemical description of the Fe-C systems shows that these systems are able to change properties depending on the oxidizer concentration: in the low concentration range it behaves as a semiconductor electrode with intercrystalline diffusion of ions, whereas in the high concentration range the double-layer's differential capacitance is decreased and the active resistance of system is increased due the presence of oxides on the metal surface.

The Fe-C mixtures are used as catalysts for many catalytic reactions, which are highly dependent on the redox state of active components. In this respect, they can change the redox properties via confinement in $Fe^{+3}$ content components [1]. Furthermore, the diffusion and aggregation of iron species through the reduction reaction have been observed, but these are retarded inside the mixture due to the spatial restriction of the carbon channels [2]. In work [3] it was found that confinement within the carbon nanotubes can modify the redox properties of encapsulated iron oxides and affect the catalytic reactivity of iron catalysts. From kinetic data and electron micrographs of the reactant  it has been determined that the rate of catalytic reactions depends on oxygen pressure: in the low pressure range the rate is determined by the intercrystalline diffusion of gas to the active surfaces of metal, and in the high pressure range – by diffusion of gas through an oxide barrier layer which covers the metal surfaces [4]. But till now, the exact nature and structure of the active catalytic sites of the iron in iron-carbon mixture is still not well understood. So, the aim of this work was

to study the possibility of generating the active catalytic phase with new electrochemical properties in the self-heating Fe-C mixtures.

### Research methodology

A mixture of powdered iron and activated carbon in the mass ratio 2:1 was investigated. The thermal analysis of the self-heating mixture was carried out on a derivatograph Q = 1500 D (Paulik-Erdey) under the linear heating conditions at a rate of $10^0$ min$^{-1}$, in an atmosphere of air and helium (inert), in the temperature range 20-1000 ° C. The initial mass of the sample was 300 mg, the sensitivity of the scale (TG) was 1 mg/div. The crucible is open corundum. The content of the component was calculated from the sample mass loss over time. The total heating time is 100 minutes. The effect of air oxygen on the change in electrochemical properties was studied in a thermo active system that was assembled in 2032 format of the elements.

The impedance spectra were taken in a two electrode cell using an Autolab-30 electrochemical modular block (PGSTAT302N Metrohm Autolab) equipped with an FRA (Frequency Response Analyzer) assembly unit within the range from $10^{-2}$ to $10^6$ Hz. The modular block was controlled by Autolab 4.9 according to the standard procedure with postprocessing in Zview 2.0. The electrochemical reactions were simulated by the equivalent circuit's method.

### Results and Discussion

The thermochemical changes in inert conditions (atmosphere of He) of the investigated objects have shown that iron and it metastable compounds regulate the implementation of oxidative exothermic reaction (table 1) in the wide temperature range (19-80 $^0$C) (fig 1). Without oxygen, the rate of the mass change and degree of samples transformation are higher in 1.5 and 9 times, correspondingly, compering to the atmosphere of air in the temperature range 19-200 $^0$C (table 1). Moreover, the maximum value of energy changes is in the temperature range up to 120 $^0$C (Fig.1). So, the system provides itself with oxidizer (oxygen) in the following way: Fe→FeO→Fe$_3$O$_4$ (FeO·Fe$_2$O$_3$).

The DTA data in an atmosphere of air showed the presence of two exothermic reactions that take place with the participation of iron compounds with different degrees of oxidation. Accordingly, the oxidation of iron powder takes place in two stages. The first stage involves the formation of a protective film on the surface of the Fe$_2$O$_3$, while the

second stage involves the oxidation of the magnetite oxygen. The diffusion of oxygen in the film of magnetite leads to recrystallization with the formation of $\acute{\alpha}$ $Fe_2O_3$- hematite structure as a result. So, the presence of oxygen blocks the bulk exothermic reaction due the high surface activity of the metastable iron oxides. In this case, the stable $Fe_2O_3$ was formed. The formation of such structures on the wustite surface decreased the temperature range of the exothermic reaction. It became 20-32 $^0$C (fig. 2). The 3-D diagrams well demonstrate the presence of such a plateau of the energy maximum in an atmosphere of helium in the temperature range 19-200 $^0$C (Fig. 3) and loss of energy potential during oxidation with oxygen (Fig.4). Experimental results confirm the change of redox reaction mechanism and catalytic activity of the Fe-C system, and kinetics data have determined that the rate of catalytic reactions depends on the oxidizer concentration (analog of oxygen pressure). So, the metal oxidation is the main adjusting gear of the exothermic catalytic reaction. And in this case, two kinds of diffusion can be expected: intercrystalline diffusion and diffusion across an oxide barrier layer which covered the metal surfaces [4]. Such differences of diffusion may be a basis for the electrochemical properties changes.

**Table 1.** Kinetics data of the thermal analysis of the self-heating mixture in an atmosphere of air and helium

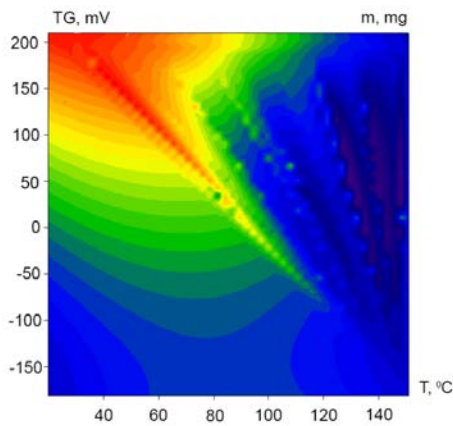| air | | |
|---|---|---|
| t, °C | $\alpha$, % | $\vec{V}$, mg/min |
| 19 – 25 | 0,2 | 0,18 |
| 25 – 200 | 1,22 | 0,19 |
| 200 – 460 | 0 | 0 |
| 460 – 593 | 12,13 | 0,31 |
| 593 – 987 | 19,4 | 1,41 |
| The residual mass of the sample after heating to 987 °C is 350,54 mg | | |
| helium | | |
| 20 – 165 | 1,84 | 0,27 |
| 165 – 330 | 0,5 | 0,08 |
| 330 – 550 | 0,77 | 0,09 |
| 550 – 650 | 0 | 0 |
| 650 – 971 | 5,64 | 0,43 |
| The residual mass of the sample after heating to 987 °C is *269,84 мг* mg | | |
| *Note.* $\alpha$ – *degree of the sample transformation,  –rate of the mass change;* | | |

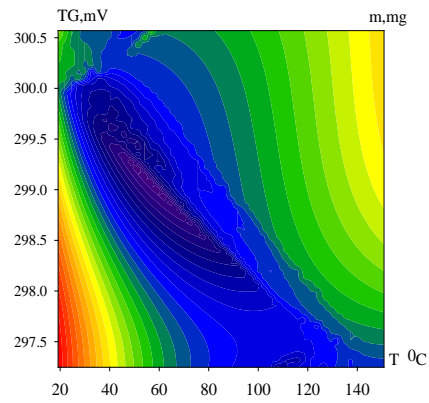**Fig 1.** Energy map of the thermochemical reaction in the atmosphere of H



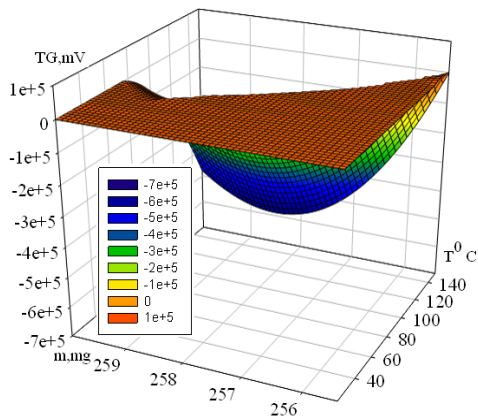**Fig 2.** Energy map of the thermochemical reaction in the presence of oxygen



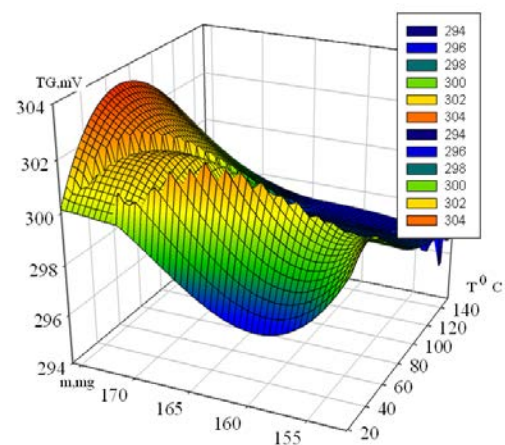**Fig.3** 3-D energy diagrams of the thermochemical reaction in the atmosphere of He



**Fig.4.** 3-D energy diagrams of the thermochemical reaction in the presence of $O_2$

Impedance spectra analysis determined that a hermetic cell (Fe-C system without oxygen) is formed electrochemical systems with relatively low active and reactive impedance (Z '< 100 Ohm, Z "< - 50 Ohm), which can be described by a model 1 (fig.4). The model is like a supercapacity equivalent electric circuit. But it contains a CPE-element instead of regular capacity. Such results support the view that the CPE behavior (or, in general, frequency dependence of capacitance) results from the energy in homogeneities which in turn affect the kinetics of the ion adsorption processes [5]. Taking into account the possibility of the intercrystalline diffusion, the decrease in the resistivity and appearance of the energy in homogeneities can be described using the CPE-element. In favor of the hypothesis of the ions intercrystalline diffusion presence indicate data of the double-layer's differential capacitance ($C(\omega) = 1/[j\omega(Z(\omega) - R_s) = 0.0017643$ F], $R_s \equiv Re(Z(\omega \to \infty))$) and

form of the impedance spectra in Nyquist Plot (linear depedence). In this case, we can use the Mott–Schottky theory for description of the double layer on the semiconductor–electrolyte junctions. This is because, in practice, this theory is often used for any semi- conductor electrodes with many and diverse corrections yielding complicated equivalent circuits introduced to eliminate the apparent frequency dependence of the Mott–Schottky lines [5].
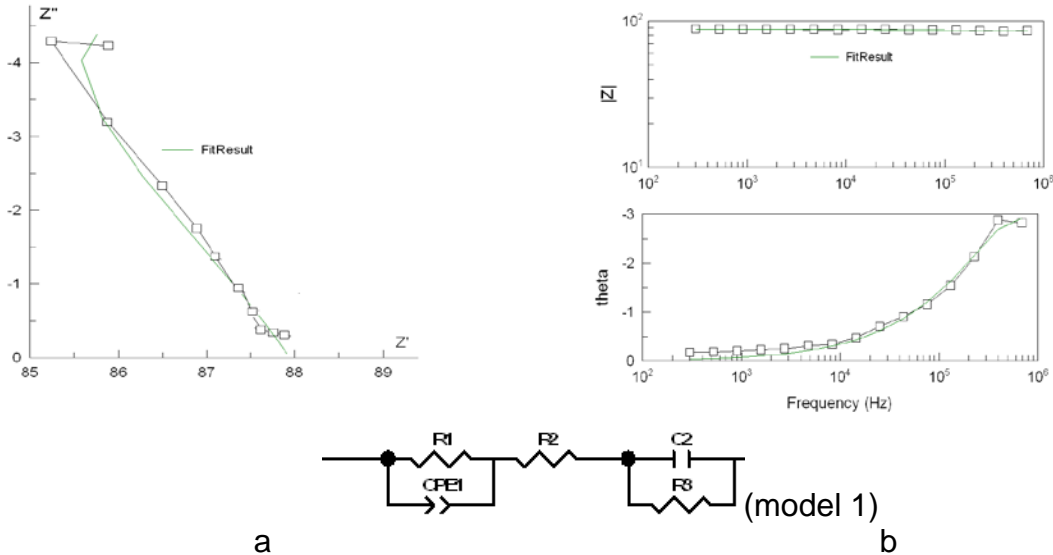


**Fig 4.** Impedance spectra of the Fe-C system in the inert conditions a - in Nyquist plot, b - diagrams Bode
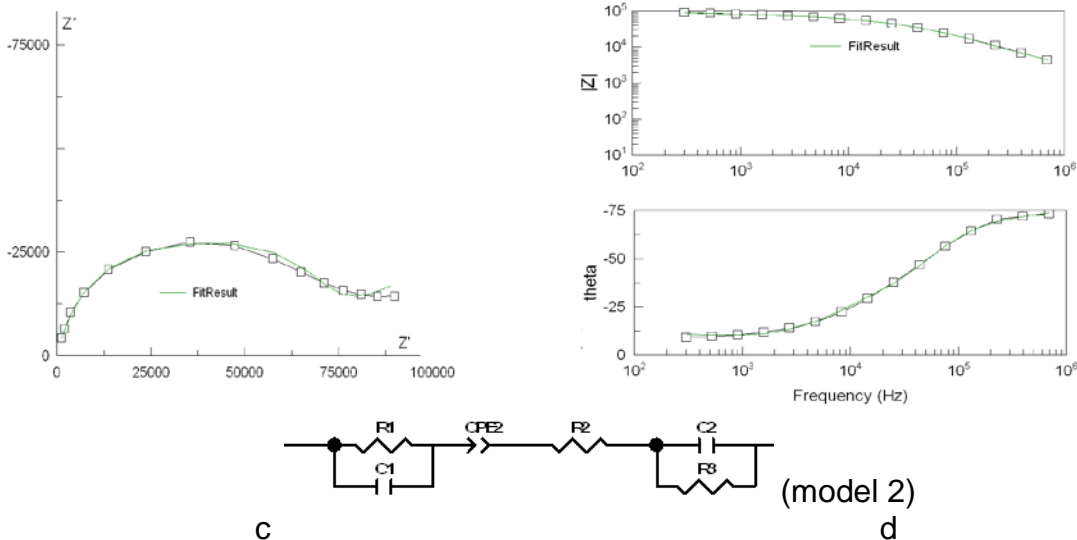


**Fig 5.** Impedance spectra of the Fe-C system in the air: c - in Nyquist plot, d - diagrams Bode

In the case of the oxygen presence CPE – element (model 2) corresponds to the energy difficulties due to the presence of redox

reaction products having semiconducting properties ($Fe_2O_3$ with spinel structure) [6]. So, the appearance of this component increases the active resistance up to $10^4$ ohm (fig.5). If the Fe-C system is considered as the system with limited diffusion across an oxide barrier layer which covered the metal surfaces (oxygen-terminated samples), the Mott–Schottky analyses yielded less coherent results and the double-layer's differential capacitance are decreased significantly. The value of such capacitance in the presence of oxygen is C = 8.0534 $10^{-11}$ F.

## Conclusions

The thermochemical changes in inert conditions (atmosphere of He) of the investigated objects have shown that iron and it metastable compounds regulate the implementation of oxidative exothermic reaction in the wide temperature range from 19 to 80 $^0$C. Thermochemical and electrochemical studies of the Fe-C systems show that these systems are able to change its catalytic and electrochemical properties depending on the oxidizer concentration: in the low concentration range it behaves like a semiconductor electrode with intercrystalline diffusion of ions, while in the high concentration range an oxide barrier layer is formed which covers the metal surfaces thus decreasing the double-layer's differential capacitance and increasing the active resistance of system.

### References

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