Mechanism of thermally stimulated current occurrence in fine heterogeneous medium on the example of grain crops

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Abstract. The mechanism of thermally stimulated current occurrence in non-equilibrium heterogeneous fine-dispersed medium was analyzed on the example of mechanically activated barley. Presence of charged defects on ground grain crops surface causes formation of enveloping water films on their surface with ordered orientation of molecules and develops a double electric layer capable of accumulating electric current in the absence of external voltage. The area of double electric layer on the interfacial boundary of the grain medium under study with rigid fixation of molecules becomes a potential obstacle capable of increasing the substance electric strength. Occurrence of thermally stimulated electric current in the analyzed medium without external voltage results from the formation of potential difference of internal electric field, and is one of the reasons for grain mass burning. It is noted that disordering the structural properties of the ground grain has a serious effect on the temperature and humidity processes in the medium and the thermally stimulated current amount. The amount of electric current depends on the size of mechanically activated particles as well as temperature and humidity conditions.

1. Introduction
The processes of spontaneous grain burning are discussed in a number of publications [1-3], however the physical mechanism of this phenomenon has not been sufficiently studied. It has been found that while feeding the grain mass in the grain dryers, partial destruction of grain shell occurs, thus grain dust with a very fine dispersion structure is formed. Grain dust, which is a broken grain shell, can easily ignite under a certain temperature and humidity conditions. The calculation procedure of convective drying of various dispersed materials is presented in [4], where physical analysis of heat and mass exchange and hydrodynamics of the considered process is suggested, mathematical description and corresponding solution of the problem are presented.

Currently, a serious attention is paid to the research of physical properties of fine materials with highly developed specific surface area using thermally stimulated spectroscopy method [5, 6]. In operation, ground barley grains are used as finely dispersed mechanically activated material. Dielectric properties of food products, including cereals, methods of their treatment and drying applying various sources of temperature effect are studied in the works [7-10]. It has been found that the presence of charged defects on the surface of ground substances, including grain structures, leads to the formation of enveloping water films on their surface and the alignment of polar water film molecules orientation, as a result a double electric layer is formed and electric current is accumulated in the absence of external voltage [11-13]. The region of the double electric layer is a potential barrier to the transition
of free water molecules and molecules, directed by the electric field of the active solid component. It forms an impermeable layer capable of increasing electrical strength of the substance. In a heterogeneous system of mechanically activated grain, there is also Coulomb interaction of charged particles present on its electrically active surface with polar molecules of a water film at interfacial boundaries. Sources of internal electric field are charged defects located on surface and inside grain, polar molecules of water film and free ions. The process of ion transfer to the active surface of the substance solid phase takes place under the influence of the internal field [11].

The purpose of this work is to investigate the features internal electric field generates and the appearance of micro-stimulated currents in finely dispersed mechanically activated grain crop samples using barley as one of the causes of the grain mass burning. The experiment was carried out applying the method of thermally stimulated spectroscopy, which allows to obtain data on the state of the electrically active medium and its structural features [5, 6].

2. Materials and techniques

In the work, thermally stimulated currents were measured for mechanically activated barley samples with different degree of particles dispersion, dependence on humidity and temperature was studied. Barley samples for the experiment were prepared by mechanical activation, which resulted in dispersion systems with particle sizes ranging from 50 to 250 \( \mu \text{m} \). The adsorption value of the samples \( \varphi = 0.5\% \) and 8\% at room temperature was used.

A sample cell (a flat capacitor with aluminum electrodes and a diameter of 1.5cm) was used for the measurements. Samples of the fixed mass grain were placed in the cell and heated without applying external voltage to the electrodes of the sample cell.

Measurement of thermally stimulated currents was performed in short-circuited sample mode with linear heating at fixed rate not exceeding 1 deg/min in temperature range between 200°C and 2600°C. The temperature test experiment of thermally stimulated currents was conducted applying the unit consisting of power supply block B 5-48 of 50V, 2A; Voltmeter-electrometer, thermocouples, cells with barley sample, two ADCs connected to personal computer. The current was recorded with a sensitive voltmeter B7-49 (measurement accuracy 10\(^{-15}\)A). The data obtained was stored in personal computer memory, processed applying well-known statistical methods and presented in diagrams.

Experimental data made it possible to calculate the main thermal and electret parameters of the analyzed medium: activation energy of charge carriers and relaxation time of structural elements, depending on the maximum of thermally stimulated current under the maximum temperature. Analysis of thermally stimulated current dynamics gives an idea of electrical and physical state of dispersed medium under study [11].

3. Results and discussions

Studies of electrical and physical properties of mechanically activated barley samples were carried out by thermally stimulated spectroscopy [6] applying a specially designed unit. Figure 1 shows thermograms of currents in the temperature range from 20°C to 260°C for the tested samples of mechanically activated fine barley with dispersion of 50\( \mu \text{m} \) and 150-250\( \mu \text{m} \).

Thermally stimulated currents in the analyzed finely dispersed medium of mechanically activated barley in the temperature range between 200°C and 2600°C have pronounced local resonance maxima, indicating non-uniformity of the studied heterogeneous system and presence of structural polarization charged defects in potential traps of the solid phase of the analyzed medium prior to thermal activation [13-15]. In the area of low temperatures from 20°C to 110°C there is a resonant current maximum corresponding to the 74°C, explained by accumulation of interfacial electret charges under the influence of the internal electric field, as well as by the peculiarities of the water component structure [14,15].

The analyzed heterogeneous fine-dispersed barley grain system has spatially non-uniform distribution of electret charges, which acquire additional energy while heating, and affect the value of thermally stimulated current. Analysis of electric current maxima on the graph confirms the complex
order in the arrangement of atoms of the dispersed medium and the presence of charges on its defects and traps [11,12].

![Figure1](image_url)

**Figure1.** Spectra of thermally stimulated currents of mechanically activated fine barley samples under 0.5% humidity of tested samples: Graph 1- for 50µm dispersion; graph 2- for 150-250µm dispersion.

It can be assumed that at low temperatures the source of free electret charges is the ionization processes in the aqueous polar matrix of the investigated system and water molecules are broken down into ions. The maximum thermal flow of a smaller and electrically active sample 1 with a dispersion of 50 µm: \(I_{\text{max}}=0.25 \times 10^{-9} \text{A}\), occurring at 74ºC, can be explained by transfer of the structured water into a volumetric state, and amplitude growth - by active manifestation of the properties of the structured water with increase of electrical activity of the fine sample. At 74ºC, the ordered structure of the aqueous matrix is thermally broken, the direction of dipoles of water molecules is disturbed, and the potential barrier holding charges near the solid surface of the grain is reduced.

In the temperature range between 121ºC and 176ºC, the presence of thermal flow maxima indicates the beginning of the solid component structure destruction. Amplitude of 1 sample current with lower dispersion degree and greater electrical activity is \(I_{\text{max}}=1.21 \times 10^{-9} \text{A}\) at \(T_{\text{max}}=121^\circ\text{C}\). At this temperature, the activation energy of the charge carriers is reduced. For a sample of barley 2 with larger particles, the maximum amplitude corresponds to \(I_{\text{max}}=0.99 \times 10^{-9} \text{A}\) at \(T_{\text{max}}=159^\circ\text{C}\). During the experiment it was found that in the temperature range between 121ºC and 176ºC, the maximum of the thermally stimulated current for the sample of greater electrical activity and smaller particle dispersion size shifted to the lower temperature range. This fact can be explained by the fact that the activation energy of charged local defects is the resulting function from the contributions of thermal and internal electric field energy. The energy of the internal electric field produced by the active surface of smaller barley grains contributes more significantly to the activation energy of local defects compared to that of the larger sample 2. Therefore, ionization of charged local complexes occurs at a lower temperature. In fact, the high temperature maximum of the thermally stimulated current of the most electrically active sample 1 appears at a lower temperature \(T_{\text{max1}}=121^\circ\text{C}\) compared to the same temperatures of the high temperature maximum of the sample 2 (figure2). Since the dominant contribution to the activation energy of charged defects is made by the thermal field, the temperature corresponding to the maximum current increases. Thus, for a less electrically active 2 sample, the maximum thermal pick values occur at higher temperatures \(T_{\text{max2}}=159^\circ\text{C}\).

Further heating of the test samples 1, 2 showed a marked increase in the amplitude of the relaxation current maxima in the high temperature range between 176ºC and 260ºC for the sample 1, indicating
the destruction of stronger solid structures. The maximum amplitude of the high temperature current maximum $I_{\text{max}} = 1.57 \times 10^{-9} \text{A}$ for a more active 1 sample under temperature $T_{\text{max1}} = 176 ^\circ \text{C}$ indicates a high concentration of accumulated electret charges at its interfacial boundaries, and the contribution of electrical energy to the activation energy of local defects is more profound. Therefore, this maximum occurs at a lower temperature $T_{\text{max1}} = 176 ^\circ \text{C}$ compared to a less active 2 sample ($T_{\text{max2}} = 231 ^\circ \text{C}$). It can be assumed that the internal electrical energy for a more active fine sample contributes more significantly to the activation energy of local defects.

The second experiment involved examining adsorption measurements of wetted samples of fine barley particles with the same dispersion as in the first experiment. All samples were subjected to the same wetting of $\beta = 8\%$. The increase in the concentration of the aqueous component in the structures under study contributes to the expansion of ion conduction channels and provides transport of most thermally released charges. It has been experimentally found that the temperature position of thermal current maxima in the low-temperature range shows dependence of the tested samples on the surface activity and concentration of the aqueous phase [11].

Figure 2 shows spectra of thermally stimulated currents for two experimentally wetted samples in the range of tested temperatures between 20ºC and 260ºC. Three intense characteristic peaks of the maximum high-amplitude thermal current appear on each graph.

![Figure 2](image)

**Figure 2.** Spectra of thermally stimulated currents of mechanically activated fine barley samples at 8% moisture content of the tested samples: graph 1 - spectra of the 1 sample (dispersion 50µm); Graph 2 - spectra of sample 2 (dispersion 150-250µm).

In the low temperature range, the detected maxima of thermal currents of samples 1, 2 are located in the temperature range between 20ºC and 110ºC. For the most electrically active sample 1 the intensive peak of a thermal current maximum which is characterized by $I_{\text{max}}=0.46 \times 10^{-9} \text{A}$ amplitude at $T_{\text{max}}=48 ^\circ \text{C}$ and $I_{\text{max}}=2.78 \times 10^{-9} \text{A}$ at $T_{\text{max}}=102 ^\circ \text{C}$ is found.

It has been experimentally determined that wetting for a larger and less electrically active sample 2 in the low temperature range results in weakening of the thermal currents amplitude intensity compared to the amplitude of the first more active sample 1. ($I_{\text{max1}} = 1.18 \times 10^{-9} \text{A}$, $I_{\text{max2}} = 0.23 \times 10^{-9} \text{A}$), which indicates a small concentration of free electret charges at interfacial boundaries in the structures under study and the presence of direction inversion of the thermally stimulated current associated with changing direction of the internal electric field intensity of the analyzed structures.

The surge in the peak thermal current amplitude of the wetted sample 2 at 89ºC is caused by an increase in the concentration of free electret charges, the source of which is the ionization processes of
the introduced aqueous component. This can be associated with an increase in the internal electric field intensity modulus and a change in the magnitude and direction of the thermal current due to wetting of test samples. The greater amplitude of the thermal maximum of current is due to the presence of a significant concentration of electret free charges caused by samples 1, 2 wetting (β = 8%), as well as the appearance of more effective electric contact interaction at the interfacial boundaries. At temperature of this peak, energy of charged structural defects decreases and is accompanied by thermal output of structural defects into conduction channels [11].

The adsorption process experiment also showed that as the electrical activity of the wetted experimental samples 1 and 2 decreased, a shift of its thermal maximums of current towards higher temperatures was found. Indeed, the first maximum of the thermally stimulated current of the sample 2 appears at a temperature $T_{\text{max}} = 89 \, ^\circ\text{C}$ and the second at a temperature $T_{\text{max}} = 127 \, ^\circ\text{C}$.

In the high-temperature range between 120°C and 260°C spectra of thermally stimulated currents of the wetted samples 1 and 2, there is a significant increase in the analyzed fine barley samples amplitude of thermal currents maxima due to thermal destruction of the structures and strong interfacial interaction.

Analysis of the dynamics of thermally stimulated currents relaxation in a given temperature range made it possible to determine the dependence of the temperature position of current maxima on the size of the fine barley particles and the concentration of the aqueous phase. Thus, for a more active 1 sample prior to wetting, the amplitude of the characteristic current thermal maximum was $I_{\text{max}} = 1.21 \times 10^9 \text{Am} - 121 \, ^\circ\text{C}$ and $I_{\text{max}} = 1.57 \times 10^9 \text{Am}$ at $T_{\text{max}} = 176 \, ^\circ\text{C}$ (figure1, graph 1), and after wetting increased to $I_{\text{max}} = 2.78 \times 10^9 \text{Am} = \ldots$. For a larger particle size 2 sample prior to humidification, the amplitude of the characteristic current thermal maximum was $I_{\text{max}} = 0.99 \times 10^9 \text{Am}$ at a temperature $T_{\text{max}} = 159 \, ^\circ\text{C}$ and $I_{\text{max}} = 0.1 \times 10^9 \text{Am}$ at $T_{\text{max}} = 231 \, ^\circ\text{C}$ (figure2, graph 2). After wetting the sample, the 2 amplitude increased to a value of $I_{\text{max}} = 1.98 \times 10^9 \text{Am}$ at $T_{\text{max}} = 127 \, ^\circ\text{C}$ to $I_{\text{max}} = 0.27 \times 10^9 \text{Am}$ at $T_{\text{max}} = 223 \, ^\circ\text{C}$. The development of peaks of these current thermal maximums is obviously associated with thermal degradation and ions release from defective areas located on the surface and in the volume of particles of mechanically activated barley. Significant amplitude of the current relaxation maximum for the more electrically active wetted sample indicates a large concentration of accumulated charges at interfacial boundaries.

As a result of the obtained experimental data analysis, it was found that mechanically activated fine barley demonstrates non-uniform physical properties depending on its particles electrical activity. There is a vivid correlation between the thermally stimulated current maxima temperature position and the intensity of the analyzed dispersed medium internal electric field with the specific surface area of the electrically active solid phase particles and the concentration of water films [11].

4. Conclusion
The mechanism of thermally stimulated current occurrence in non-equilibrium heterogeneous fine-dispersed medium was analyzed on the example of mechanically activated barley. It has been found that one of the causes of the grain mass temperature increase is the thermally stimulated currents occurring in the non-equilibrium heterogeneous fine medium in the absence of external voltage. It is shown that the occurrence of electric current in the absence of external voltage results from the formation of a potential difference of the internal electric field in the medium under study and can lead to "burning" of the grain mass.

The contact area between the electrically active solid and polar liquid components in the analyzed medium of mechanically activated barley creates a new interfacial structure in the form of a double electric layer capable of accumulating thermally stimulated currents under the influence of potential gradients of its own stable internal field.

The appearance of thermally stimulated currents in the grain mass with no external voltage is evidence of the internal potential difference formation in the medium; the presence of ion conductivity channels and free charge carriers, the sources of which are polar matrix ions and charges of the solid phase which is one of the causes of the grain mass burning.
The amount of thermally stimulated current is substantially dependent on the amount of particle dispersion, humidity level and temperature mode, and therefore increases with particle size of the dispersed medium decrease and humidity and temperature increase respectively.

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