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The strenuous state of the contact at the sliding - flip pairs

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Abstract: The exact determination of strain on the load application area, regards to changing material or shape is one of the main problems of the mini structure constructions, which it does not interfere with the classical methods of linear elasticity. The main purpose of this article is to demonstrate accomplishments in the knowledge of linear elasticity with different mathematical methods, in order to penetrate into the area or into the contact lining, taking into consideration the friction between the bodies in contact. The methods and hypotheses are related to the analysis of different classical half-plane problems in loads of different types of linear elasticity. This material shows a clear original solution of the strained state in the contact area including the surface lining; it serves as a solution to the various contact plan problems. The details and the elements of the vehicles are part of a broad field, which should be optimized considering different analytical solutions and using various computer programs. These solutions can be installed in their structure. Classical methods in the details apply only when the hypotheses on studied subjects are being met, such as Material Resistance studying the Rod. A detail with a length of ten times greater than the transverse dimension. That's the reason why extreme problems or problems out of the different hypotheses are solved and proven in practice with the most creative and sophisticated methods. The solution given in this article is an important contribution to constructive calculations, which is also associated with other works carried out by me on the friction coefficient on the flip-flop slippery contact.

Keywords: STRINGS, ELLIPTICAL COORDINATES, CONTACT HERZIT, CONTACTLESS CONTACT, SURFACE CONTACT

1. Subplant loaded with normal and tangential loads

The Fig. 1 depict a normal and tangential load in half planes.

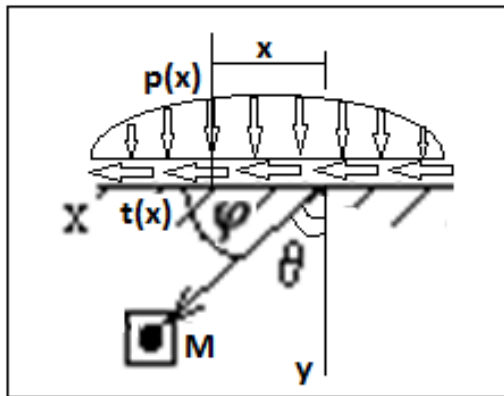


Fig.1 Normal and tangential load in half planes

For the most appropriate normal load is to be shifted to a bi-harmonic function $F(z)$ and then to the harmonic functions Φ and Ψ where $F(z) = \Phi + y \cdot \Psi$ and $z = x + i \cdot y$. The strains from the strain relief will be [1-3].

$$\sigma_{xx} = \frac{\partial^2 F}{\partial y^2}; \sigma_{yy} = \frac{\partial^2 F}{\partial x^2}; \sigma_{xy} = -\frac{\partial^2 F}{\partial x \partial y}$$

Knowing that the harmonic functions satisfy the condition

$$\nabla^2 \Phi = \frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} = 0, \text{ we get}$$

$$\Psi = -\frac{\partial \Phi}{\partial y}; \varphi = \frac{\partial \Psi}{\partial y} \rightarrow \varphi = -\frac{\partial^2 \Phi}{\partial y^2} = \frac{\partial^2 \Phi}{\partial x^2} \quad (1)$$

Afterward we get:

$$\sigma_{xx} = \frac{\partial^2 F}{\partial y^2} = \varphi + y \cdot \frac{\partial \varphi}{\partial y}; \sigma_{yy} = \frac{\partial^2 F}{\partial x^2} = \varphi - y \cdot \frac{\partial \varphi}{\partial y}; \sigma_{xy} = -\frac{\partial^2 F}{\partial x \partial y} = -y \cdot \frac{\partial \varphi}{\partial x} \quad (2)$$

After collecting normal strains, the first strain tensor invariant will be:

$$\varphi = \frac{\sigma_{xx} + \sigma_{yy}}{2} \quad (3)$$

The most convenient tangential load is to go to a bi-harmonic function as below:

$$F(z) = \Phi + x \cdot \Psi, \text{ ku } z = x + i \cdot y. \quad (4)$$

Strengths from strain solution will be:

$$\sigma_{xx} = \frac{\partial^2 F}{\partial y^2} = \psi - x \cdot \frac{\partial \psi}{\partial x}; \sigma_{yy} = \frac{\partial^2 F}{\partial x^2} = \psi + x \cdot \frac{\partial \psi}{\partial x}; \sigma_{xy} = -\frac{\partial^2 F}{\partial x \partial y} = -x \cdot \frac{\partial \psi}{\partial y}; \psi = \frac{\sigma_{xx} + \sigma_{yy}}{2} \quad (5)$$

In the case of normal and tangential load these functions will be as below:

$$\varphi = -P \cdot \frac{\sin \theta}{\pi r}; \psi = -T \cdot \frac{\cos \theta}{\pi r}; \bar{F}(z) = \varphi + i \cdot \psi = -\frac{1}{\pi r} (P \cdot \sin \theta + i \cdot T \cdot \cos \theta) \quad (6)$$

when $P = T$ group together into the complex variable z

$$\bar{F}(z) = -\frac{P \cdot i}{\pi z} = -\frac{P \cdot i}{\pi r e^{i\theta}} = -\frac{P \cdot i e^{-i\theta}}{\pi r} = -\frac{P \cdot i (\cos \theta - i \sin \theta)}{\pi r} \quad (7)$$

In the case when the P and T forces are located at the 'u' distance from the origin we have:

$$\bar{F}(z) = \frac{P \cdot i}{\pi(u-z)} \quad (8)$$

In case of distributed load we will integrate:

$$\bar{F}(z) = \int \frac{p(u) \cdot i}{\pi(u-z)} du \quad (9)$$

where φ is the real part of $\bar{F}(z)$ and ψ is the imaginary part of $\bar{F}(z)$.

For normal load we have:

$$\sigma_{xxN} = \varphi + y \cdot \frac{\partial \varphi}{\partial y}; \sigma_{yyN} = \varphi - y \cdot \frac{\partial \varphi}{\partial y}; \sigma_{xyN} = -y \cdot \frac{\partial \varphi}{\partial x} \quad (10)$$

For the tangential load we have:

$$\sigma_{xxT} = \psi - x \cdot \frac{\partial \psi}{\partial x} = 2 \cdot \psi - \sigma_{xyN}; \sigma_{yyT} = \psi + x \cdot \frac{\partial \psi}{\partial x} = \sigma_{xyN}; \sigma_{xyT} = -x \cdot \frac{\partial \psi}{\partial y} = \sigma_{xxN} \quad (11)$$

2. The usage of elliptical coordinates

In the x and y axes system, we have different functions such as strains, deformations, and displacements, which are very complicated. The differential equations that they have emerged may present different difficulties to be solved. Another system of axes is the elliptical coordinate's ξ, η . These functions can come up with simpler formulas as well as with the solution of the differential equations from which the equation have emerged to be lighter. Fig. 2 depict Elliptic coordinates in the contact problem.

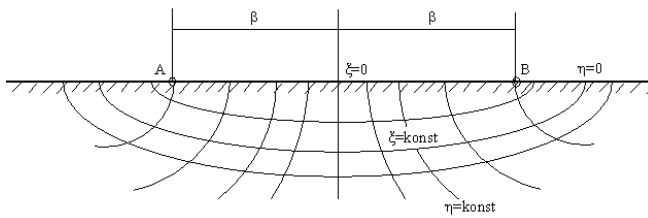


Fig.2 Elliptic coordinates in the contact problem

In the complex variable $z = x + i \cdot y$ or $\zeta = \xi + i \cdot \eta$ for the transformation

$$z = \beta \cdot \cosh \zeta = \beta \cdot \frac{e^{\xi} + e^{-\xi}}{2} = \beta \cdot \frac{e^{(\xi+i\eta)} + e^{-(\xi+i\eta)}}{2} = \beta \cdot \frac{e^{\xi} \cdot e^{i\eta} + e^{-\xi} \cdot e^{-i\eta}}{2}$$

$$x = \beta \cdot \cosh \xi \cdot \cos \eta \text{ dhe } y = \beta \cdot \sinh \xi \cdot \sin \eta$$

3. The integral solution for the symmetric term (Herc's fiery contact)

We analyze the case of contact with normal and tangential load according to the problem of Herc, see Fig. 3.

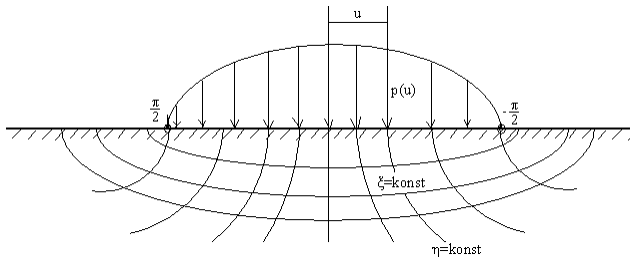


Fig.3 Herculean contact in elliptical coordinates

$$p(u) = C_1 \cdot \cos \theta = \frac{C_1}{\beta} \cdot \sqrt{\beta^2 - u^2} \text{ dhe } u = -\beta \cdot \sin \theta \quad (12)$$

From the mathematical analysis we draw:

$$\int \frac{\sqrt{\beta^2 - u^2}}{u - z} du = \sqrt{\beta^2 - u^2} - z \cdot \sin^{-1} \left(\frac{u}{\beta} \right) + \sqrt{z^2 - \beta^2} \cdot \cos^{-1} \left(\frac{\beta^2 - z \cdot u}{\beta \cdot (u - z)} \right) \quad (13)$$

So we have the equation:

$$\bar{F}(z) = \frac{i}{\pi} \cdot \int \frac{p(u) \cdot du}{u - z} = \frac{i}{\pi} \cdot \int_a^b \frac{C_1 \cdot \sqrt{\beta^2 - u^2}}{\beta \cdot (u - z)} du = -C_1 \cdot i \cdot (\cosh \zeta - \sinh \zeta) = -C_1 \cdot i \cdot e^{-\zeta} = -C_1 \cdot i \cdot e^{-\xi} \cdot (i \cdot \cos \eta + \sin \eta) \quad (14)$$

with its real and imaginative part:

$$\varphi = -C_1 \cdot e^{-\xi} \cdot \sin \eta \text{ dhe } \psi = -C_1 \cdot e^{-\xi} \cdot \cos \eta \quad (15)$$

4. Sample preparation

In the case of rough rolling contact we have both pressure terms. We analyze the second term of pressure as it was first analyzed at Herc's contact, see Fig. 4.

$$p(u) = -C_2 \cdot \sin(2 \cdot \theta) = 2 \cdot C_2 \cdot \frac{u}{\beta^2} \cdot \sqrt{\beta^2 - u^2} \text{ and } u = -\beta \cdot \sin \theta$$

We define the potential function for this pressure:

$$\int_a^b \frac{\sqrt{\beta^2 - u^2}}{\beta \cdot (u - z)} \cdot u \cdot du = u \cdot \left[\sqrt{\beta^2 - u^2} - z \cdot \sin^{-1} \left(\frac{u}{\beta} \right) + \sqrt{z^2 - \beta^2} \cdot \cos^{-1} \left(\frac{\beta^2 - z \cdot u}{\beta \cdot (u - z)} \right) \right] - \left[\frac{\pi \cdot \beta^2}{2} - \pi \cdot (\beta^2 - z^2) - \pi \cdot (\beta + z) \cdot \sqrt{z^2 - \beta^2} \right] \frac{\beta}{-\beta} = \pi \cdot \beta^2 \cdot \frac{\sinh(2\zeta) - \cosh(2\zeta)}{2} = -\frac{\pi \cdot \beta^2}{2} \cdot e^{-2\zeta}$$

$$\bar{F}(z) = \frac{i}{\pi} \cdot \int_{-\beta}^{\beta} \frac{p(u)}{u - z} \cdot du = \frac{i}{\pi} \cdot \frac{2 \cdot C_2}{\beta^2} \cdot \left(-\frac{\pi \cdot \beta^2}{2} \cdot e^{-2\zeta} \right) = -C_2 \cdot i \cdot e^{-2\zeta} \quad (20)$$

and the formative reinforcement of functions:

$$\varphi = -C_2 \cdot e^{-2\zeta} \cdot \sin(2 \cdot \eta); \psi = -C_2 \cdot e^{-2\zeta} \cdot \cos(2 \cdot \eta) \quad (21)$$

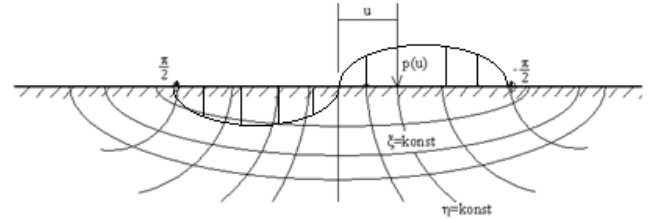


Fig.4 Contact with antimetric term

5. Strings on the lining of contact bodies

Laboratory The Fig. 5 depict a pressure at rolling contact for $\lambda = 0.424$.

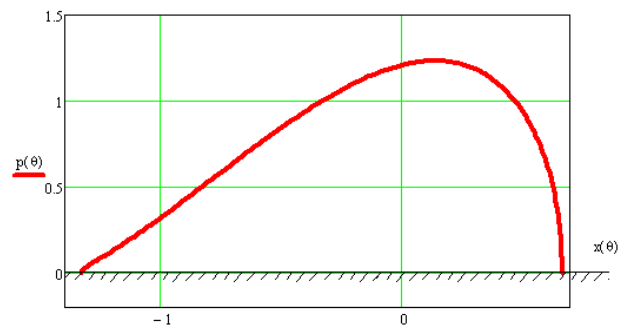


Fig.5 Pressure at rolling contact for $\lambda = 0.424$

In this case we have rotation (flip), so we have both terms, therefore the analytical solution will be:

$$p_n(\theta) = C_1 \cdot \cos \theta - 0.424 \cdot C_1 \cdot \sin(2 \cdot \theta)$$

From reference pressure we have simplifications:

$$\overline{p_n(\theta)} = \frac{p_n(\theta)}{C_1} = \cos \theta - 0.424 \cdot \sin(2 \cdot \theta); \bar{\tau} = \frac{t - \alpha}{\beta} = -\sin \theta [-90^\circ \div 90^\circ]$$

In case of total slide we draw:

$$p_t(\theta) = \mu \cdot [\cos \theta - 0.424 \cdot \sin(2 \cdot \theta)]; \mu \rightarrow \text{the coefficient of friction between the two bodies in contact}$$

The contact surface in elliptical coordinates is divided into three parts. The CD part where $\eta = \pi$, the contact AB part, which depends directly on the oppressive force $\xi = 0$ and the part BD where $\eta = 0$.

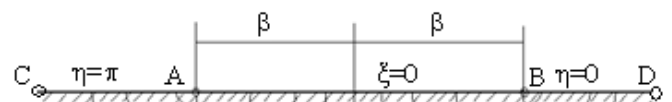


Fig.6 Surface of the bodies in contact and its elliptical variables

When flipping in real contact, the most loaded case is realized when we have full slide. The reinforcements in this case for the lining will be:

Area CA: $\eta = \pi$ from Eq. (23), (25), (29), (30):

$$\begin{aligned}\sigma_{xx1N} &= 0; \sigma_{xx1T} = 2 \cdot \mu \cdot C_1 \cdot (\theta^{-\xi}); \sigma_{xx2N} = 0; \sigma_{xx2T} = -2 \cdot \mu \cdot C_2 \cdot \theta^{-2\xi} \\ \sigma_{yy1N} &= 0; \sigma_{yy1T} = 0; \sigma_{yy2N} = 0; \sigma_{yy2T} = 0 \\ \sigma_{xy1N} &= 0; \sigma_{xy1T} = 0; \sigma_{xy2N} = 0; \sigma_{xy2T} = 0\end{aligned}$$

Area AB: $\xi = 0$ by ek (23), (25), (29), (30):

$$\begin{aligned}\sigma_{xx1N} &= -C_1 \cdot \sin \eta; \sigma_{xx1T} = -2 \cdot \mu \cdot C_1 \cdot \cos \eta; \sigma_{xx2N} = -C_2 \cdot \sin(2 \cdot \eta); \sigma_{xx2T} = -2 \cdot \mu \cdot C_2 \cdot \cos(2 \cdot \eta) \\ \sigma_{yy1N} &= -C_1 \cdot \sin \eta; \sigma_{yy1T} = 0; \sigma_{yy2N} = -C_2 \cdot \sin(2 \cdot \eta); \sigma_{yy2T} = 0 \\ \sigma_{xy1N} &= 0; \sigma_{xy1T} = -\mu \cdot C_1 \cdot \sin \eta; \sigma_{xy2N} = 0; \sigma_{xy2T} = -2 \cdot \mu \cdot C_2 \cdot \sin(2 \cdot \eta)\end{aligned}$$

Zone BD: $\eta = 0$ by ek (23), (25), (29), (30):

$$\begin{aligned}\sigma_{xx1N} &= 0; \sigma_{xx1T} = -2 \cdot \mu \cdot C_1 \cdot (\theta^{-\xi}); \sigma_{xx2N} = 0; \sigma_{xx2T} = -2 \cdot \mu \cdot C_2 \cdot \theta^{-2\xi} \\ \sigma_{yy1N} &= 0; \sigma_{yy1T} = 0; \sigma_{yy2N} = 0; \sigma_{yy2T} = 0 \\ \sigma_{xy1N} &= 0; \sigma_{xy1T} = 0; \sigma_{xy2N} = 0; \sigma_{xy2T} = 0\end{aligned}$$

By analyzing the surface lining we distinguish in the passive body, the maximum strain at the trailing edge of the contact path which is equal to $\sigma_{1,max} = 2 \cdot (1 + \lambda) \cdot \mu \cdot p_H$. It is known that destruction starts at the points that are pulled and these are found at the ends of the contact path, see Fig. 7.

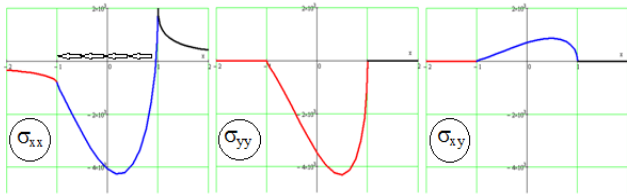


Fig.7 Struts on the passive body surface lining in contact for case $C_1 = 3500 \frac{N}{mm^2}, \mu = 0.2$

By analyzing the surface lining we distinguish in the active body that the maximum retraction strain is located at the other end of the contact path with a smaller value $\sigma_{1,max} = 2 \cdot (1 - \lambda) \cdot \mu \cdot p_H$, see Fig. 8.



Fig.8 Strands on the surface of the active body in contact with the case $C_1 = 3500 \frac{N}{mm^2}, \mu = 0.2$

6. The skeleton of the tooth at the toothed wheel

Skeleton is an injury from tiredness in contact with the tooth surface, is a progressive destruction of cyclic strains and has the features of fatigue destruction [4-6]. Oily wheels in the environment of oil are always damaged by the skull, especially this damage appears in the area from the pole to the toes. According to the coefficient of friction literature in this case (in oil environment) varies by type of oil at the limits $0.05 \div 0.06$ [5]. When the oil is absent varies in the range of $0.09 \div 0.4$, so the maximum tangential strain appears on the surface and the discussion ends. It starts the destruction of the fatigue contact.

In a couple of sprockets we distinguish the active wheel that the movements comes from and the passive wheel that the movement goes. In addition, we recognize the active tooth with the highest tangential velocity and the passive tooth with lower tangential velocity because the normal speed is the same. At the beginning of the active tooth, the active wheel is active and at the end of the gear the active tooth is active wheel. This helps us to set the direction of the friction forces, starting from the active tooth, always against it and the opposite tooth according to the principle of counteracting action.

Seeing the tangential speed game, we conclude that when the contact point is located on the part from the foot to the poly of the gear of each tooth of each wheel, the maximum tensile strengths in the traction are impacted by frictional forces. This strain is in tune and explains every disaster, especially from fatigue contact. From both bodies, one of them appears to be in charge, and this is in the tooth area up to the poly Fig.9 and Fig.10.



Fig. 9 The skeleton in the wings of the teeth

Active Wheels Active 1 Passive Wheels Active Wheel 2 Active wheel. Passive wheel

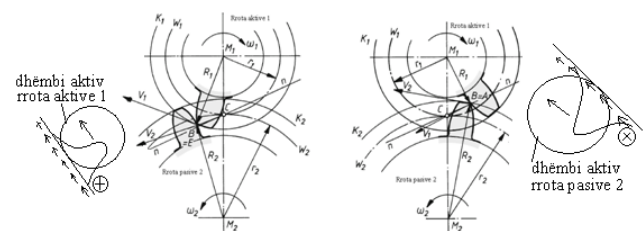


Fig.10 Determining the frictional forces direction

The maximum value of the pulled force for the passive tooth and the active tooth are respectively $\sigma_{1,pasiv,max} = 2 \cdot (1 + 0.424) \cdot \mu \cdot p_H$ and $\sigma_{1,aktiv,max} = 2 \cdot (1 - 0.424) \cdot \mu \cdot p_H$. Therefore, we conclude that the destruction always starts from the surface due to the friction and the tendency to flip the tooth.

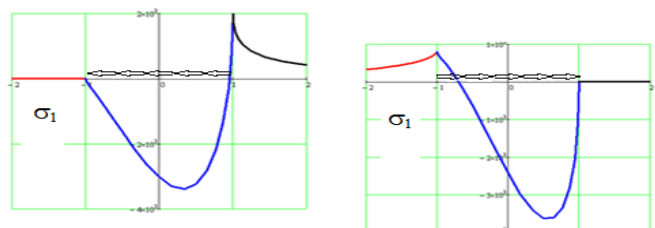


Fig.11 Main strain on the body surface and counter-contact surfaces

7. Conclusions

From the harshness of the rough contact and its application to the toothed wheel we conclude that:

- Analytical determination of stiff contact state.
- At the end of the contact line always appears a pulling strain due to friction.
- The passive body is loaded more in tow than the active body due to friction and flip.
- Friction is the main cause of the skirmish.
- The maximum peak strength on the surface lining depends directly on the friction coefficient and the Hercule pressure.
- The skeleton starts from the pole and goes straight to the end of the tooth because in this area the maximum peak pull strength $\sigma_s = 2.848 \cdot \mu \cdot p_H$ appears.
- Calculation of the tooth skeleton are merely calculation of fatigue contact.

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Comparison of the Precision of Dry Sieve Analysis versus Wet Sieve Analysis for Some Selected Natural Clay Varieties

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Abstract: Clay is a specific soil type that composed with relatively finer particles usually less than 0.002mm according to most of standard definitions including the behaviours of cohesive and the clay particles may have different sizes less than 0.002mm and most of occasions the clay bulk is contaminated with some more coarse particles such as sand and silt even though those particles are comprised in a same deposit or a same massive body. Most of clay varieties are frequently condign in the advanced technological uses. Therefore, the investigation of the particle sizes of some of clay and categorization are important tasks in the selection of a clay type for some particular technological application. The well known methods for the grain size analysis are the wet sieve analysis and dry sieve analysis in order for cohesive soils and non-cohesive soils as usual. In the existing study, there were anticipated to compare the accuracy of dry sieve analysis results with the wet sieve analysis results of three different selected clay varieties in Sri Lanka. As the experiential works those clay samples were separately analyzed using a sieve range of 2mm- 0.037mm and pan (<0.037mm) using dry sieve method. Also those clay types were wet sieve analyzed with respect to the sieve size of 0.075mm. According to dry sieve analysis results the finer portions (<0.075mm) were obtained as ~17%, ~6% and ~16% from clay 1, clay 2 and clay 3. The results of wet sieve analysis showed ~60%, ~37% and ~72% of finer portions (<0.075mm) in clay 1, clay 2 and clay 3 while the average grain sizes (D50) of them were 0.25mm, 0.27mm and 0.19mm. When comparing of those results the minimum deviation between wet sieve analysis result and dry sieve analysis result was found from clay 2 which is having maximum average grain size (D50) while the maximum deviation was observing from clay 3 which is having minimum average grain size (D50).

Keywords: Anthill clay, Brick clay, Roof tile clay, Wet sieve analysis, Dry sieve analysis

1. Introduction

Clay types have been identified as the specific varieties of soils because of the uncommon visible and physic-chemical characteristics of such clay in the comparison of those characteristics against the common characteristics of abundant soils. As a physical characteristic, particle size would be a descriptive parameter based upon the uses of such clays and soils in the industrial purposes. In the consideration of the analysis of particle sizes of soils the sieve analysis is the well-known standard method that used to classify the relevant group of soil such as the clay, gravel, silt etc. However, based upon experimental activities and past research experiences, there were defined two standard sieve analysis techniques that depending on the particle sizes of the soil type or the specific soil category as follows [1, 2, 3, 4, 5, 6].

- Dry sieve analysis- Coarse grained soils such as sand, gravel, pebbles, cobbles etc.
- Wet sieve analysis- Fine grained soils such as clay, silt, ultrafine clay etc.

According to the methodologies of both wet sieve analysis and dry sieve analysis, it is possible to emphasize some important contrarieties.

In the wet sieve analysis technique, the unknown dry soil sample is separated into a series with respect to know sized while applying an external vibrational forces through a shaker. In the selection of this method, the following primary characteristics of the unknown soil type will be considered [4-10].

- Non-cohesive soil
- Relatively coarse grained soils

In the dry sieve analysis method, the unknown dry soil sample is separated as two or more stages as follows.

- Primary stage- Separation of the coarse portion and the finer portion of the soil

Usually the unknown soil sample is dissolved in distilled water on a known size of sieve. The critical separation size would be the size of used sieve.

- Secondary stage- Size analysis and classifications of the separated portions in respectively such as the dry sieve analysis for the coarse portion and the hydrometer analysis for the finer portion.

The required critical separation size would be decided by the researcher based upon the aims and objectives of the research. Based upon the requirements of the analysis, the relevant standard sieve size would be selected. In the selection of the critical separation sieve sizes the standard defined particle size of the required soil type could be used as a reference value as follows [1-10].

- Clay – <0.075mm (USCS Standards)
- Sand - 0.075-4.75 (USCS Standards)

The sizes of soils are not the fixed values and it is possible to be varied in size according to the type of soils based upon a few of main factors as follows [2-8].

- Weathering conditions (erosion)
- Climatic conditions such as the temperature, wind, rain pattern etc.
- Geomorphological conditions
- Anthropogenic activities such as the vegetation

Clay is an abundant earth material at around large number of locations in the world including various characteristics from one location to other one. The experimental studies of the accuracies of those scientific methods for unknown materials are the essential chapters on the research and development activities.

In the existing research, there were expected to analyze and compare the status of bot wet sieve analysis and dry sieve analysis outcomes using three selected different clay types that available in three different locations in Sri Lanka.

2. Materials and Methodology

The representative clay samples were collected from three different locations of Sri Lanka and the collected clay types were nominated using the names that based on their typical uses and origin. A brief description about such clays is given in the Table 1.

Table 1: A brief description of the selected clays

Clay Type	Uses	Collected Area	General Characteristics
Anthill Clay (Clay 1)	Not recorded	Matale	Cohesive clay, reddish brown and relatively finer grained clay
Brick Clay (Clay 2)	Brick industry	Maduragoda	Less cohesive clay, brown and relatively coarse grained clay
Roof Tile Clay (Clay 3)	Roof tile industry	Dankotuwa	Much cohesive clay, yellowish brown and relatively finer grained clay

The representative portions of the collected clay samples are shown in the Fig.1.



Fig. 1. (a) Roof tile clay (b) brick clay and (c) anthill clay

2.1. Dry Sieve Analysis

Some representative portion of each clay type was selected and the selected clay portions were oven dried for 24 hours under the temperature of 110°C based upon the purpose of the removal of water content/moisture content from the clays.



Fig. 2. Drying oven

The dried clay samples were separately crushed using a ceramic crucible based upon the purpose of the breaking of clogs of clay particles. In the crushing, it was not used any of high performance comminution machinery such as the ball mills, crushers etc. Each clay sample was weighed using an analytical balance.

The crushed dry clay samples were separately poured on to a flat surface and the final representative clay sample from each clay type was selected using coning and quartering method as shown in the Fig.3.

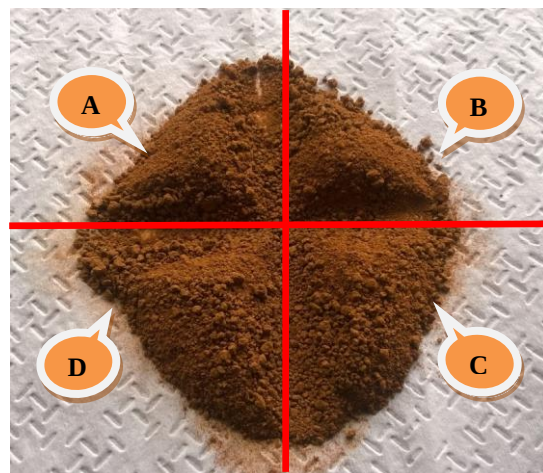


Fig. 3. Coning and quartering method

Coning and quartering method is a well-defined sample selection method from a large portion which is applicable for the solid materials such as soils, powdered minerals etc.

The selected representative clay samples were separately analyzed using a set of standard sieves and relevant equipment as shown in the Fig.4.



Fig. 4. Sieve set and sieve shaker

After 10 minutes shaking period, the retained clay weight of each sieve was measured an analytical balance. The particle size distribution curve was plotted with respect to each clay type based upon the observed data [1-6].

2.2. Wet Sieve Analysis

The representative clay samples were prepared using the same methodology except the step of crushing. Each representative clay sample was weighed using an analytical balance.

Each representative clay sample was washed on sieve in the size of 0.075mm using distilled water as the finer portion is washed out and the coarse portion is remaining on the mesh. The remained coarse portions were oven dried for 24 hours under the temperature of 110°C and each of dried coarse portions was weighed using an analytical balance [5-10].



Fig. 5. 0.075mm standard sieve

The dried coarse portion was dry sieve analyzed using the same methodology that discussed in the previous chapter and the finer portion was sent for the hydrometer analysis.

3. Results and Discussion

The dry sieve analysis results of anthill clay are shown in the Table 2.

Table 2: Dry sieve analysis results of anthill clay

Sieve Size (mm)	Weight retained on each sieve (g)	Percentage of weight retained (%)	Cumulative percentage of weight retained (%)	Cumulative percentage of weight passed (%)
2	0.02	0.04	0.04	99.96
0.5	10.34	20.32	20.36	79.64
0.25	15.61	30.68	51.04	48.96
0.149	12.39	24.35	75.39	24.61
0.074	3.91	7.68	83.08	16.92
0.037	7.86	15.45	98.53	1.47

<0.037 (pan)	0.75	1.47	100	0.00
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The particle size distribution curve of anthill clay is shown in the Fig.6.

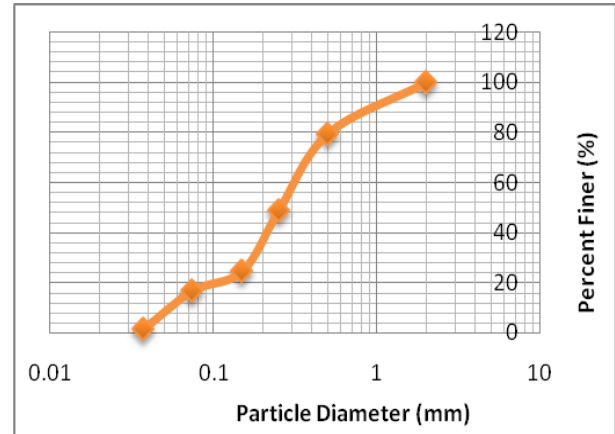


Fig. 6. Particle size distribution curve of anthill clay

According to the above graph the average particle diameter (D_{50}) of anthill clay was recorded as

The wet sieve analysis results of anthill clay are shown in Table 3.

Table 3: Wet sieve analysis results of anthill clay

Aggregates	Weight Percentage (%)
Coarse Aggregates (>0.075mm)	~40
Finer Aggregates (<0.075mm)	~60

The dry sieve analysis of the coarse portion of anthill clay are shown in the Table 4.

Table 4: Dry sieve analysis results of the coarse portion of anthill clay

Sieve Size (mm)	Weight retained on each sieve (g)	Percentage of weight retained (%)
2	0.01	0.04
1.18	0.71	2.95
0.59	7.92	32.89
0.42	3.26	13.54
0.25	4.99	20.72
0.15	4.1	17.03
0.075	2.89	12.00

<0.075 (pan)	0.2	0.83
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When comparing of both wet sieve analysis and dry sieve analysis results of anthill clay, there were observed the great difference in the results for the finer portion (<0.075) in both dry sieve analysis and wet sieve analysis results. According to the dry sieve analysis method (experimental method), it was observed ~ 17% of finer portion with respect to the weight since the more accurate value was observed as ~ 60% under the wet sieve analysis method (well defined method for clays). In addition, that the soils weights which were retained in other sieves showed the dissimilarities in both dry sieve analysis and wet sieve analysis methods [1,2,3,4,6,10].

The dry sieve analysis results of brick clay are shown in the Table 5.

Table 5: Dry sieve analysis results of brick clay

Sieve Size (mm)	Weight retained on each sieve (g)	Percentage of weight retained (%)	Cumulative percentage of weight retained (%)	Cumulative percentage of weight passed (%)
2	0.01	0.02	0.02	99.98
0.5	10.41	20.30	20.32	79.68
0.25	17.13	33.41	53.74	46.26
0.149	13.43	26.19	79.93	20.07
0.074	7.09	13.83	93.76	6.24
0.037	2.47	4.82	98.58	1.42
<0.037 (pan)	0.73	1.42	100	0.00

The particle size distribution curve of brick clay is shown in the Fig.7.

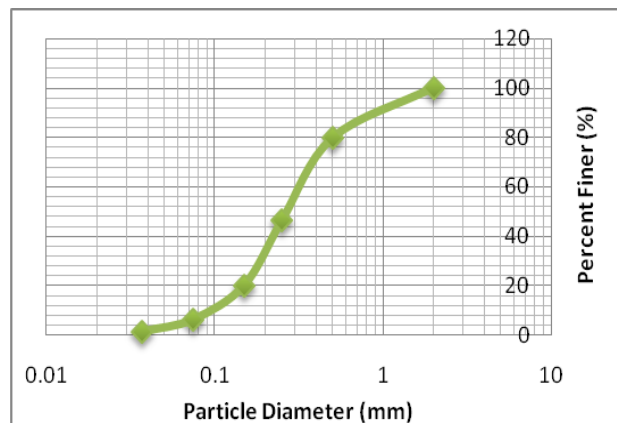


Fig. 7. Particle size distribution curve of brick clay

According to the above graph the average particle diameter (D_{50}) of brick clay was recorded as

The wet sieve analysis results of brick clay are shown in Table 6.

Table 6: Wet sieve analysis results of brick clay

Aggregates	Weight Percentage (%)
Coarse Aggregates (>0.075mm)	~63
Finer Aggregates (<0.075mm)	~37

The dry sieve analysis of the coarse portion of brick clay are shown in the Table 7.

Table 7: Dry sieve analysis results of the coarse portion of brick clay

Sieve Size (mm)	Weight retained on each sieve (g)	Percentage of weight retained (%)
2	1.94	5.13
1.18	1.94	5.13
0.59	7	18.51
0.42	3.71	9.81
0.25	7.45	19.70
0.15	8.57	22.66
0.075	6.53	17.27
<0.075 (pan)	0.68	1.80

In the comparison of both results of wet sieve analysis and dry sieve analysis of brick clay, there were obtained ~6% of finer portion under the dry sieve analysis and ~37% of finer portion under the wet sieve analysis method. Also there were observed the dissimilarities in between the results of wet sieve analysis and dry sieve analysis of brick clay with respect to each sieve size [1-8].

The dry sieve analysis results of roof tile clay are shown in the Table 8.

Table 8: Dry sieve analysis results of roof tile clay

Sieve Size (mm)	Weight retained on each sieve (g)	Percentage of weight retained (%)	Cumulative percentage of weight retained (%)	Cumulative percentage of weight passed (%)
2	0.16	0.31	0.31	99.69
0.5	11.8	23.17	23.48	76.52
0.25	7.97	15.65	39.13	60.87
0.149	11.71	22.99	62.12	37.88
0.074	11.12	21.83	83.96	16.04
0.037	7.05	13.84	97.80	2.20
<0.037 (pan)	1.12	2.20	100	0.00

The particle size distribution curve of roof tile clay is shown in the Fig.8.

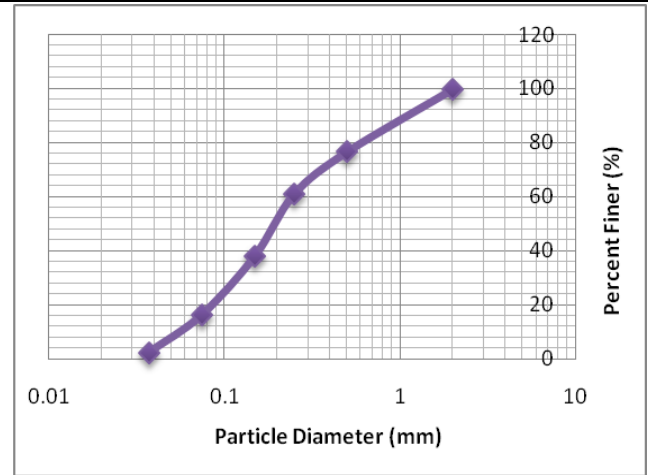


Fig. 8. Particle size distribution curve of roof tile clay

According to the above graph the average particle diameter (D_{50}) of roof tile clay was recorded as

The wet sieve analysis results of roof tile clay are shown in Table 9.

Table 9: Wet sieve analysis results of roof tile clay

Aggregates	Weight Percentage (%)
Coarse Aggregates (>0.075mm)	~28
Finer Aggregates (<0.075mm)	~72

The dry sieve analysis of the coarse portion of roof tile clay are shown in the Table 10.

Table 10: Dry sieve analysis results of the coarse portion of roof tile clay

Sieve Size (mm)	Weight retained on each sieve (g)	Percentage of weight retained (%)
2	0.35	2.14
1.18	0.28	1.71
0.59	2.61	15.98
0.42	1.07	6.55
0.25	2.1	12.86
0.15	3.57	21.86
0.075	4.62	28.29
<0.075 (pan)	1.73	10.59

In the consideration of the observed values for the finer portions under both wet sieve analysis and dry sieve analysis methods, there were obtained ~16% of finer percent under the dry sieve analysis method and ~72% of finer percent under the wet sieve analysis method. When considering the relevant results for other sieve sizes there were observed the variations as usual [1, 2, 3, 4, 5, 7, 8].

Table 11: Deviations of results for the finer portion both wet sieve analysis and dry sieve analysis

Clay	Finer Portion in Wet Sieve Analysis (%)	Finer Portion in Dry Sieve Analysis (%)	Deviation (%)	Average Grain Size (D_{50})/ mm
Anthill Clay (Clay 1)	~60	~17	~43	0.25
Brick Clay (Clay 2)	~37	~6	~31	0.27
Roof Tile Clay (Clay 3)	~72	~16	~56	0.19

In the comparison of the values in above table, there can be identified some correlation between the average grain size (D_{50}) of a soil/clay and the deviations of the results for the finer portion of particle according to the weight that obtained under both methods of wet sieve analysis and dry sieve analysis. Usually it is possible to expect some relatively higher deviations of such results with respect to the soils/clays that having lower average particle size (D_{50}) [2, 3, 4, 5, 6, 8].

The dry sieve analysis method would be a common method to analyse both coarse soils and finer soils although that there might be consisted some errors in results that obtained under the dry sieve analysis method for finer soils such as the clays. However, the dry sieve analysis method can be used for both coarse soils and finer soils to have some approximate conception on the soil/ clay and it is possible to detect the requirement of wet sieve analysis method for such soil/clay type by referring the average grain size (D_{50}) value of such soil/clay which is determined under the dry sieve analysis method while comparing of that value with the standard or experimental reference values for the soil classification in particle size [1-6].

In the dry sieve analysis of finer soil verities, it is better to perform the experiment with relatively lower weight of soil samples because in the existing research there were found some experimental errors in the continuing of sieve analysis with respect to intermediate sieves when the sample was too large.

4. Conclusion

In the considerations of the major outcomes of the wet sieve analysis and wet sieve analysis methods of three different clay types, mainly there were observed some higher deviations (errors) based on the results that obtained under both wet sieve analysis and dry sieve analysis methods for the finer portions of clay according to the weights. When comparing those deviations with the average grain sizes (D_{50}) of clays, there were seen the important correlations between the experimental deviation and average grain sizes (D_{50}) of clay because the experimental deviation was relatively lower in coarse grained clays/soils with relatively higher in average grain sizes (D_{50}).

5. Acknowledgement

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Features of creation of multiprobe system for nanometric measurements of geometrical and mechanical properties of surfaces of microsystem devices

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Abstract: The article considers the peculiarities of the technology of creating a multiprobe system for nanometric measurements of geometric and mechanical properties of the surfaces of microsystem devices. This system is built on the sites of domain-dissipative structures formed by the method of combined electron-beam micromachining on piezoelectric ceramics of the grade "lead zirconate-titanate". The fundamental problem of creating such a nanoinstrument – measuring probes is the difficulty of determining the exact location of the contact regions of these probes. A fundamentally new method of high-precision formation of contact regions by the electroplating capillary method is considered. It is shown that the application of this method will speed up 3.5 – 5.5 times the process of measuring geometric and mechanical surface parameters, as well as the sensitivity of the measurement process by 10 – 18%, which, in general, increase the productivity and reliability of determining these parameters of surfaces of microsystem devices on average – by 15 – 25%.

Keywords: MULTIPROBE SYSTEM, NANOMETRIC MEASUREMENTS, MICROSYSTEM DEVICE, DOMAIN-DISSIPATIVE STRUCTURE, PROBE, PIEZOELECTRIC CERAMICS

1. Introduction

Piezoceramic elements and devices based on them have recently been increasingly used in such fields of science and technology as precision instrumentation, medicine, hydroacoustics, aerospace and shipbuilding [1]. The high accuracy, reliability, sensitivity and control flexibility of such devices, the possibility of their implementation in miniature dimensions allow the use of piezoelectric elements as measuring elements for diagnosing the molecular composition of various gases and liquids, even under high pressure, temperature, vacuum and aggressive environments, and in some cases (for example, when measuring the pressure of the coolant at nuclear power plants) piezoelectric element is the only possible measuring instrument.

Another region of metrological measurements that is impossible without the use of piezoceramic materials is scanning probe microscopy, where such materials are used as the main measuring elements in the measuring unit, as well as the main element of the precision supply unit of the measuring instrument to the sample [2, 3].

The main advantage of using piezoceramic elements in measuring devices is due to their special structure, which allows to implement in one such element fundamentally different schemes, for example, for simultaneous measurement of temperature, pressure and humidity. However, the specificity of the manufacture of such elements negates the possibility of their miniaturization. The way out of this situation is seen in the formation of domain-dissipative structures in piezoelectric ceramics by creating ordered nanostructures on its surface.

One possible variant of such a measuring element is a piezoceramic chip with thin consoles formed on its surface. The composition and shape of the tip of the consoles are selected based on the condition of deposition of molecules of the test gas (liquid). The intrinsic oscillations of the molecules cause the console to oscillate, which in turn causes an electric pulse to form on the piezoceramic chip. By the nature and duration of such a pulse, an idea of the molecular composition of the test substance is formed. However, the complexity of manufacture and the narrow range of measured values do not allow the widespread use of such measuring elements in practice.

As shown in [4 – 6], ordered thermal nanostructures on the surfaces of piezoceramic elements can be obtained by thermal deposition in vacuum. Further action on such surfaces by the electron flow of the tape form [7, 8] leads to the formation in piezoelectric ceramics of zones (domain-dissipative structures) with different values of the piezomodule d_{31} and the coefficient of electromechanical coupling K , which, in turn, allows you to create a piezoelectric circuit, limited by the volume of such a single zone.

However, the main difficulty in creating probes on such ordered structures is the need for high-precision formation of micrometric conductive sections of a given shape and location.

In the course of previous experiments [9, 10] it was shown that a significant influence on the formation of ordered nanostructures has not only the thickness of the applied coatings, but also the geometric characteristics and chemical purity of the material to be deposited.

Therefore, the electroplating capillary method is promising for obtaining such contact regions.

Another important issue that needs to be addressed is the choice of method of control of the obtained structures and elements on them [11].

Among the existing non-destructive methods of control, which can be used to determine both the state of the surface of piezoelectric elements (its microgeometry and purity) and the size of the structures formed on it, the most promising is the method of atomic force microscopy, which has high accuracy (up to 1 nm); sensitivity (of the order of 10^{-12} N) and performance. Therefore, the development of technology for creating a multi-probe system for nanometric measurement of geometric and mechanical properties of surfaces of microsystem devices and the study of microgeometry and surface condition, as well as identifying the boundaries of individual regions in piezoceramic elements using atomic force microscopy is an important task.

The aim of the work is to study the peculiarities of creating ordered domain-dissipative structures in piezoelectric ceramics with the subsequent formation of contact regions and measuring probes using a combined galvanic capillary method with subsequent electronic micromachining, which allows to create miniature elements of multiprobe measuring and measuring surface properties of microsystem devices.

2. Experimental research

The experimental part of the work was carried out in specialized laboratories: "Laboratories of vacuum technology and electron beam processing methods", "Laboratory of Applied Optics and Atomic Force Microscopy" of the Training and Research Center "Micronanotechnology and Equipment", established at Cherkasy State Technological University.

The method of combined technology to create a multi-probe system was as follows. Initially, electronic microprocessing of piezoelectric surfaces consisted of two stages and consisted in the formation of a thin homogeneous metal (Ni) coating up to 1000 nm thick on the surface of piezoceramic elements of the ZTP grade by thermal deposition in vacuum $(2...3) \cdot 10^{-3}$ Pa. The formation of ordered structures (respectively, domain-dissipative structures) on the thus obtained coatings was carried out electronically, when the flow of low-energy electrons affected the surface of such coatings through a removable mask and led to partial melting and evaporation of the coating material. In this case, the control of the electron flow power in the process of such combined microprocessing allowed to simultaneously separate zones with

different values of the piezomodule d_{31} and the coefficient of electromechanical coupling K and, at the same time, to polarize these zones in a given direction.

The next step after the creation and polarization of metallized nickel-plated domain-dissipative structures in piezoceramics is the formation of measuring probes on the surfaces of these structures. This formation is carried out by electroplating capillary method, the essence of which was the electrochemical deposition of Ni and W ions from a liquid solution of the following composition: $\text{NiSO}_4 \cdot 7\text{H}_2\text{O} : \text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O} : \text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O} : \text{NH}_4\text{OH} = 2 : 5 : 6 : 3$.

In the first stage, a thin film (buffer layer) of Ni powder, which is used for the manufacture of piezoelectric electrodes (Powder Nanotechnologies LLC, Cherkasy), was applied by resistive deposition. Modes of the coating process: film thickness $h = 60 \dots 80$ nm; evaporator current $I = 20$ A; deposition time $t = 2.6 \dots 4.8$ s; the average size of the precipitated particles is $0.6 \dots 1.1$ μm . The deposition of the buffer layer was associated with the need to increase the cohesive strength formed on the coating of the probe and create a more uniform coating.

In the second stage, under the same deposition modes and deposition time $t = 5.6 \dots 8.4$ s, ordered structures were applied through a removable molybdenum mask. Subsequent low-energy electron microprocessing of the obtained coatings (accelerating voltage $U_a = 0.8 \dots 1.1$ kV; electron current $I_e = 250$ mA; duration of electronic action $t = 0.8 \dots 3.3$ s) led to evaporation of the buffer layer and, at the same time with this, to the formation of a homogeneous ordered coating on the piezoelectric surface [12].

The deposition was carried out at a solution temperature of $65 \dots 75$ $^{\circ}\text{C}$, current density of $1 \dots 5$ A/dm², pH = 6...9; used anodes – platinum, deposition time 4.5... 5.5 hours (under conditions of constant temperature and pH of the solution).

Probes were grown by electrochemical deposition of probe materials made of platinum titanium or nickel, which had the shape of a thin wire, which was placed in the liquid medium of the working electrolyte in a thin glass capillary (ratio of wire diameter to capillary diameter, as 1:10...1:15). Control of operating modes and geometrical parameters of deposition was carried out by means of the automatic control system (ACS) specially developed with participation of authors, Fig.1.

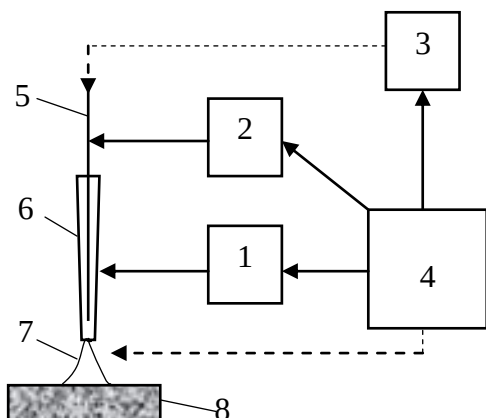


Fig. 1. Block diagram of the ACS operating modes and geometric parameters of the technology of electrochemical deposition of the probe: 1 – block supply capillary to the deposition surface; 2 – block precision feed wire; 3 – control unit of electric current of galvanic deposition; 4 – microprocessor automatic control system; 5 – wire cathode for deposition of metals on the surface; 6 – capillary with working fluid for deposition of metals on the surface; 7 – liquid conduction channel of ions of the precipitated material; 8 – deposited surface.

As the material is deposited on a given area of the ACS automatically increases the distance from the deposited surface (pos.8) to the capillary with the working fluid (pos.6). This leads to a reduction of the meniscus of the liquid channel (pos.7), thereby – thinning the perimeter of each subsequent deposited layer of the substance. Another advantage of the developed ACS is the ability to

accurately determine the boundaries of metallized areas on the surface of the piezoceramic element, which were obtained in the first stage (by the method of resistive deposition). The deposition process continues until there is a break in the electrical circuit due to rupture of the meniscus (pos.7) when the capillary (pos.6) from the deposited surface (pos.8) to a sufficient distance.

The combined electronic microprocessing was performed on a modified technological electronic equipment UVN-71 in one technological cycle in two stages. The processing tool was a tape-shaped electron flow with a length and width of the electron flow on the surface of the material, respectively, 60 mm and 1.5 mm. The objects of the study were samples of piezoelectric ceramics ZTP-19 (parallelepiped bars $3 \times 2 \times 1$ mm), made in 2018 and taken from one batch of samples in the amount of 10 samples.

Studies of the surface of piezoelectric ceramic elements, as well as the study of the boundaries of the formed structures after combined electron microprocessing were performed using a scanning electron microscope JEOL JSM-6700F (Japan) in the center of collective use of the Ukrainian representative office "Tokyo-boeki" (Kyiv), and also with the help of the atomic force microscope "NT-206" in the International Training and Research Center "Micronanotechnology and Equipment". Silicon probes "Ultrasharp CSC12" were used. The atomic force microscope included a micropositioning system and a built-in Logitech long-focusing optical microscope, which were used to position the measuring system of the device in certain areas of the sample surface. Measurement of the microrelief of the surface of the samples was performed in a statistical mode on the surface areas, with a maximum size of 13×13 μm , in accordance with the developed methods and recommendations.

3. Discussion of research results

The conducted researches of the received ordered nanostructures on the created sites of elements of piezoelectric ceramics of the ZTP grade allowed to establish the following.

By applying the galvanic capillary method on the prepared metallized surfaces of individual sections on the piezoelectric ceramic elements, a conical W-Ni structure is formed, which can be used as a measuring probe for nanometric means (for example, scanning probe microscopy devices), Fig.2.

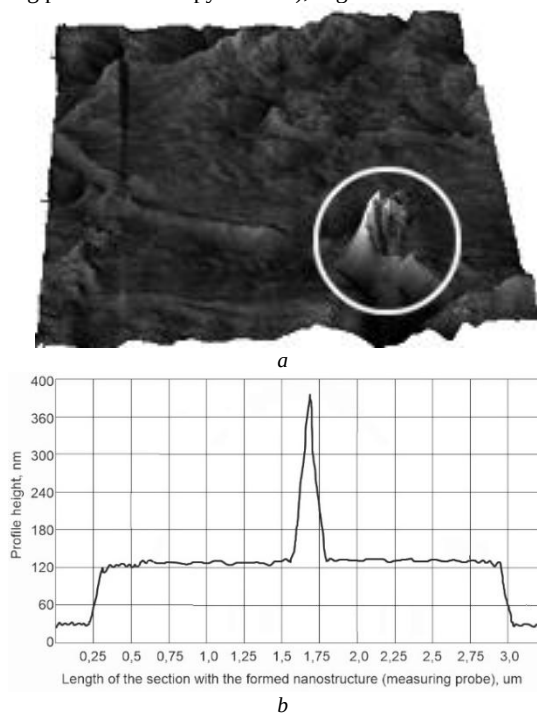


Fig. 2. Topogram (a) and profile (b) of the ordered nanostructure (probe) created on the site of piezoelectric ceramics formed by the combined technology

As can be seen from Fig. 2, the use of a combined method to create a multiprobe system of nanometric measurements allows to obtain measuring elements (nanoprobes) on such surfaces of high precision shape and size, which can be easily adjusted by modes developed by ACS (see Fig. 1).

In this case, the action of low-energy electron flow of the tape form directly on the surface of the piezoelectric ceramics leads to the formation in the volume of the piezoceramic material of zones of high density with a reduced value of free dipoles. This determines the boundaries of domains with a certain direction of the

polarization vector (the size of such domains is usually determined by the size of the ordered nanostructure on the ceramic surface).

It is likely that this decrease is due to the intense evaporation (sublimation) of the piezoceramic matrix material under the action of a concentrated energy source – the electronic flow. This is indicated by the decrease in the porosity of the piezoceramic surface after electronic exposure to it. As a result of the conducted researches the sizes of the formed structures (that is, zones with various values of d_{31} and K) which make 2,2...8,0 mkm were established, Fig.3.

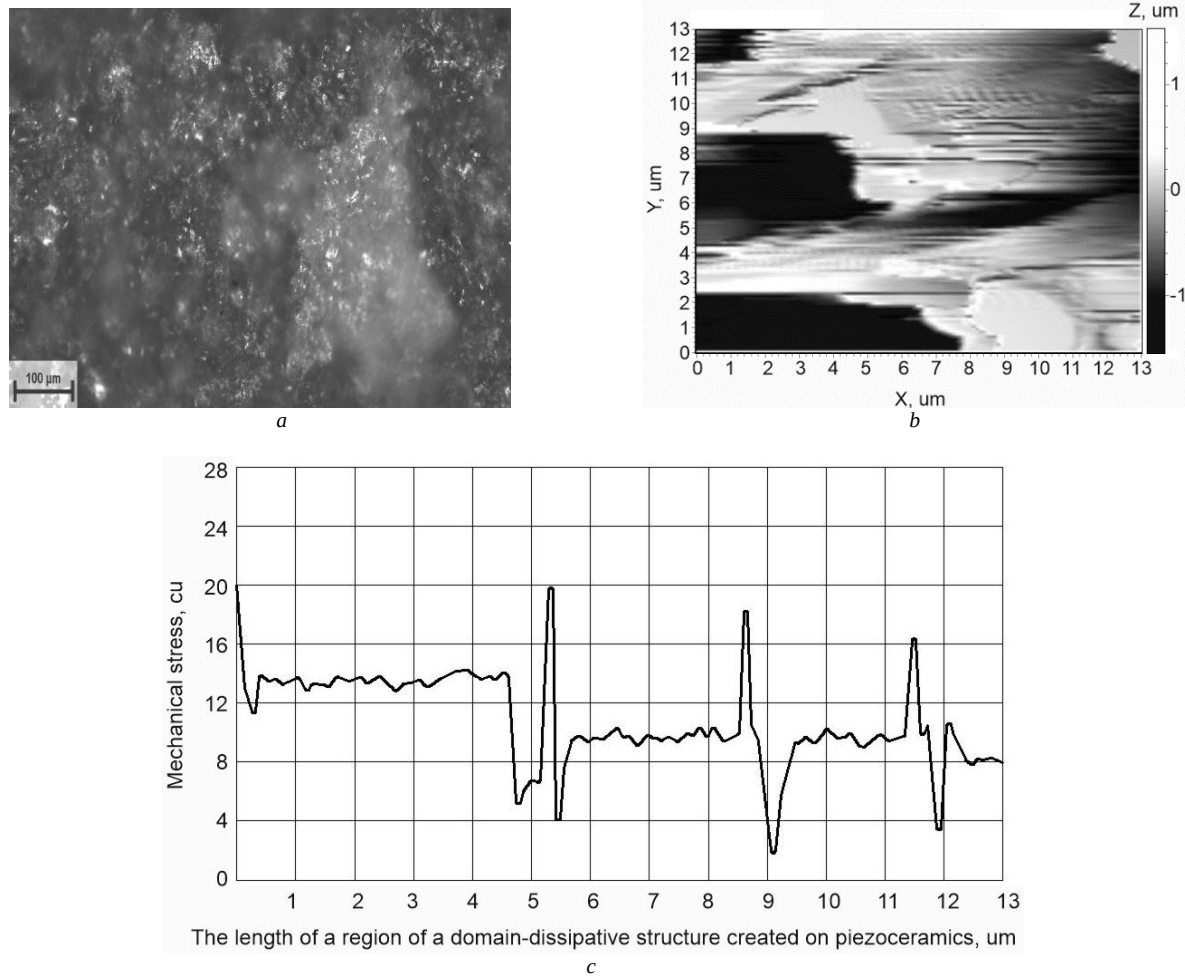


Fig. 3. Fragment of the surface of the sample of piezoceramics ZTP-19 with the domain-dissipative structures formed in it: a) micrograph of the surface section. JEOL JSM-6700F; b) a map of the distribution of domain-dissipative structures in the surface of the sample; c) the shape of the boundary of the domain-dissipative structure at the surface of the sample. NT-206 (lateral force mode)

5. Conclusion

It is shown that the use of the combined galvanic capillary method with subsequent electronic microprocessing will speed up 3.5 – 5.5 times the process of measuring geometric and mechanical parameters of the surface, as well as the sensitivity of the measurement process by 10 – 18%, which, in general, increase productivity and the reliability of determining these parameters of the surfaces of microsystem devices on average – by 15 – 25%.

The study of ordered domain-dissipative structures allowed to establish the conditions for the formation of the boundaries of these structures by the combined action of the electron flow on piezoelectric ceramics. The coefficient of electromechanical coupling in these zones was 0.44...0.48, and the piezomodule d_{31} increased insignificantly (by $4 \cdot 10^{-7}$ cm/CtV), which is characteristic of piezoceramics of the ZTP system. However, the action of the electron flow leads to a decrease in surface porosity by 3...5%, as well as an increase in its microhardness by 0.5...0.8 MPa.

Based on the obtained results, it is planned to further study the electrodynamic and electromechanical characteristics of blast-dissipative structures and probes formed on these structures from piezoelectric ceramics ZTP-19 by combined galvanic capillary method with subsequent electronic microprocessing.

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Complex study of the bioaerosol composition of the atmosphere over urban areas based on lidar monitoring during the quarantine COVID-19

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Abstract: A comprehensive study of the air condition in urban areas was conducted, based on lidar monitoring. The subject of monitoring are two districts of Sofia the capital of the R.Bulgaria. The time period of the study is May-June 2020 and coincides with the introduced quarantine period in connection with the COVID-19 pandemic. The study includes lidar monitoring of the selected urban areas taking into account the mass concentration of particulate matter (PM). The method is combined with in situ sampling taking into account also the size control in μm – PM2.5 and PM10. The data are compared with those from the indications for the period of the licensed laboratories of the Ministry of Environment and Water and the Civil Network. A physicochemical study of the phase composition, structure and dispersion of the collected PM was performed by the methods of powder X-ray diffraction and Mössbauer spectroscopy. Predominant pollen and spore contamination was reported using Cascade Impactor measurements. Most part, the PMs studied show a conglomerate of several particles.

Keywords: BIOAEROSOL, PARTICULATE MATTER (PM), LIDAR MONITORING, PM SAMPLING

1. Introduction

Atmospheric pollution is a huge problem for the people living in big cities and is relevant through such planetary problems as global warming and damage to the ozone layer. Air pollution and urban air quality are listed as two of the world's worst toxic pollution problems in the 2013 and interest in it has been growing so far [1, 2, 3]. The present-day scientific interest over following the advances in measurement technologies [4. 5. 6. 7. 8. 9. 10.], which have allowed for monitoring the processes in the atmosphere and understanding of the biogenic composition and of the physicochemical properties of atmospheric particles. Particulate matter (PM) emitted by vehicles in urban traffic, seasonal heating and industrial activities, can greatly affect environment air quality and have direct implications on human health. This paper talks over the most recent results of air quality investigation at some residential districts of Sofia-the capital of R. Bulgaria within the application of Lidar monitoring of scanning the horizontal aerosol distributions and the vertical long-distance transport of air masses at operational distances exceeding 25 km. The studies were expanded with local sampling based on spatio-temporal data from lidar monitoring and indepth study of the bio-chemical and physical properties of PM. These studies are a natural continuation of our work covered in the book "Atmospheric Air Pollution Monitoring" [11].

2. Methods, instruments, and procedures

The lidar mapping was performed by a lidar system installed on the Lidar station of Institute of Electronics. The site at residential district Mladost is located at a distance about 3 km and Dragan Tsankov blvd. is at a distance of 5.5 km from the lidar. This lidar system is capable of scanning the horizontal and vertical aerosol distributions and transport of air masses with a spatial resolution of 30 m and a beam divergence of ~ 1 mrad at operational distances of about 25 km. The laser emitter (wavelength of 510.6 nm) is a pulsed CuBr vapor laser with a repetition rate of 10 KHz at a 15-ns pulse duration. The receiving system comprises a Carl Zeiss Jena Cassegrain telescope (aperture of 20 cm, a focal distance of 1 m), a 2-mm-wide focal diaphragm, an interference filter with 2-nm-wide passband, and an EMI 9789 photo-multiplier tube operating in a photon-counting mode. The receiving system is fully computerized for collecting and processing the lidar data using a PCO 1001 1024-channel digital interface system for signal strobing and accumulation.

The PM sampling were realized using Andersen Cascade Impactor [12]. For enumeration of microbiota into the atmospheric

air, an active sampling with FSC-A6 1CFM impactor was engaged. Glass Petri dish (ϕ 90x15 mm) with 27 ml sterile nutrient media was positioned beneath each stage. Nutrient agar with cycloheximide was used for bacteria and YGC agar for fungal enumeration. The Petri dishes were incubated for 48h at room temperature (25°C). The positive hole method and expressed as CFU/m³ was used for total colony counts (Andersen, A.A, 1958). The control and selection of particles by size and mass concentration in this experiment was expanded through systematic use during lidar experiments and in the daily experimental practice of the Microcontroller SDS 011 – PM2.5 и PM10. Additionally, the material collected on the filters and the stage after three hours of aspiration during the lidar monitoring was studied by SEM and EDAX. Mössbauer analysis was made using a Wissenschaftliche Elektronik GmbH apparatus, working at a constant acceleration mode; ⁵⁷Co/Cr source, α -Fe standard. The parameters of hyperfine interactions of the Mössbauer spectral components were determined by computer fitting.

3. Results and discussion

The city of Sofia has a well-developed control network of local licensed stations for daily pollution control in selected points of the town. The subject of this study is to compare the network information with the lidar measuring during the months May and June 2020, which are part of the quarantine period of the COVID-19 pandemic. The measurement of pollution for the period shows a relatively low concentration of PM, which is due to understandable reasons of limited traffic and relatively warm weather for the season (average monthly temperature in the range of 16-20°C), which significantly reduces the use of heating appliances, respectively the use of solid fuels. The limited traffic opens a good opportunity to study the contribution of organic particles and especially those related to the flowering of plants, which is typical for the second haft of May and the beginning of June. In the second haft of June, significant relief was introduced in quarantine measures and industrial life returned to its traditional activities. Although the pollution did not exceed the critical values [13], we conducted indepth studies of the PM and microbial contents (Mladost and Lozenets), where more than 160 thousand citizens live.

3.1. Lidar monitoring

Analyzing the PM in aerosol loadings formed in the vicinity of the grounded level of the atmospheric urban areas and experimentally measured of the mass concentration of the aerosol by the lidar technique were able to draw the important conclusion. Two major lidar parameters were calibrated, namely, the extinction

coefficient $\alpha(r)$ and the backscatter coefficient $\beta(r)$, in terms of the aerosol mass concentration following the well-known method [10,13] and making use of the mass concentration M_a data obtained by the sampling device. For the lidar ratio $LiR = \alpha(r)/\beta(r)$ we adopted the typical value of $LiR = 50$ [10,13]. The parameters $\beta(r)$ and $\alpha(r)$ were calculated using the lidar equation under the assumption of a horizontally-homogeneous atmosphere:

$$P(r) = P_0 \frac{c\tau}{2} C \frac{\beta(r)}{r^2} \exp\left[-2 \int_{r_0}^r \alpha(r) dr\right] \quad (1)$$

where $P(r)$ is the power of the detected laser radiation backscattered from the atmosphere from a distance $r = \frac{ct}{2}$ after a period of time t following the moment of laser pulse emission, and τ is the pulse duration. Under the homogeneity assumption, the extinction coefficient $\alpha(r)$ is calculated as

$$\alpha(r) = -\frac{1}{2} \frac{dS(r)}{dr}, \text{ where } S(r) = \ln[r^2 P(r)] \quad (2)$$

Calibration dependencies of the mass concentration in $[mg/m^3]$ of, respectively, $\alpha(r)$ and $\beta(r)$ was developed. In both cases, the linear fit ($Y=A+B.x$) shows acceptable values of the standard deviation (less than 4 %) and the correlation coefficient (over 0.92). The plots can be used directly for calibrating the lidar maps, shown above, in mass concentration.

The lidar observation schedule complied with the generally accepted manner of measuring the aerosols mass concentration by air-quality monitoring systems. The sampling device pumps atmospheric air through the filter (typically a volume of 60–100 m^3) for an interval of about a few hours. Thus, the laser beam was stationary and directed to pass above the aspirator at a height of $h_{PM} < \delta R$, $\delta R \sim 30m$ being the lidar's radial resolution. The height of placing the aspirator was also chosen to comply with this condition, $h_{asp} < \delta R$. The lidar signals represent the number of backscattered photons $L_{phot}(k, \delta R, \tau_m)$, where $k=1..K_{max}$, $K_{max} = R_{max}/\delta R$, and $\tau_m = 5min$ is the time of photons accumulation. The total time of measurement lasted from one to several hours, depending on the particular weather situation. The computer system processes the input data by solving the lidar equation (1), with its output being profiles of the backscatter coefficient $\beta(k, \delta R)$ or the extinction coefficient $\varepsilon(k, \delta R)$, as calibrated in terms of aerosols mass concentration (see Fig. 3 above). The set of lidar profiles obtained for the entire period of measurement is used to construct 3D lidar maps, with the x axis presenting the accumulation time with a step of $\tau_m = 5min$ and the y axis, the distance from the lidar with a step δR . The z axis corresponds to the color-coded coefficients of backscatter or extinction.

The lidar monitoring of the selected areas was carried out with a starting point – Lidar station of the Institute of Electronics, as the laser beam is horizontal at a height of about 40 m and its direction is marked on the city map (see Fig.1). The lidar measurements were also performed with inclined lidar drilling with a variable angle to the horizon, as the height at the end of the route reaches a height of 2 km. Fig.1b shows a lidar map in the form of a corner sector of daily observation (19.05.2020), which well illustrates the capabilities of the lidar and is a typical lidar image for the studied period. Fig.1a for comparison shows the lidar map of a typical image for April 2019.

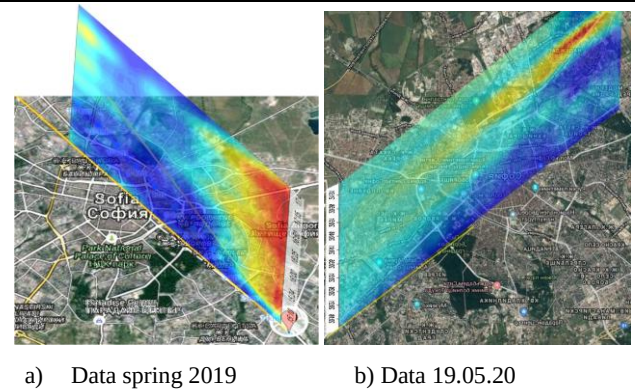


Fig. 1 a) Lidar sector mapping of pollution measured in April 2019 and b) measured in May 2020 (graduation from light blue to dark brown shows an increase in the mass concentration of PM)

Figures 1a and 1b well illustrate the difference between the pollution found by the lidar during the quarantine period and the conventional state of the atmospheric pollution in the same caisson but with heavy traffic. Apparently in the COVID-19 quarantine period the surface atmospheric layer has a very low concentration of PM. The data from the lidar monitoring shown in Fig.1 make it possible to obtain fast and accurate information in time-space coordinates. It is evident that for the studied period the pollution in the ground layer of the urban atmosphere is insignificant, but the lidar makes it possible to report pollution in the higher layers of the atmosphere.

The dependence of the aerosol extinction coefficient in the surface atmosphere on the distance to the Lidar station was also investigated. This coefficient is one of the most accurately measured optical parameters of the atmosphere and is used to calibrate lidar signals at mass concentration [11]. The data shows that the surface aerosol atmosphere is almost homogeneous at distances up to over 8 km from the location of the lidar and varies in small ranges from 0.01 to about 0.03 micrograms per cubic meter. At these extinction values, the atmosphere can be considered clean during the quarantine period, which is mainly due to the greatly reduced car traffic, as well as the reduced industrial activity of the citizens due to the state of emergency. It can be expected that by May and the beginning of June 2020 the air quality has improved.

3.2. Particle size distribution studies

In order to better assess the accuracy of lidar monitoring, in parallel with daily pollution measurements were made using electronic sensors type Microcontroller SDS 011, which detects pollution with PM2.5 and PM10. The controllers were located at a height of 10 m from the ground. Our measurements were compared with data from licensed stations and those of the civil network.

Below in Fig.2 shows histograms that illustrate well the approach to these measurements. Data from 05 and 06 May 2020 were selected, in which relatively high pollution was reported. This is a time when the merger of two weekends ends and during which there was an increase in car traffic of vacationers returning to the capital. Our measurements are compared with the data from the nearest measuring points of the licensed network of the Ministry of Environment and Water and of the civil network of the Cleanliness Movement. The results were obtained using an electronic tester type Microcontroller SDS 011 for PM2.5 and PM10. The survey was conducted daily in May and June 2020. Fig.2 illustrate the approach in measuring pollution.

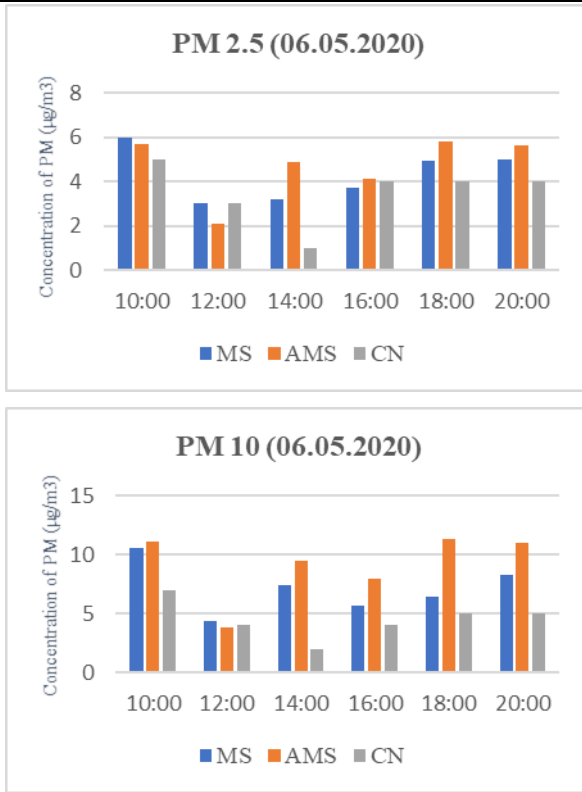


Fig. 2 Data about the PM2.5 and PM10 for three points of the district Mladost (MS – mobile sensor data, Mladost 1; AMS – licensed air monitoring station data, Mladost 1; CN – civil network data, Mladost 2).

In our measurements, the influence of the parameters – temperature, humidity, wind speed and atmospheric pressure – was taken into account in parallel. The data are shown in Table 1.

Table 1: Meteorological data during the measurement

	T (°C)	Relative humidity (%)	Wind (m/s)	Atmospheric pressure (hPa)
10:00	7	80	3.1	1014
12:00	9	82	3.1	1014
14:00	9	82	3.6	1015
16:00	8	87	5.7	1015
18:00	7	80	2.0	1016
20:00	9	71	5.1	1014

From the above data it can be seen that in practice we have two maximums of pollution – in the morning until 10.00 h and after 18.00 h. These peaks are repeated systematically on a monthly basis. In practice, the measurements of pollution with controllers coincide well with the lidar data for relatively high air purity (low mass concentration of PM) and similarity of pollution in large urban areas. This finding gave us reason to unify the measurements with those of the licensed stations near which our results were compared. For this purpose, a method for calibration was developed.

3.3. Calibration of sensor data

Below we will describe the algorithm applied for calibration of sensor data. The measured data are presented as time series, denoted by:

$$X(t_k), t_k = t_0 + \Delta k, k=1..N \quad (3)$$

where Δ is the sampling interval, t_k are the successive sampling instances, N is the total number of single measurements and $T_m = N \cdot \Delta$ is the full measurement time. Moreover, the variables $X(t_k)$ present the sensor measured separately PM2.5 & PM10 mass concentrations in ($\mu\text{g}/\text{m}^3$).

Following the expression in (3) the reference data can be presented as well by

$$Y(t_k), t_k = t_0 + \Delta k, k=1..N \quad (4)$$

They are collected simultaneously by the officially calibrated Station (IOS) of the Sofia Municipality, disposed nearby to about 70m. The reference sensor data are given as well separately for the both particle types PM2.5 & PM10 respectively.

In the further analysis we will accept the aerosol field, carrying the aerosol PM2.5 & PM10 particles in the region of measurements as approximately uniform and stationary during the measurement time T_m . Then, we could calculate separately from (3, 4) the total mass concentrations for the both types PM2.5 and PM10, given by :

$$MX^{PM2.5} = \sum X^{PM2.5}(t_k) k=1..N; MX^{PM10} = \sum X^{PM10}(t_k) k=1..N; \quad (5)$$

$$MY^{PM2.5} = \sum Y^{PM2.5}(t_k) k=1..N; MY^{PM10} = \sum Y^{PM10}(t_k) k=1..N; \quad (6)$$

where $MX^{PM2.5}$, MX^{PM10} in (4) are the sensor's measured total mass concentrations and $MY^{PM2.5}$, MY^{PM10} in (5) are the corresponding total mass concentrations, measured by the Municipality reference Station. As seen in (4) and (5) the calculated total mass concentrations are averaged quantities over the entire measurement time T_m at the assumption for the uniform and stationary aerosol field.

One can now calculate the calibration coefficients to the sensor time series in (3) using the ratios R_0^{PM} for both particle types PM2.5 & PM10 respectively, using (4), (5) and given by:

$$R_0^{PM2.5} = MY^{PM2.5} / MX^{PM2.5}; R_0^{PM10} = MY^{PM10} / MX^{PM10} \quad (6a)$$

At least, using the expressions in (6) the calibrated quantities $X_{cal}(t_k)$ in the sensor measured PM mass concentrations $X(t_k)$ can be presented by

$$X_{cal}^{PM}(t_k) = R_0^{PM} \cdot X^{PM}(t_k), t_k = t_0 + \Delta k, k=1..N, \quad (6b)$$

The effects of the calibration algorithm above developed on the time history of the measured time series $X^{PM2.5}(t_k)$ and $X^{PM10}(t_k)$ by the both types of sensors: of IE-BAS and the Civil network are presented on Fig.3a to 3e below. Here the plot in Fig.3a presents ratio of both mass concentrations of PM2.5/PM10, measured by the Reference station used also for the calibration of other two groups of sensors. As seen, the ratio PM2.5/PM10, averaged over the entire period from March 7 to March 25 is of order of 0.48-0.5, which is typical for the clear atmosphere conditions. Moreover, the time-variations of the same ratio PM2.5/PM10, displayed as time series are given in Fig.3b. As seen, some non-strong air pollution are detected during the first half of the measurement period, when the same ratio is of order of 0.5, remaining relatively constant on the 0.5 level up to the end of the measurement period.

The effects of the calibration algorithm are further demonstrated on the next Fig. 3c3 to 3c5. Here the ratio PM2.5/PM10 is calculated from the non-calibrated data, acquired by the sensors in the civil network. As seen in Fig.3c3, here the PM2.5/PM10 varies within the limits of 0.4 to 0.6 for the first period as in Fig. 3c2. Then, during the last quarantine period the same ratio is rapidly increased up to the values of 1.6. As seen in Fig.3b such of high increase of the ratio PM2.5/PM10 was not observed in the previous Fig.3b. The next Fig.3c demonstrates the time history of the same ratio PM2.5/PM10 calculated from the same data as in previous figure, but after their calibration, according to the above Calibration algorithm. As seen, the variations of the same ratio within the first period remains within the same limits as in the first two figures. Moreover, the step increase of the ratio PM2.5/PM10 on the final quarantine period is missing here. This result is very important as it demonstrate the effectiveness of the Moreover, the same behavior of the ratio PM2.5/PM10 is displayed on the last Fig.3e, where the calibrated data from the IE sensors are shown. We will note that the mean ratios, calculated from calibrated data remains very close as shown in all of figures. As a conclusion, it could be stated, the calibration algorithm here developed could be useful in many cases

for calibration of sensors over large networks, using a single reference station.

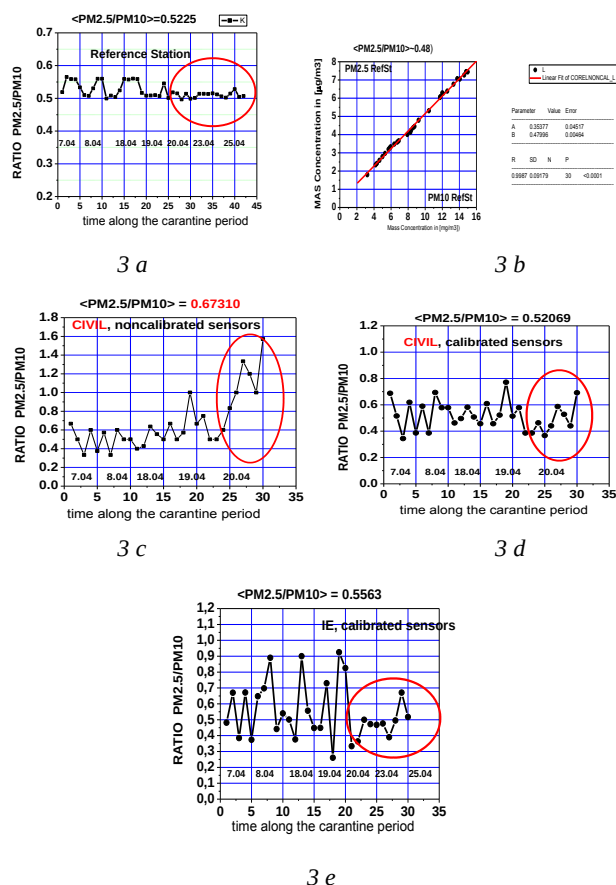


Fig. 3 Summarized calibrated data from our measurements for May and June 2020 for PM2.5 and PM10 pollution (Sofia's districts Mladost and Lozenets)

3.4. Crystallochemical features of PM

The recorded X-ray diffractograms show that the examined PMs are X-ray amorphous. No crystalline phases were detected. One of the diffractograms is presented on Fig.4 and well illustrate the structural features of the PM.

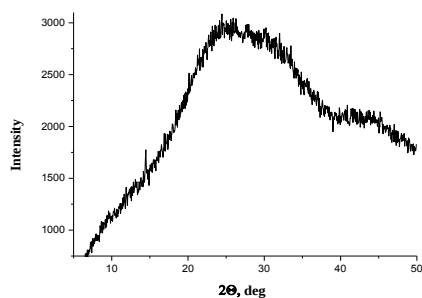


Fig. 4 X-ray diffraction pattern of PM, which illustrates their amorphousness and absence of crystalline phases.

Mössbauer's analyzes of the studied PMs show the presence of iron ions in the second valence of oxidation, mostly in the atmosphere of district Lozenets, while equal amounts of divalent and trivalent iron were registered in the samples from district Mladost. The absence of sextet (magnetic) components and the presence of a predominant amount or entirely divalent iron is characteristic of PM with natural origin – mineral or biologic. Which can explain the amorphous structure illustrated in fig.4.

3.5. Quantitative characteristics of the microbial component in the selected locations

Quantitative analysis was performed to determine the total number of cultured microorganisms as follows: aerobic heterotrophic bacteria (NA medium) and fungi (YGC medium). Samples were collected twice for each month (1 and 4 weeks) by means of a six-stage cascade impactor and performed in triplicate for each sample.

The results of the analysis show a significantly higher number of bacteria compared to that of fungi in both time intervals of the study. When comparing the data from this analysis over time: May, 2020 and June, 2020, a significant increase in the number of the two studied groups is reported. As already mentioned, the first interval tested in May is characterized by extremely low anthropogenic pressure due to the quarantine sanitary-epidemiological restrictions for the period (Fig. 5).

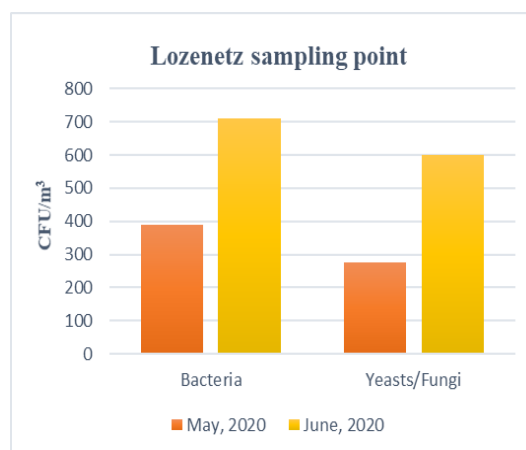


Fig. 5 Quantitative characteristics of the microbiota in Lozenets location

Cascade impactor aspiration methods are currently considered to be one of the most suitable for quantifying the microbial component, as they provide information on the size distribution of bioaerosol particles. The distribution of bioaerosols, respectively their precipitation and stability depend to a large extent on the size of the bioaerosol particles. The data from the comparative analysis of bacteria and fungi depending on the size of the bioaerosol particles in the above location are given in Table 2.

Table 2: Quantitative characteristics of bacteria and fungi depending on the size of bioaerosol particles in Lozenets location

Location Lozenets				
Size of bioaerosol particles (µm)	Bacteria (CFU/m³)		Fungi (CFU/m³)	
	May	June	May	June
I – 0.65 – 1.1	3.1±0.2	8.5±0.3	0	0
II – 1.1 – 2.2	13.2 ±0.1	39.5±0.2	8.1±0.1	91.3±0.3
III – 2.1 – 3.3	75.8±0.5	125.2±0.1	45.2±0.1	161.1±0.1
IV – 3.3 – 4.7	99.6±0.4	160.4±0.1	95.2±0.1	205.3±0.1
V – 4.7 – 7.0	90.3±0.1	171.8±0.2	37.5±0.1	78.2±0.1
VI – > 7.0	110.5±0.3	207.2±0.3	90.2±0.2	42.5±0.2

The results obtained show domination of bacterial bioaerosol particles with sizes over 7.0 µm, followed by those with sizes 4.7 - 7.0 µm; 3.3 - 4.7 µm and 2.1 - 3.3 µm. The cascade impactor does not allow the ingress of a particle larger or smaller than the corresponding level of the pores. This proves that the association of microbial cells with PM, leading to the formation of an aggregate of a certain size. The analysis of the size distribution of the fungal bioaerosol particles reveals the highest share of particles with sizes 2.1 - 3.3 µm and 3.3 - 4.7 µm.

4. Conclusions

In general, the following main conclusions are outlined: 1. Quarantine period has led to a sharp reduction in PM pollution. Traffic and the use of solid fuel for heating are strongly reduced and this is underlined by the data on lidar monitoring for the same period in 2019 and the increase in pollution while easing the quarantine measures (after 13.06.20). 2. The greatly reduced presence of PM due to traffic and heating has opened up a good opportunity to take into account the presence of microbial contamination in the ground layers of the atmosphere. 3. Their presence is either as well-formed microbially contaminated PMs in the form of bioaerosols associated with inorganic PMs. 4. The amount of microbiota (bacteria and fungi) increases significantly after the relief of the quarantine period, which shows a direct relationship between the inorganic and microbial content of PM.

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Experiment on charging an electric vehicle LiFePO₄ battery after over-discharge

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Abstract: The efficiency and technical and economic properties of the electric cars depend mainly on the rechargeable traction battery. LiFePO₄ batteries belongs to the lithium-ion type and has a number of advantages such as high capacity, long life cycle, resistance to fire at high temperatures or shock. They have safe and stable over-charging and over-discharging performances. This paper describes the process of charging the individual cells of an electric car battery after their over-discharge.

Keywords: LITHIUM IRON PHOSPHATE (LiFePO₄) BATTERY, OVER-DISCHARGE, CHARGING, ELECTRIC VEHICLE

1. Introduction

Early vehicles were created to meet the transport needs in the settlements. Due to low speeds and low mileage, in the middle of the 19th and the beginning of the 20th century the use of electric cars and cars with internal combustion engine was equal, but social and technical factors gave an advantage in the development of cars [1]. The harmful effects of emissions from internal combustion engines, the reduction of fossil fuel resources and improvements in electric vehicle technology have led to an increase in the production of electric vehicles at the beginning of the 21st century. The conversion of a car with an internal combustion engine into an electric car is one of the possibilities for creating environmentally friendly cars [2]. The efficiency and technical and economic indicators of the electric car depend mainly on the rechargeable battery. Rechargeable batteries used in electric cars and hybrid cars can be: lead, nickel-cadmium, nickel-metal hydride, lithium-ion, lithium-polymer, metal-air, sodium-sulfur, sodium-metal chloride [3, 4]. Lithium-iron phosphate batteries (LiFePO₄) belong to the lithium-ion and have a number of advantages such as high theoretical capacity, long cycle life, resistant to ignition at high temperatures or shock. The life cycle of a lithium-ion battery is more than 2000 charge / discharge cycles and can reach tens of thousands at shallow discharge depths. Cycle life is the number of complete discharge and charge cycles that can be expected from the battery before it reaches its end-of-life (EOL) [5]. The cells LiFePO₄ have a nominal voltage 3.2 V per cell and discharge-charge voltage range of 2.0 V – 3.6 V according to [6]. When converting a conventional car into an electric car, several lithium-ion cells can be connected in series, thus providing a higher voltage or in parallel (greater capacity) or both. In the electrical circuits of the lithium-ion battery there are always small differences between the cells due to the production tolerances. To increase safety and increase the life of a newly supplied lithium-ion battery, the cells must be pre-balanced and the entire battery pack pre-charged. It is mandatory to install a battery management system for the lithium-ion battery - BMS, i.e. BMS performs the battery monitoring function. The BMS monitors the following parameters of the battery cells during charging and discharging: currents, voltages, internal temperature of the battery or the environment. If any of the parameters approaches or exceeds the normal limits, the BMS generates an audible or visual alarm and sends a signal to the input of the protection devices, which will disconnect the battery from the load or the charger [7]. In some electric vehicles, especially those converted during long stays, the battery is over-discharged caused by consumers such as the alarm system, the auxiliary battery, the consumption of BMS, leaks and others. The probability of this happening increases with the forced need for a long stay, for example in the conditions of COVID-19 quarantine.

According to [6], an important advantage of lithium-iron phosphate batteries is that they have reliable and stable performance when recharged, i.e. even if the lithium-iron phosphate battery is discharged to 0 V, there will be no damage or accident. However, in [8] charge-discharge experiments of lithium iron phosphate (LiFePO₄) battery packs have been performed. Their conclusion is that the over-discharge has a huge impact on the utilizable capacity and cycle life of the batteries. In particular, over-discharge may completely damage the battery when the voltage drops to 0 V, but

the battery does not ignite, explode or smoke. The authors of this publication have also performed experiments on over-discharged cells with high-current charging, using the on-board charger of the electric car. In this experiment, some of the cells deformed (swollen).

In this work the process of charging the battery of an electric car after over-discharging of the individual cells is described. Charge experiments of lithium iron phosphate (LiFePO₄) battery have been performed on an electric car. Based on the theory and the conducted experiment, a method has been proposed for restoring the battery of an electric car after over-discharge, using a low current to charge the individual cells to reduce the damage to the battery.

2. Object of Research and Used Equipment

An object of research was the battery of a converted car with a gasoline engine into an electric car with an induction electric motor. The electric motor power is 25 kW/120 Nm, the battery is 100 Ah LiFePO₄ and nominal voltage 3.2 V per cell. The battery pack consists 30 series-connected cells (Fig. 1) as the nominal voltage of the whole battery is 96 V and stored energy 9.6 kWh.



Fig. 1 The battery pack and BMS information display.

The used cells in this work are model SP-LFP100AHA and their characteristic is shown in Fig. 2.

The characteristic shows that when discharged, the cell voltage drops sharply when reaching the moment of complete discharge. At low discharged currents the branch is steeper. During a long stay without the electric car in motion, when the consumption is minimal covering the needs of the alarm system, BMS, leaks, etc., it is difficult to predict the moment of complete discharge of the battery. In such cases, there is a risk of completely over-discharge the battery. The experience has shown that when charging a fully discharged battery with the high current on-board charger 16 A, good results are not achieved, therefore the authors have used a charger for individual charging of cells with lower current (2 A).

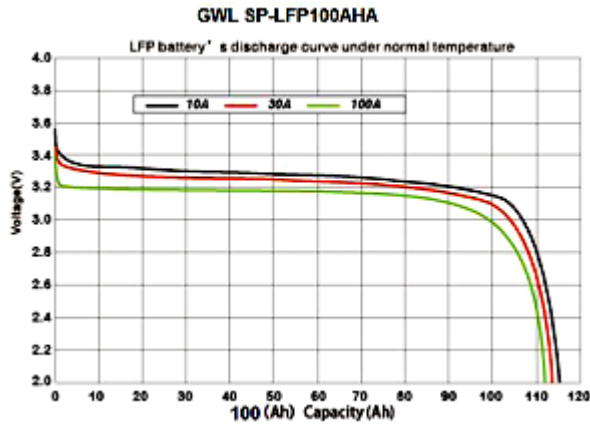


Fig. 2 Characteristic of a cell model SP-LFP100AHA [9].

To charge the individual cells the used charger is IMAX B6 LiPro Balance Charger (see Fig. 3) which according to the manufacturer is suitable for charging and balancing lithium-ion cells without the risk of over-charging.



Fig. 3 The used balance charger discharger.

The charger has the ability to charge different types of cells, such as the LiFe charging program, provides the following parameters:

- Voltage level: 3.3 V/cell;
- Max. charge voltage: 3.6 V/cell;
- Allowable fast charge current: 4 C or less;
- Discharge voltage cut off level: 2.0 V/cell or higher.

3. Experimental Procedure

An experiment was performed to charge 30 over-discharged cells. Their measured initial voltage is shown in Tab. 1. The total battery voltage after over-discharging the cells is 56 V.

Table 1: Battery condition after over-discharging.

Battery, №	Voltage, [V]	Battery, №	Voltage, [V]
1.	0.50	16.	2.10
2.	0.86	17.	2.10
3.	1.26	18.	2.13
4.	1.26	19.	2.14
5.	1.31	20.	2.16
6.	1.34	21.	2.18
7.	1.39	22.	2.18
8.	1.40	23.	2.22
9.	1.71	24.	2.22
10.	1.75	25.	2.25
11.	1.88	26.	2.27
12.	1.88	27.	2.28
13.	2.05	28.	2.30
14.	2.08	29.	2.35
15.	2.08	30.	2.39

When these values are found, the wires of the battery are disconnected. The auxiliary battery was disconnected on the fifth day, as a decrease in its voltage was observed.

In the daily measurements of the cells, an increase in their voltage is noticed, probably due to their charging by the auxiliary battery until the fifth day when it is disconnected. An increase in voltage is also observed after that and the authors believe that it is due to charging by cells that are already charged by the charger. The connection between the individual cells to carry out this process probably takes place via the BMS wires.

In Fig. 4 the increase in voltage in one of the cells due to recharging by BMS is shown.

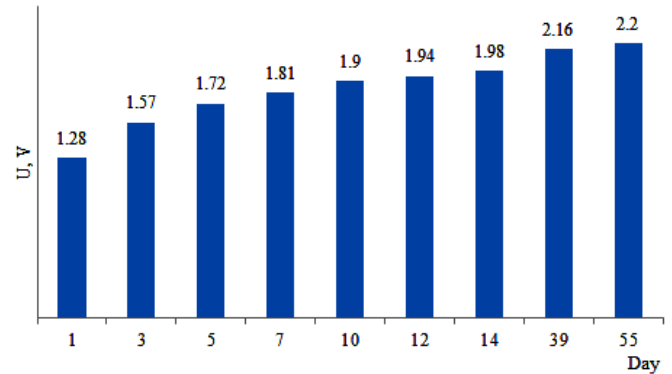


Fig. 4 Recharging a cell by BMS.

In Fig. 5 the change in voltage level of a cell charged on the fourteenth day is shown.

From the first to the twelfth day the recharging process by BMS can be seen. As can be seen in Fig. 5 after charging on the fourteenth day, a constant voltage was maintained (over a long period of 65 days). In this way, all 30 cells of the battery were charged.

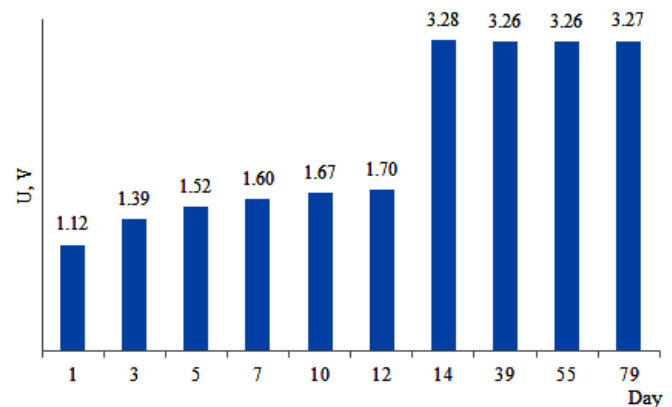


Fig. 5 Voltage level of a cell charged on the fourteenth day.

After loading all the cells, their condition was checked and no deformation (swelling) of the cells was found. The on-board charger was used for final charging, thus achieving 100 % charge of the entire battery. This was followed by test drives, initially over short distances (5÷10 km), which alternated with recharging the battery with the on-board charger. The distance traveled during the test drives gradually increased, reaching 50÷60 km at a residual energy in the battery of 20÷30 %. These values correspond to the initial ones before allowing the cells to be over-discharge.

In Fig. 6 is shown the charger socket while charging the electric car with the on-board charger.



Fig. 6 Charging the electric car with the on-board charger.

4. Conclusions

This article describes the process of charging the cells of a battery of an electric car after over-discharge and a method for charging the individual cells with low current to reduce the damage to the battery was proposed. Test drives with the electric vehicle were carried out. The same mileage was reached as before the over-discharge of the battery. This proves that this method achieves good battery recovery. The disadvantage of this method is its long duration, as the cells are charged one by one individually. The duration of the recovery charging process can be reduced by using more than one charger of this type.

Acknowledgement

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Production of powders of copper alloy (copper 85, tin 5, lead 5, zinc 5) by spraying a melt with a gas flow

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Abstract: The study of the process of producing copper alloy (copper 85, tin 5, lead 5, zinc 5) powders of grade by the method of induction melting and spraying with a melt gas flow is presented.

KEYWORDS: SPRAYING OF METAL MELT WITH A GAS FLOW, POWDER OF THE COPPER ALLOY (COPPER 85, TIN 5, LEAD 5, ZINC 5), INDUCTION MELTING, RESEARCH

1. Introduction

Bronze powders (copper alloy (copper 85, tin 5, lead 5, zinc 5) grade are widely used for spraying coatings by the gas-thermal method on the working surfaces of parts operating under friction and wear conditions. One of the main ways to produce spherical powders for spraying is spraying an overheated metal melt with a gas flow [1–3]. The method of producing metal powders by spraying a melt is technologically advanced, universal and highly efficient. However, in the process of induction melting, the copper alloy (copper 85, tin 5, lead 5, zinc 5) multicomponent alloy is significantly depleted in zinc due to the large difference in its melting temperatures with the melting points of the main component. A large number of techniques have been developed to reduce the loss of alloying components during melting and casting of the alloy. Their main recommendations are as follows [4–6]: to avoid overheating of the melt [7]; to use deoxidizers; to use fluxes.

Zinc and zinc-based alloys are very sensitive to overheating. Excessive overheating of zinc melts is always undesirable, since it causes the oxidation of zinc and alloying elements; it contributes to the saturation of the melts with hydrogen and oxide non-metallic inclusions. In addition, limitations on permissible overheating temperatures of zinc melts are due to the low boiling point of zinc and the evaporation of zinc. The losses of metals from evaporation depend on the pressure of the saturated vapor of the liquid metal: the higher the vapor pressure, the greater their losses during the preparation of alloys [8]. At the moment when the vapor pressure of the metal becomes equal to the external pressure, boiling of the metal begins, i.e. evaporation occurs not only from the surface, but throughout the entire volume. Deoxidizers are used to reduce the oxides that make up the alloy. One of the most common methods of deoxidation of powder of copper alloy (copper 85, tin 5, lead 5, zinc 5) is melting the alloy in graphite crucibles. Fluxes are used to protect the alloy from oxidation and to separate non-metal impurities that enter the metal. For the protection of copper-zinc alloys, fluxes are used consisting of materials such as glass, sodium chloride, calcium sulfate, calcium fluoride, barium chloride, borax, and etc.

However, all the applications of the above methods are impractical in the implementation of processes for producing spherical powders by spraying the melt with a gas flow. Thus, the recommendation not to overheat the melt contradicts one of the main requirements of the powder spraying process, i.e. melt overheating by at least 250 °C [9]. The use of deoxidizers and fluxes in the process of spraying powder is possible with a significant complication of the process and a decrease in its productivity, since before supplying the melt to the spraying unit, it is necessary to completely remove the slag. It is technically difficult to implement. At the same time, if the slag gets into the spraying unit, it clogs the nozzle, which requires stopping the entire spraying process and spending a significant amount of time and additional resources. In addition to losses in value terms, zinc vapor brings a

significant danger to human health. Thus, the development of ways to reduce zinc losses is an urgent and important task.

The purpose of the work is to study the effect of the melt overheating temperature, the diameter of its outflow jet and the gas pressure in the spray nozzle on zinc waste in the process of producing powders of copper alloy (copper 85, tin 5, lead 5, zinc 5) by induction melting and spraying the metal melt with a gas flow.

2. Experimental results and discussion

The production of experimental samples of sprayed copper alloy (copper 85, tin 5, lead 5, zinc 5) grade included the following basic operations [10, 11]: weighing the initial components, loading the components into an induction melting furnace and heating, spraying a jet of the melt, removing the powder from the equipment and drying, sieving powder.

1) *Weighing the initial components* (scrap copper – 83.48 %, tin – 4.91 %, lead – 4.91 %, zinc – 6.7 %). Copper scrap without tinsplate and soldering, plate zinc anodes, tin of O1 grade, lead sheets of C1 grade in the state of delivery were used as the initial components.

2) *Loading the components into an induction melting furnace and heating.* The melt was overheated with respect to the main component by 117 – 317 °C: the melt temperature was 1200, 1300, and 1400 °C. Two load variants were tried. According to the first variant, copper was heated to a specified temperature and melted. Then, slag was removed from the surface of the melt and tin and lead were introduced. When the melt reached the specified temperature, the most low-melting component, i.e. zinc, was introduced. According to the second variant, all the components were melted simultaneously: zinc sheets were twisted together with lead plates. Tin and copper were placed outside.

3) *Spraying a jet of the melt.* Within no more than 30 seconds from the moment of readiness, the melt entered the metal receiver. From the metal receiver, the melt freely flowed through a hole of a certain diameter in the form of a vertically falling jet into the spray zone, where it was dispersed into fine droplets by a gas flow. The sprayed droplets of the melt, due to the forces of gravity, moved into the water, where their final cooling took place. Figure 1 shows the equipment for spraying powders, and Figure 2 schematically shows a nozzle for spraying a jet of the melt. The hole diameter was 4, 6 and 8 mm; the pressure drop was 0.3 and 0.7 MPa.

4) *Removing the powder from the equipment and drying.* The sprayed powder was removed from the plate and dried at a temperature of 110 – 120 °C.

5) *Sieving powder.* The dried powder was sieved into fractions, and its chemical composition was examined.



Fig. 1 Equipment for spraying powders

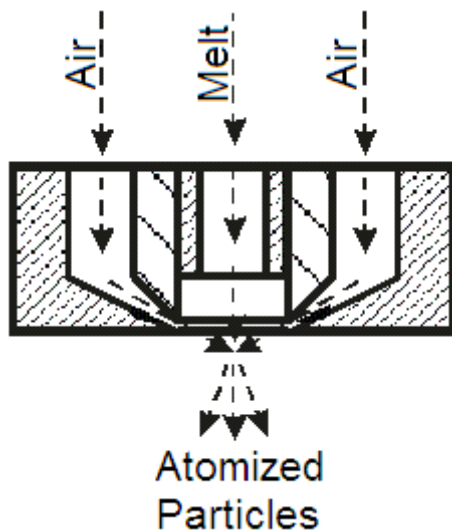


Fig. 2 The nozzle for spraying

According to the above technology, pilot batches of experimental samples of powders were produced and the effect of the melt overheating temperature, the diameter of the melt jet and the gas pressure on the value of zinc waste was investigated.

Table 1 shows the effect of overheating temperature on zinc waste at different sequence of introducing components into the melt.

Table 1 Effect of overheating temperature on zinc waste

Sequence of introducing components	Sequential introduction of components (variant 1)			Simultaneous introduction of components (variant 2)		
Overheating temperature, °C	117	217	317	117	217	317
Zinc content in the charge mixture, %	6,7	6,7	6,7	6,7	6,7	6,7
Zinc content in the powder, %	2,70	2,59	1,14	2,60	2,32	1,10
Waste, %	59,7	61,34	82,99	61,19	65,37	83,58

An analysis of the obtained data indicates that the overheating temperature has a primary effect on zinc waste. In this case, the

powder spraying technology according to variant 1 is preferable due to lower zinc losses. Further, the experimental samples were produced according to variant 1, i.e. with the sequential introduction of the components. Moreover, taking into account that excessive zinc waste is observed at a melt temperature of 1400 °C (overheating temperature is 317 °C), and at a melt temperature of 1200 °C (overheating temperature is 117 °C), a low output of good powder is observed. Then the melt was heated to a temperature of 1300 °C (overheating temperature is 217 °C).

The effect of the overheating temperature on the form factor and the output of a good powder for experimental samples produced at overheating temperatures of 1200 and 1300 °C was determined (the temperature of 1400 °C was not considered according to the data in Table 2 due to the large waste of zinc). Form factor FF was assessed by the method described in Ref. [12]:

$$FF = \frac{4\pi A}{L_0^2}, \quad (1)$$

where A – particle projection area, mm; L_0 – projection perimeter, mm.

The evaluation of the sphericity of the particles was carried out by determining the number of powder particles in the investigated fraction with a form factor of 0.8 or more on a certified automatic image analyzer “Mini-Magiscan” (“Joyce Loebel”, England) (Figure 3). The output of good powder was determined as a percentage in relation to the weight of the charge mixture for preparing the melt (Table 2).



Fig. 3 Automatic image analyzer “Mini-Magiscan” (“Joyce Loebel”, England)

Table 2 Effect of overheating temperature on a form factor and output of good powder

Over-heating temperature, °C	Good powder output, %	Particle content with a form factor not less than 0.8, %		
		Powder particle size, μm		
		(-1000+630)	(-400+200)	(-1000+630)
1200	88,5	69,0	81,0	90,0
1300	94,0	93,0	94,0	96,0

Figure 5 shows the appearance of powder of copper alloy (copper 85, tin 5, lead 5, zinc 5), produced by the developed technology, and not dispersed into fractions.

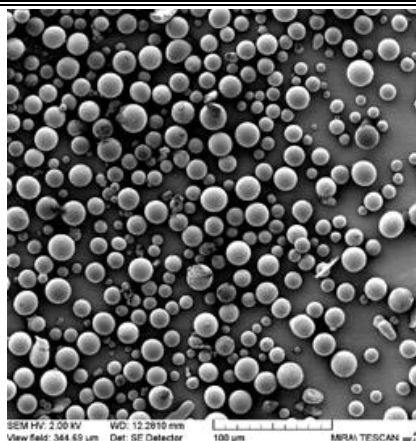


Fig. 5 The appearance of the produced particles of powders of copper alloy (copper 85, tin 5, lead 5, zinc 5)

The analysis of the obtained data indicates that the overheating temperature of 1300 °C is optimal for producing the required shape and chemical composition of the powder according to all parameters under study.

The effect of spraying modes of the melt (the diameter of the nozzle hole through which the melt flows and the gas pressure in the spray nozzle) by the gas flow on the zinc content was studied. The research results are presented in Table 3.

Table 3 Effect of the diameter of the melt jet and the pressure drop of the gas on zinc waste

Melt flow diameter, mm	4	4	8	8	6	6
Gas pressure in the nozzle, MPa	0,3	0,7	0,3	0,7	0,3	0,7
Zinc content in powder, %	2,58	2,6	2,58	2,59	2,6	2,6
Waste, %	61,49	61,19	61,49	61,34	61,19	61,19

The analysis of the obtained data has shown that the modes of the spraying process of the metal melt by a gas flow have practically no effect on the content (losses) of zinc in the process of producing a spherical sprayed powder.

Conclusion. It has been experimentally confirmed that when producing zinc-containing sprayed powders using the traditional technology of melting charge mixture materials, excessive zinc waste is observed, i.e. more than 60%. The optimal temperature 1300 °C for heating the melt for further research has been established -. The melt flow diameter and gas pressure do not affect zinc losses.

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Fabrication, structure and use of nanocellulose as reinforcement in polymer composites

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Abstract: Nanocellulose is defined as term refers to the cellulosic materials with defined nano-scale structural dimensions. Nanocellulose can be mainly categorized into three main types; nanocrystalline cellulose (NCC), nanofibrillated cellulose (NFC), and bacterial nanocellulose (BNC). The special attention is the size of nanocellulose fiber which generally contains less than 100 nm in diameter and several micrometers in length. The NCCs have very attractive fundamental properties such as high strength and stiffness, low density, biodegradability, transparency, and extremely low thermal expansion property. They have extremely strong mechanical properties, e.g., a Young's modulus of 130-140 GPa. As a results of the recent developments in the nanotechnology in the last decade, nanocellulose has garnered much attention for its use in biocomposites, biofilms, medicine, coatings, thermoplastic and thermosetting resins. The production cost of nanocellulose is gradually decreasing due to increasing utilization by many industries all over the world. In this study, structure of use of nanocellulose and its use in polymer composites was reviewed.

KEYWORDS: NANOCELLULOSE, POLYMER COMPOSITES, REINFORCING FILLER, NATURAL FIBERS

1. Introduction

The preparation of polymer nanocomposites using nanocelluloses has been found to be of growing interest due to the unique characteristics of those nanomaterials, such as numerous surface -OH groups and their associated ease of surface modification, high strength, (potentially) low cost, and renewability. However, those nanomaterials also suffer from certain disadvantages, including high moisture adsorption and poor compatibility with the hydrophobic polymer matrix [1].

Nanocelluloses are natural materials with at least one dimension in the nano-scale. Cellulose nanofibers (CNFs) (Fig. 1). The CNFs can be produced from any kind of plant cell walls by simple mechanical methods or a combination of both chemical and mechanical methods. The word "nanocellulose" generally refers to cellulosic materials with one dimension in the nanometer range. They exist in nature as nano-structured materials, so called cellulose nanofibers (CNFs) [2]. The significance of forest biomaterials has been sharply increasing due to their abundance and substitutability and as a potential alternative to petroleum resource. Thus, high-quality utilization of forest biomaterial and their developments have intensively been requested for the next generation to ensure our future environmentally-friendly biomaterials.

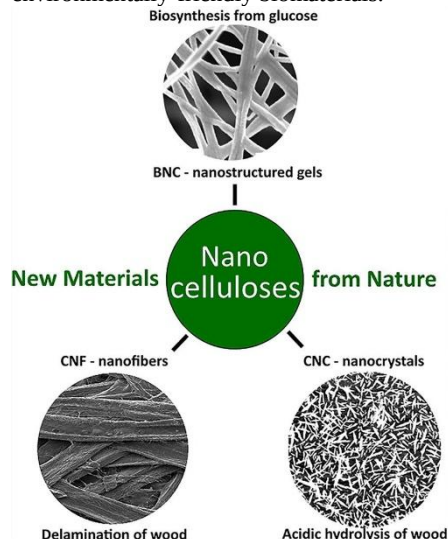


Figure 1. Types of nanocellulose [3].

Bio-nanocomposites are a new concept of combined and applied materials, which are produced using reinforcement particles with at least one dimension at the nanoscale. Cellulose microfibril is the major constituent of plant cell walls and has a width about 10-30nm in diameter with crystalline domain and amorphous region [4]. In wood cell walls, the cellulose microfibril was surround by hemicellulose and lignin

Research field of forest biomaterials has been dealing with many aspects of the utilization, significance, understanding and promotion of forest resources and industries [1]. Recently, researchers in the world have focused on these inherent strength and performance of CNFs and on the applications for a new class material (Fig 2). With advances in the ability to prepare and characterize CNFs, CNFs has been using for a wide variety of applications including polymers, textiles, cosmetics, food products, and nanocomposite materials as well as medical applications. Among those applications, light-weight and high-performance CNF-reinforced nanocomposites have attracted great attention. Light-weight, high-performance CNF-reinforced nanocomposites are expected to become the next generation of green materials, since they have the potential to replace conventional petroleum-based materials in a wide range of applications. CNFs provide benefits such as improved strength and stiffness with little sacrifice of toughness, reduced gas/water vapor permeability, a low coefficient of thermal expansion, and a large heat-deflection temperature [5]. The reinforcing effects of CNF on the properties of nanocomposite have been intensively studied [6,7].

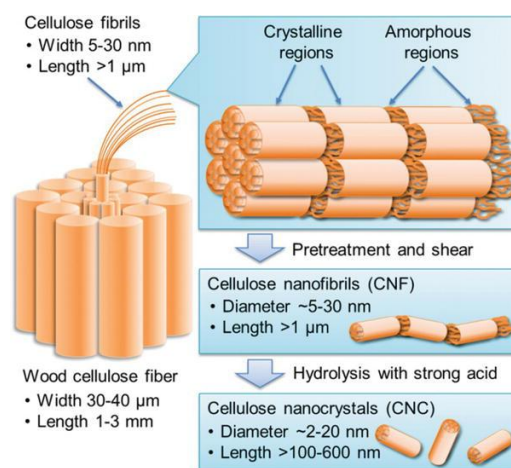


Figure 2. Dimensions of nanocellulose [

Preparation and properties of cellulose nanofibers

Generally, there are two representative CNFs, nanocrystalline cellulose (NCC) and microfibrillated cellulose (MFC). NCC is generally prepared by acid hydrolysis under strict conditions and has high crystallinity and low aspect ratio. The product, microfibrillated cellulose (MFC), exhibits gel-like characteristics. NCC suspensions have liquid-crystalline properties. In contrast to MFC and NCC, which are prepared from already biosynthesized cellulose sources, a third nanocellulose variant, bacterial nanocellulose (BNC), is prepared from low-molecular-weight resources, such as sugars, by using acetic acid bacteria of the

genus *luconacetobacter* [1]. The usage areas and SEM images of CNCs, CNFs, and BC are presented in Figure 3 [9].

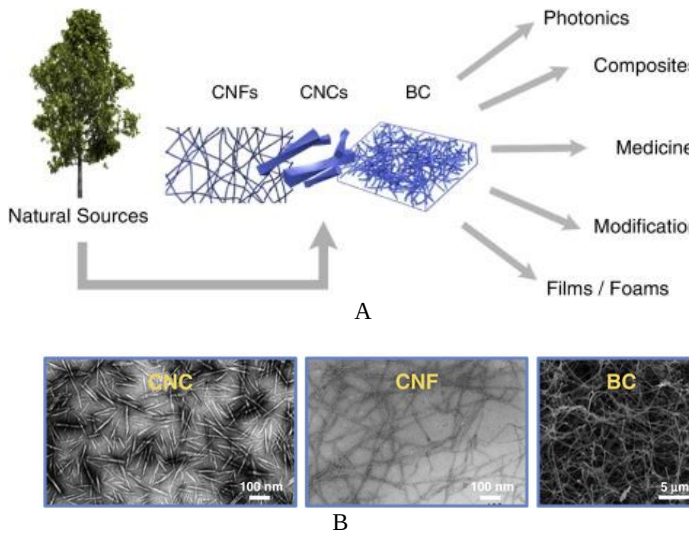


Figure 3. Some usage areas (A) and representative SEM images (B) of the three types of nanocellulose: CNCs, CNFs and BC [9].

Cellulose nanocrystal preparation by acid hydrolysis (chemical treatments)

The amorphous regions around the cellulose microfibrils could be destroyed by acid hydrolysis under controlled conditions, keeping the crystallites intact [5]. The acid hydrolysis is selective in cellulose fibrils, resulting in colloid suspensions of cellulose nanocrystals. The presence of sulfate groups resulting from the acid hydrolysis treatment when using sulfuric acid to prepare cellulose whiskers (CNW) Nanocrystalline cellulose (NCC) induces the stability of the ensuing aqueous suspension. Using HCl for hydrolysis increases the thermal stability of cellulose nanostructures, but chloride ions are easily removed by repeated washings with water. Whiskers of cellulose are primarily obtained by acid hydrolysis, with strong acids such as sulphuric and hydrochloric, which leads to nanocrystals ranging between 100 and 400 nm in length and less than 10 nm in width [1]. Chemical treatment with sodium chlorite solution was cyclically applied five or more times under acidic conditions at 70 °C for an hour to remove lignin [1]. Liquid, gel, and powder forms of NCC are shown in Figure 4.

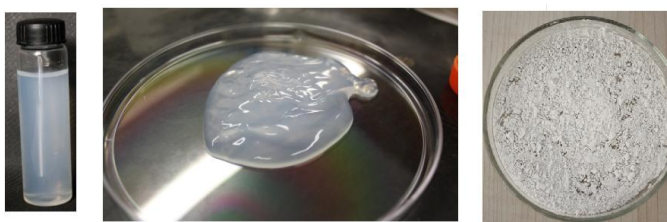


Figure 4. NCC at 5 wt% solution; at 12% wt solution; and NCC powder (by spray-dried) [7].

Conventional preparation methods for CNFs are on the basis of mechanical treatment by using wet disk-mill, high-pressure homogenizer, cryocrushing, and other processes, after removing the matrix polymer from the lignocellulosic resources. Abe et al. [8] introduced a method to prepare CNFs with a uniform width of 15 nm from Radiata pine using wet disk-milling (WDM) after leaching hemicellulose with 6 wt% potassium hydroxide and delignification with acidified sodium chlorite solution. The sample was kept in a water-swollen state, after the removal of the matrix polymers, to avoid the generation of hydrogen bonding

between the microfibril bundles after the removal of the matrix. Recently, microfibrillated cellulose (MFC) in nano scales has attracted attention in many different research areas, especially nanocomposite development, by virtue of its impressive mechanical properties [1].

Micro/nanofibrils (nanocrystalline cellulose (NCC), nanofibrillated cellulose (NFC)) isolated from natural fibers have garnered much attention for the use in composites, coatings, resins, and film because of high specific surface areas, renewability and unique mechanical properties in the past two decades. Nanocrystals are ricelike, needle-shaped and strong with diameters in the 5- to 10-nm range and lengths on the order of 100 to 200 nm, depending on the source. In contrast, nanofibrils, which tend to have roughly 5-nm diameters, as spaghetti-like because they are longer (a micrometer or more), flexible, and easily entangled [10]. Nanocellulose-based materials have high strength and low weight. The highest grades have attributes that offer great reinforcing strength and/or optical clarity, while lower grades can offer increased strength and improved properties at lower costs [11].

Bacterial nanocellulose

As opposed to the existing methods for achieving nanocellulose by way of mechanical or chemo-mechanical processes, Bacterial cellulose (BC) is made by bacteria through biosynthesis of cellulose and fabricates bunches of microfibril. These bunches of microfibril have remarkable crystallinity (up to 84–89%), and an appropriate elastic modulus. Although bacterial cellulose is produced in nature, it can be produced from cultures in laboratories as a large-scale process. By controlling culturing conditions, the resulting cellulose can be tailored to have specific desirable properties. (BC) is more preferred over plant cellulose for edible applications; which is available in relatively pure form and no chemical process are required for the isolation of BC. In this regard, the bacterial nanocellulose produced by genus *Gluconacetobacter* (*Gluconacetobacter xylinus*) is recognized for its preferable properties. Superior mechanical and thermal properties, high crystallinity and water holding capacity are the reasons of specialty of bacterial nanocellulose [12]. The cellulose crystal is one of the strongest and stiffest organic molecules, with a modulus of 145 GPa and a strength estimated at 7500 MPa. The extension to break of a NCC is estimated to be only 2%. NCCs have high surface areas (~250 m²/g), are hydrophilic, and are quite amenable to surface derivatization [6].

Nanocellulose is regarded as a good alternative to improve the qualitative properties of biopolymers due to positive characteristics such as biodegradability, renewable, abundance and inexpensive cost, low density, strength and high durability as well as the possibility to derive from agricultural wastes and food industries. Global nanocellulose market was valued US\$ 160.98 Mn in 2017 and is estimated to reach US\$ 687.97 Mn by 2026 at a CAGR of 17.51% [20]. Based on their dimensions, functions, and preparation methods, which in turn depend mainly on the cellulosic source and on the processing conditions, nanocelluloses may be classified in three main subcategories (Table 1) [9].

Table 1. The family of nanocellulose materials [9].

Type of nano cellulose	Selected reference and synonyms	Typical sources	Formation and average size
Microfibrillated cellulose (MFC)	Microfibrillated cellulose, nanofibrils and microfibrils, nanofibrillated cellulose	Wood, sugar beet, potato tuber, hemp, flax	Delamination of wood pulp by mechanical pressure before and/or after chemical or enzymatic treatment diameter: 5–60

			nm length: several micrometers
Nanocrystalline cellulose (NCC)	Cellulose nanocrystals, crystallites, whiskers, rodlike cellulose microcrystals	Wood, cotton, hemp, flax, wheat straw, mulberry bark, ramie, Avicel, tunicin, cellulose from algae and bacteria	Acid hydrolysis of cellulose from many sources diameter: 5–70 nm length: 100–250 nm (from plant celluloses); 100 nm to several micrometers (from celluloses of tunicates, algae, bacteria)
Bacterial nanocellulose (BNC)	Bacterial cellulose, microbial cellulose, biocellulose	Low-molecular-weight sugars and alcohols	Bacterial synthesis diameter: 20–100 nm; different types of nanofiber networks

The NCCs have very attractive fundamental properties such as high strength and stiffness, low density, biodegradability, and extremely low thermal expansion property. They have extremely strong mechanical properties, e.g., a Young's modulus of 130–140 GPa [1] (Table 2).

Table 2. The comparison of tensile properties of cost of nanocrystalline cellulose (NCC) and other synthetic fibres [14].

Material	Density g/cm ³	Tensile strength (MPa)	Tensile modulus (GPa)	Cost (\$/kg)
Hi Strength steel	7.9	600	210	~1
Aluminum 6061-TL	2.7	275	70	~2
E-glass	2.5	3500	80	~2
Carbon fiber	1.8	4000	230	~20
Nanocrystalline cellulose	1.5	7500	135	4-10

Industrial applications of cellulose nanofibers

Recently, researchers in the world have focused on these inherent strength and performance of CNFs and on the applications for a new class material. With advances in the ability to prepare and characterize CNFs, CNFs has been using for a wide variety of applications including textiles, cosmetics, food products, and nanocomposite materials as well as medical applications. Among those applications, light-weight and high-performance CNF-reinforced nanocomposites have attracted great attention. Cellulose nanocomposites exhibit mechanical, thermal, optical, physiochemical and barrier properties far better than pure polymers. The potential application of cellulose nanoparticles as reinforcements in polymers provides a new direction for the development of better composites accompanying with added value [15]. Nanowhiskers act as efficient reinforcement due to high aspect ratios, surface areas and high modulus. Common benefits observed in tensile strength, elongation rate, elevated thermal decomposition

Industrial usage areas of nanocellulose in the market are given below:

- Improved paper and packaging products
- Reinforced polymers
- Advanced composite materials

- Hydro-fracking and oil drilling fluids
- High-strength spun fibers and textiles
- Films for barrier and other functions
- Coatings, paints, lacquers, and adhesives
- Switchable optical devices
- Pharmaceutical and drug delivery
- Bone replacement and teet repair
- Improved building products

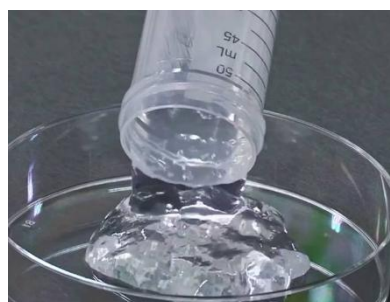
Advantages of nanocellulose

- Abundantly available
- Low weight
- Biodegradable
- Non-toxic and optical transparency
- Cheaper
- Renewable
- Unique mechanical properties
- Good thermal stability
- High specific surface area
- Modest abrasivity during processing
- Highly absorbent when used as a basis for aerogels or foams.
- very high tensile strength – 8-10 times that of steel
- Stiffer than Kevlar®
- Electrically conductive

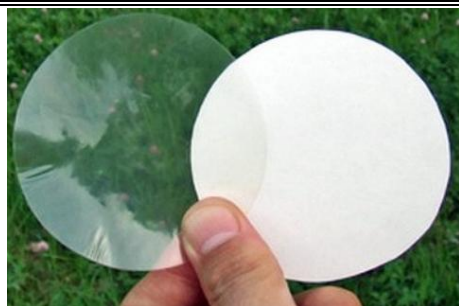
Drawbacks of nanocellulose

- Substantial hydrophilicity
- Poor compatibility

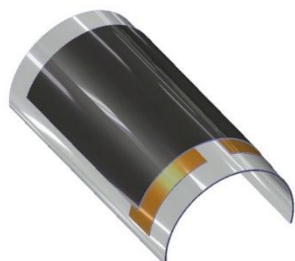
Additives for foods, cosmetics th advances in the ability to prepare and characterize CNFs, it has been using for a wide variety of applications including textiles, cosmetics, food products, and nanocomposite materials as well as medical applications. Among those applications, light-weight and high-performance CNF-reinforced nanocomposites have attracted great attention. As a nanoscale filler, CNFs provide benefits such as improved strength and stiffness with little sacrifice of toughness, reduced gas/water vapor permeability, a low coefficient of thermal expansion, and a large heat-deflection temperature [1]. Sehaqui et al. [16] developed rapid preparation procedure for large, flat, smooth, and optically transparent cellulose nanopapers using a semiautomatic sheet former. The gel “cake” is peeled from the membrane and stacked first between two woven metal cloths and then two paper carrier boards [17]. The application of the nanopaper-making strategy to cellulose/inorganic hybrids demonstrates the potential for “green” processing of new types of nanostructured functional materials [1]. Chun et al. [18] developed eco-friendly cellulose nanofiber paper-derived separator membranes (CNP separators) for use in lithium-ion batteries (Fig. 6). The CNP separator has been substantially improved the ionic conductivity, electrolyte wettability, and thermal shrinkage. With its transparency, strength and optic properties, nanocellulose is being researched by Pioneer Electronics as a replacement for glass for flexible screens [9].



Plant-derived nanocellulose is an eco-friendly new material.



A



B.



C.

Figure 6. A: Transparent film from nanocellulose. B: Nanofiber paper-derived separator membranes (CNP separators) for use in lithium-ion batteries. Body Armor Applications of NCC [25,26].

Engineers can significantly reduce the weight of a plastic composite without sacrificing strength (benefiting auto manufacturing, for instance) or keep the mass of plastic the same while dramatically increasing strength. When properly aligned, nanocellulose offers an alternative to even stronger applications, like replacing Kevlar® from DuPont. It is being investigated by the Department of Defense to use in body armor and ballistic glass [19]. With these optical and other properties it is a unique additive for inks, paints, dyes or glazing adding strength while enhancing color brilliance. Crystal structure of nanocellulose is consisting from packed array of needle-like crystals. These crystal structures are incredibly tough and their strength value is nearly eight times higher than stainless steel. Therefore, nanocellulose can be perfect building material for the future body armor studies [20].

Resin is one of the important factors affecting mechanical and physical properties of wood-based composites. Urea-formaldehyde (UF) resin is commonly used in the manufacture of plywood, laminated veneer lumber, particleboard, and fiberboard etc. The advantages of UF resins are low cost, water solubility, easy use (under a wide variety of curing conditions), relatively low cure temperature, microorganisms resistance, low abrasion hardness, excellent thermal properties, and clear or light color (especially of the cured resin) [21]. Due to these advantages, wood-based composite industry utilizes UF as a common resin, worldwide. However, the mechanical performance of resin bonds between the UF and wood is limited, in particular humid conditions. Since the elastic modulus of cured UF bond lines is high, the deformation of the resin layer under mechanical loading is usually small. As a result, stress concentrations along the bond line of a wood resin joint are generated that reduce the overall strength of the joint [22]. UF-resins are a widely used class of low-priced wood resins, which are well known for their pronounced brittleness and their tendency to develop microcracks

which limits their mechanical performance. The combination of low price and poor mechanical performance makes UF an ideal candidate for studying the effect of added filler [22].

Ayrlimis et al. [21] reported that the tensile shear strength of the specimens slightly increased with the incorporation of (MFC 0-1 wt%) while it considerably increased as the amount of MFC increased from 1 to 3 wt%. As compared to the control specimens, the tensile shear strength of the specimens increased by 5.7% as 3 wt% MFC (5% suspension in water) was incorporated into the UF-adhesive. However, the further increment (5 wt%) in the MFC content decreased the tensile shear of the specimens (-14.3% of control specimen). The specific surface area of the MFC was 86 m²/g. It was estimated that the high specific surface area of 5 wt% MFC was one of the main reasons decreasing the bond performance of the UF-adhesive. The improvement in the bonding performance of the UF-resin indicates that the addition of a certain amount of MFC in the UF-resin improves the mechanical performance of wood resin bonds, thus opening up new fields of application for UF, which is currently used only in the non-structural field.

Ayrlimis et al. [23] aimed to understand the effect of relationship between the molar ratio of UF adhesive and MFC on mechanical properties of laminated veneer lumber (LVL) and adhesive characteristics of UF adhesive. LVLs were produced using different molar ratio UF adhesives having different amounts of microfibrillated celluloses (MFCs). Adhesive characteristics, gel time, viscosity, and acidity of the E0 and E1 class UF adhesives with the MFCs were determined. The bending properties and tensile shear strength of the LVLs were investigated. At the same content of the MFCs, the bonding performance of the E0 class UF adhesive improved more than that of the E1 class UF adhesive. The higher bond strength for the UF adhesive containing the MFCs could be explained by the possible reaction between the methylol groups of the UF adhesive and the hydroxyl groups of the cellulose. Substantial increases in the gel time and viscosities of the UF adhesives were observed as the amount of MFCs increased in the adhesive. The gel time of the UF adhesives increased with increasing amount of the MFCs.

Due to the large quantity of materials used in buildings, and their constant exposure to indoor air, there is a growing concern regarding the effects of these indoor pollutants on the health and comfort of the building occupants. Building materials can release wide range of pollutants. One of the hazardous pollutants of the indoor air are volatile organic compounds (VOCs) emitted from wood-based panels, which can cause indoor air related health problems. Ayrlimis et al. [24] investigated the formaldehyde emission and TVOC emitted from the laminated veneer lumber (LVL) produced with the different grade UF resins (super E0, E0, and E1 grades) modified with different amounts of the MFC using a thermal extractor. The formaldehyde emission from the LVLs produced with the SE0 grade UF resin considerably decreased with increasing MFC content at 25 °C while this was not observed for the E0 and E1 grade resins. The results revealed that the MFC did not work for decreasing of formaldehyde emission of the LVLs produced with the E0 and E1 resins at 35 °C and 45 °C. However, the VOCs emitted from the LVLs considerably decreased with the incorporation of the MFC at environmental temperatures of 25 °C and 35 °C, except for 45 °C. The MFC was not effective to reduce the VOCs from the LVLs at higher temperatures. The xylene was the highest detected compound in all samples, followed by ethylbenzene and toluene. Styrene, however, was not detected at all in any of the LVLs. The use of MFC in the UF resin can be environmentally friendly solution for reducing the VOCs from the wood-based panel used for indoor furniture.

CONCLUSIONS

Nanocellulose haven been widely used in polymer composites for a long time due to its unique properties. It is commercially produced in many countries due to its excellent properties. Polymer composite industry is the most pronounced

sector which use the nanocellulose as reinforcing filler because it is based on abundant resources, economic, renewable, and commercially processable. Nanocellulose is a material of the future with potential for replacing synthetic materials which cause environmental pollution. Many countries have focused on the nanocellulose researches to produce strategic materials in near future. The research and development on the BNC, CNF, and CNC has rapidly increased in recent years. In particular, it is estimated that the potential use of CNC will increase in the production of high performance materials in near future.

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Synthesis of energy-efficient control methods of the electromechanical disintegrator operating modes

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Abstract: The present trend in the development of highly efficient technological equipment for the production of nanomaterials is being analysed. It is associated with the synthesis of energy-efficient control methods for the operating modes of electromechanical disintegrator of multifactorial action. As a result of genetic modelling, the deterministic relationship between the genetic information of generative electromechanical chromosomes, structure of the resulting magnetic flux in the active zone of electromechanical disintegrator and its functional operating modes has been established. According to the results of structural synthesis, methods for technical implementation of energy-efficient modes of material processing, which ensure the increase of productivity of the electromechanical disintegrator, have been optimized and developed. The credibility of theoretical results was confirmed by experimental studies.

Keywords: GENETIC MODELING, STRUCTURAL SYNTHESIS, CONTROL METHODS, OPERATING MODES, ELECTROMECHANICAL DISINTEGRATOR, ACTIVE ZONE, DISCRETE FERROMAGNETIC PARTICLES, NANOMATERIALS, ENERGY-EFFICIENCY, PRODUCTIVITY.

1. Introduction

The creation of highly efficient technological equipment for the production of powder materials and homogeneous mixtures of the nanoscale range is one of the priority areas of modern science and technology. The importance of such research is determined by the widespread use of nanopowder materials and technologies in such important fields as electronics, pharmaceuticals, chemical industry, materials science, and others. This indicates the relevance and novelty of research in this area.

It is known that the energy efficiency of ultra-fine grinding processes and the quality of finished products is determined by the type of process equipment. The vast majority of existing equipment is based on the use of the mechanical principle of action (hammer grinders, spherical mills, and disintegrators). The peculiarity of such equipment is their high energy consumption and low energy efficiency. Therefore, the problem of creating new types of energy-efficient equipment for the implementation of nanotechnology remains open. According to experts, one of the promising areas for improving energy efficiency, intensification of processes in ultra-fine grinding technologies is the creation and use of electromechanical mills [1] and electromechanical disintegrators (EMDs) of multifactor action [2].

EMDs belong to a new class of highly efficient technological equipment, in which technological processes of materials processing are carried out by converting electromagnetic energy of inverse magnetic fields into energy of mechanical motion of discrete ferromagnetic particles (DFPs), which is carried out directly in the active zone of the disintegrator. EMDs find practical application in the implementation of a wide range of technologies: fine and ultrafine grinding of materials; production of nanopowders; homogeneous mixing and preparation of composite mixtures; production of multicomponent fuel mixtures; dispersion of liquid-phase and heterogeneous systems; acceleration of chemical reactions (oxidation, regeneration, neutralization, etc.), intensification of microbiological processes, wastewater treatment, etc. [3, 4]. According to the results of multifactorial action on the processing substance in the technologies of ultrafine grinding (especially in the nanometre range), the physical properties of materials can change significantly and acquire qualitatively new, sometimes unique properties.

According to the results of the analysis of industrial operation and the results of experimental studies on the prototypes of EMDs, a number of specific phenomena and effects that accompany the operating modes of EMDs have been detected [5]. Since the trajectory of the working bodies is determined by 6 degrees of freedom, during the operation of EMDs there appears a problem of controlling the uniformity of distribution and intensity of DFPs, which is directly related to the efficiency of processing, ingredient processing, energy-efficient processing modes and quality of the

output product. The lack of flexible control of processing modes does not allow to carry out technological processing of materials at the optimal level. The complex functional relationship between geometric and electromagnetic parameters, the complexity of the collective motion of the DFPs and the turbulence of the treated medium in the active volume are virtually unanalysable and significantly complicate the mathematical modelling of physical processes in EMDs. The presence of this set of significant differences requires the development of new systems approaches to the analysis of physical processes and the synthesis of EMD structures with specified operational properties.

The analysis of data of industrial operation and results of experimental researches of EMDs allow to allocate the following directions of increase of their efficiency [6, 7]:

- optimization of EMD operation modes;
- compensation of negative influence of final electromagnetic effects;
- optimization of spatial geometry and electromagnetic parameters of DFPs;
- optimization of geometric relations;
- synthesis of competitive technical solutions of EMDs;
- optimization of input parameters of supply voltage.

In the following paper, based on the generalization of the results of industrial operation, experimental data and analysis of physical processes and phenomena accompanying the operating modes of EMDs, the purpose is to synthesize structural energy-efficient ways to control the operation modes of EMDs and propose ways to implement them.

2. Features of electromagnetic processes

The specific nature of the structure and features of electromagnetic processes that ensure the operation of double winding EMDs [8, 9], cause significant differences in their operating modes from disintegrators and mills of mechanical and electromagnetic types. These differences are caused by:

- the presence of a two-way system of inductors with counter-orientation of travelling or rotating magnetic fields on active surfaces, phase shifted by an angle $\gamma = \pi/3$;
- a relatively large value of the non-magnetic (inter-inductor) gap $\Sigma\delta$, which houses the working chamber (WCH) with DFPs and process environment;
- the limiting ratio of the value of the non-magnetic gap to the length of the pole division ($\Sigma\delta/\tau \approx 0,6 \div 0,7$);

- discrete structure of ferromagnetic working bodies, the characteristic geometry of which is much smaller than the length of the pole division ($l/d \ll \tau$);

- complex spatial motion (6 degrees of freedom) of the DFPs, the idealized motion of which consists of the rotational motion of the elementary DFP relative to its centre of mass ($n_p = 3000$ rpm, provided $f = 50$ Hz) and the rotational motion of the particle on a circular trajectory ($n_r \approx 3000$ rpm), within the corresponding pole division τ ;

- multifactorial complex action of a number of physical factors on the processed technological environment (Fig. 1), which includes intensive mechanical grinding and mixing, the action of high-gradient alternating magnetic field and high-potential electrostatic charge field, the influence of surface acoustic waves, local thermal overheating as well as the influence of accompanying processes of electrolysis and cavitation (subject to the presence of liquid ingredients);

- a wide variety of genetically acceptable Species of the functional class of EMDs, the quantitative composition of which significantly exceeds the species diversity of electric machines [10].

The working process of machining is characterized by high-frequency collisions of DFPs with each other, with particles of the substance and the walls of the working chamber, which causes a sharp change in the trajectory of their movement, the emergence of alternating accelerations and accompanied by processes of dispersion, mechanical activation, intensive mixing and others (Fig. 1).

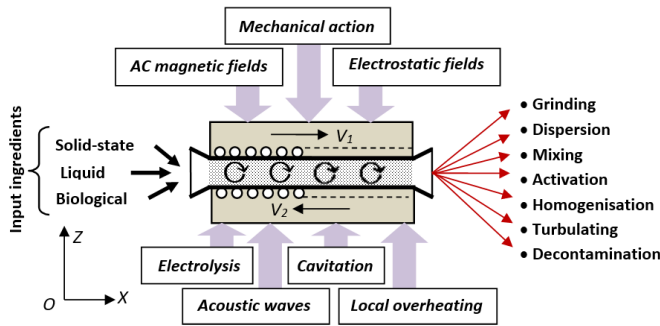


Fig. 1 Main physical factors and processes that determine the technology of ingredient processing in the active volume of electromechanical disintegrator.

The presence of the mentioned set of factors (Fig. 1) determines the complex effect on the processed environment, which intensifies the technological process, provides a change of physical properties of the processed substances and significantly expands the range of applied technologies.

3. The genetic model of the structure formation of the resulting magnetic field

The integral function of synthesis F_S must take into account the following set of partial requirements:

- 1) The presence of a dual-inductor system with equivalent geometry and mass of active parts ($2M_{AI}$);
- 2) Electromagnetic method of excitation of inductors active surfaces (Φ_{EM});
- 3) Dual-inductor version of the magnetic system with independent power supply of m -phase distributed windings ($2N_1$);
- 4) Electromagnetic inversion of the inductors $V_1 = (-V_2)$ travelling magnetic fields;
- 5) The presence of nonmagnetic WCH with the discrete ferromagnetic working bodies (nN_2);

6) A number of pole divisions of the windings in the OX coordinate ($N_r \geq 2$).

The search space for R^n synthesis is limited by the electromagnetic chromosomes of 2.2y subgroup of the first major period in the periodic structure of genetic classification [11]. Chromosome-isotopes [12] and their hybrid compositions are not taken into account. Given these partial requirements and constraints, the vector of the integral search function in the multidimensional feature space R^n takes the form:

$$F_S = [2M_{AI}; \Phi_{EM}; 2N_1; V_1 = (-V_2); nN_2; N_r \geq 2]. \quad (1)$$

The structure of an ideal homological series [13] of subgroup 2.2y contains six base-level electromagnetic chromosomes

$$H_{02y} = (C_{CL}, C_{KN}, C_{PL}, C_{TP}, C_{SF}, C_{TC}). \quad (2)$$

The synthesis of the genetic model can be performed on the basis of the parental chromosome C_{PL} with the genetic code of the PL 2.2y, which determines the boundaries of the structure of the dominant Species of double-winding EMDs [6, 7]. The given search function (1) corresponds to a multilevel genetic model (Fig. 2). The synthesis of the model is carried out using genetic synthesis operators (replication, intra-Species hybridisation, spatial and electromagnetic inversion and mutation). The sequence of application of genetic operators is determined in accordance with the logic of genetic modelling "from simple to complex", by gradually complicating the parent chromosome [14].

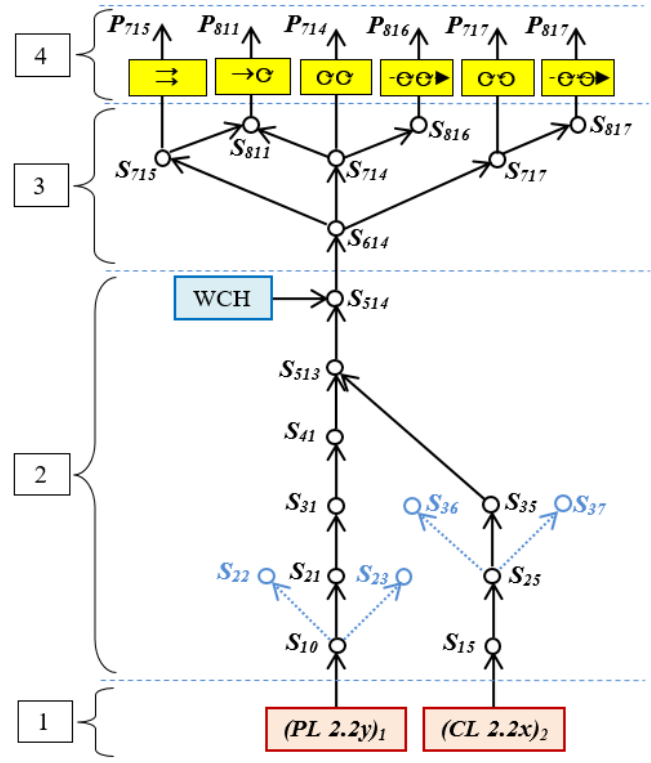


Fig. 2 Genetic model of synthesis of the resulting magnetic field structures in the EMD active zone: $(PL\ 2.2y)_1$ – parent chromosome; $(CL\ 2.2x)_2$ – secondary chromosome; WCH – working chamber; S_{10} – S_{514} – information chromosomes; S_{614} – S_{817} – generative chromosomes; P_{714} – P_{817} – populations of technical solutions that satisfy the functions of synthesis; 1–4 – levels of genetic organization of structures.

The synthesized model reproduces the multilevel process of complication of the parental chromosome in accordance with the logic of genetic synthesis for a given function F_S and taking into account the given constraints. The structure of the model (Fig. 2) contains four levels of genetic complexity:

1) chromosomal level, which is represented by the generative (parental) y -oriented chromosome $(PL\ 2.2y)_1$ and the secondary chromosome $(CL\ 2.2x)_2$;

2) the level of the genome of the Species, represented by genetically modified information chromosomes $S_{10}-S_{514}$ of increasing level of complexity, modelling the process of structure formation of EMD active parts and its combination with nonmagnetic WCH , which has the status of another genetic nature;

3) the level of structural detailing (up to τ) of the generative chromosome S_{614} , which allows to determine possible variants of the structures of the resulting magnetic field in the EMD active zone;

4) population level ($P_{714}-P_{817}$), which models the deterministic relationship of generative chromosomes with synthesized variants of the resulting magnetic field structure in the active volume (are indicated by graphic primitives in Fig. 2).

4. The results of the genetic modelling

The results of genetic analysis of the structure formation model (Fig. 2) are given in Table 1.

The modelling results show that there is a deterministic relationship between the structure of generative electromagnetic chromosomes ($S_{714}-S_{817}$), the structure of the resulting magnetic field and the modes of operation of the EMDs (Table 1), which gives the opportunity of pre-selection and technical implementation of control methods for material processing through appropriate adaptation of the structure of the magnetic system and changes in the relative orientation and velocity of DFPs.

Analysis of the results of decoding the microgenetic program (Table 1) shows that each generative chromosome corresponds to a specific structure of the resulting magnetic field and mode of operation:

- mode No. 1 with inverse travelling fields $V_1 = (-V_2)$ and the coordinated orientation of the DFPs vortex zones fixed by the OX coordinate (S_{714} chromosome):

$$S_{714} = \{2[(PL\ 2.2y)_1]^{-1} \cdot R_{OZ} : I_{OX} : (R_{\tau})_1\} \times \{n(CL\ 2.2x)_2 : M : R_V\} \times (WCH); \quad (3)$$

- mode No. 2 with the coordinated orientation of the travelling fields $V_1 = V_2$ (S_{715} chromosome):

$$S_{715} = \{2[(PL\ 2.2y)_1]^{-1} \cdot R_{OZ} : I_{OX} : (R_{\tau} : I_{\tau})_2\} \times \{n(CL\ 2.2x)_2 : M : R_V\} \times (WCH); \quad (4)$$

Table 1: The results of decoding the genetic program of structure formation of the resulting magnetic field in the nonmagnetic gap of EMDs.

Chromosome number	Structural formula of a chromosome	Chromosome status	Structure of the resulting field
Level 1. Parental chromosome			
$PL\ 2.2y$	$(PL\ 2.2y)_1$	Parental (primary)	—
$CL\ 2.2y$	$(CL\ 2.2x)_2$	Secondary	—
Level 2. Genome structure			
S_{10}	$2(PL\ 2.2y)_1 : R$	Replicated ($K_R = 2$), information	—
S_{21}	$2(PL\ 2.2y)_1 : R_{OZ}$	Oriented isomer (OZ), information	—
S_{31}	$2[(PL\ 2.2y)_1]^{-1} : R_{OZ}$	Spatially inverse, information	—
S_{41}	$2[(PL\ 2.2y)_1]^{-1} : R_{OZ} : I_{OX}$	Electromagnetically inverse (OX), information	—
S_{15}	$n(CL\ 2.2x)_2 : M$	Mutated, secondary, information	—
S_{25}	$n(CL\ 2.2x)_2 : M : R$	Replicated secondary, information	—
S_{35}	$n(CL\ 2.2x)_2 : M : R_V$	Spatial isomer (V_{XYZ}), information	—
S_{513}	$\{2[(PL\ 2.2y)_1]^{-1} : R_{OZ} : I_{OX}\} \times \{n(CL\ 2.2x)_2 : M : R_V\}$	Hybrid (paired), information	—
S_{514}	$\{2[(PL\ 2.2y)_1]^{-1} : R_{OZ} : I_{OX}\} \times \{n(CL\ 2.2x)_2 : M : R_V\} \times (WCH)$	Combined, information	With a coordinated orientation of fixed vortex zones
Level 3. Structural detailing of S_{614} chromosome			
S_{614}	$\{2[(PL\ 2.2y)_1]^{-1} : R_{OZ} : I_{OX} : R_{\tau}\} \times \{n(CL\ 2.2x)_2 : M : R_V\} \times (WCH)$	Replicated ($K_{R\tau} \geq 2$), information	With a coordinated orientation of fixed vortex zones
S_{714}	$\{2[(PL\ 2.2y)_1]^{-1} : R_{OZ} : I_{OX} : (R_{\tau})_1\} \times \{n(CL\ 2.2x)_2 : M : R_V\} \times (WCH)$	Isomer 1, generative	With a coordinated orientation of fixed vortex zones ($\odot \odot$)
S_{715}	$\{2[(PL\ 2.2y)_1]^{-1} : R_{OZ} : I_{OX} : (R_{\tau} : I_{\tau})_2\} \times \{n(CL\ 2.2x)_2 : M : R_V\} \times (WCH)$	Isomer 2, generative	With a coordinated orientation of travelling fields ($\Rightarrow$)
S_{717}	$\{2[(PL\ 2.2y)_1]^{-1} : R_{OZ} : I_{OX} : (R_{\tau} : I_{\tau})_3\} \times \{n(CL\ 2.2x)_2 : M : R_V\} \times (WCH)$	Isomer 3, generative	With an alternate orientation of fixed vortex zones ($\odot \ominus$)
S_{811}	$\{2[(PL\ 2.2y)_1]^{-1} : R_{OZ} : I_{OX} : (R_{\tau} : I_{\tau})_4\} \times \{n(CL\ 2.2x)_2 : M : R_V\} \times (WCH)$	Isomer 4, generative	With a combined orientation of travelling and vortex zones ($\Rightarrow \odot$)
S_{816}	$\{2[(PL\ 2.2y)_1]^{-1} : R_{OZ} : I_{OX} : R_{\tau} : M_{\tau}\} \times \{n(CL\ 2.2x)_2 : M : R_V\} \times (WCH)$	Mutated, generative	With a coordinated orientation of moving vortex zones ($\odot \odot \rightarrow$)
S_{817}	$\{2[(PL\ 2.2y)_1]^{-1} : R_{OZ} : I_{OX} : R_{\tau} : I_{\tau} : M_{\tau}\} \times \{n(CL\ 2.2x)_2 : M : R_V\} \times (WCH)$	Mutated, generative	With an alternate orientation of moving vortex zones ($\odot \ominus \rightarrow$)

- mode No. 3 with the inverse travelling fields $V_1 = (-V_2)$ and alternate orientation of the fixed OX coordinate of the DFPs vortex zones (S_{717}):

$$S_{717} = \{2[(PL2.2y)_1]^{-1} \cdot R_{OZ}; I_{OX}; (R_r; I_{2r})_3\} \times \{n(CL2.2x)_2; M; R_V\} \times (WCH); \quad (5)$$

- mode No. 4 with alternating sequence of zones with travelling and inverse fields by OX coordinate (S_{811}):

$$S_{811} = \{2[(PL2.2y)_1]^{-1} \cdot R_{OZ}; I_{OX}; (R_r; I_{2r})_4\} \times \{n(CL2.2x)_2; M; R_V\} \times (WCH); \quad (6)$$

- mode No. 5 with the inverse travelling fields $V_1 \neq (-V_2)$ and the coordinated orientation of the travelling fields by the OX coordinate of the DFPs vortex zones (S_{816}):

$$S_{816} = \{2[(PL2.2y)_1]^{-1} \cdot R_{OZ}; I_{OX}; R_r; M_r\} \times \{n(CL2.2x)_2; M; R_V\} \times (WCH); \quad (7)$$

- mode No. 6 with the inverse travelling fields $V_1 \neq (-V_2)$ and the alternate orientation of the travelling fields by the OX coordinate of the DFPs vortex zones (S_{817}):

$$S_{817} = \{2[(PL2.2y)_1]^{-1} \cdot R_{OZ}; I_{OX}; R_r; I_{2r}; M_r\} \times \{n(CL2.2x)_2; M; R_V\} \times (WCH). \quad (8)$$

According to the results of structural synthesis, methods of technical realization of energy-efficient modes of materials processing have been optimized and developed. This increases the productivity of electromechanical disintegrators, the efficiency of which is confirmed by experimental studies on flat double-winding EMD samples in technologies of coal-water slurry fuel preparation [15] and the activation of Portland cement [16].

5. Conclusions

1. For the first time a genetic model of structure formation of EMD active parts with three-level structural detailing has been developed, which allows synthesis and analysis of genetically acceptable magnetic field structures in the active zone of the disintegrator at the stages of search design.

2. For the first time a deterministic connection between the genetic information of generating electromagnetic chromosomes and the corresponding structure of the resulting magnetic field in the EMD active zone substance has been established, which significantly simplifies the task of synthesis and analysis of magnetic field structures.

3. According to the results of genetic modelling and synthesis, processing modes, which provide a change in the mutual orientation of the vortex zones and a uniform distribution of working bodies and control of the intensity of their movement in the working volume of EMDs, have been optimized.

4. According to the results of research, methods of technical implementation of material processing modes, which provide the implementation of energy-efficient processing modes and increase the productivity of EMDs of multifactorial action, have been developed.

5. The reliability of the results of theoretical studies is confirmed by experimental studies, the results of which show that the use of the proposed methods of controlling the modes of operation of EMDs in technologies for production of coal-water slurry mixture and activation of cement increases their efficiency.

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Effects of various fire retardants on mechanical and fire properties of plywood

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Abstract: Effects of various fire retardant (FR) chemicals on mechanical and fire properties of plywoods were investigated. Boron compounds such as, borax and boric acid; and phosphate compounds such as, monoammonium phosphate and diammonium phosphate were used as fire retardant chemicals in the plywood panels. An exterior liquid phenol formaldehyde resin with 47% solids content was used as adhesive. The 2.2 mm thick Tetraberlinia wood veneers were treated with the liquid solution of FR chemicals. The plywoods having 5-layers were produced from the treated wood veneers. The mechanical properties of the plywoods produced with treated veneers was found to be lower than that of the control group. Among the treated plywoods, The plywoods treated with borax had highest mechanical properties, followed by diammonium phosphate (DAP), monoammonium phosphate (MAP), and, boric acid, respectively. The FR chemicals improved the fire resistance of the plywoods. The chemicals showed individually different effects related to improvement of fire resistance of the panels. For example, the OSB panels treated with diammonium phosphate were the latest ignited group (52.8 s) which were followed by the panels treated with boric acid (49.2 s), borax (44.5 s), and monoammonium phosphate (41.2 s), respectively. As compared to the control group (7.5 cm), the plywoods treated with borax (3.6 cm) had the shortest flame length after burner was turn off, followed by diammonium phosphate (4.2 cm), boric acid (5.1 cm), and monoammonium phosphate (5.8 cm).

KEYWORDS: WOOD-BASED PANELS, FIRE-RETARDANTS, BORON COMPOUNDS, TECHNOLOGICAL PROPERTIES, PLYWOOD

1. Introduction

Plywood is a wood-based panel which is widely used in construction industry. Since plywood is commonly used buildings, its fire resistance is very important to decrease fire risk and prevent to human death. It is well known that one can significantly improve the fire performance of wood-based composites by chemical treatment and thereby widen the options for their utilization. Three methods are commonly employed to provide wood-based products with improved fire-resistance and reaction-to-fire: chemical impregnation, incorporation of flame retardants into the adhesive, and flame-retardant coatings [1]. For chemical impregnation, the most widely used flame-retardant chemicals for treating wood-based products are inorganic salts that contain elemental phosphorus or boron. Boron compounds such as borax and boric acid are considered to be effective flame retardants that exert less impact on mechanical properties compared with some other flame retardant chemicals [2,3]. Phosphates such as mono- and diammonium phosphates, and ammonium polyphosphate are another group of fire retardants [4]. The phosphates are one of the oldest known fire-retardant systems. They are usually included in proprietary systems used for wood. For example, monoammonium phosphates (MAP) have been used in extinguishers for a long time in many places such as cars and homes, plants. Boron and phosphate compounds are widely used as FR chemicals in wood composite industry. In this study, the effect of loading level of boron and phosphate compounds on the mechanical and fire properties of plywood was investigated.

2. Materials and methods

2.1. Materials

2.1.1. Wood material

Commercial rotary veneers (2.2 mm thickness) of *Tetraberlinia bifoliolata* roundwood as raw material in the production of plywood production were supplied from a commercial plywood company, Kuris Plywood Company, in Istanbul, Turkey. The veneers without defect were sized to 490 mm x 490 mm by saw. The moisture content of the veneers was 7-8% based on the oven-dry weight of wood.

2.1.2. Resin

Phenol-formaldehyde (Polifen47) resin was supplied from Polisan The Chemical Company in Dilovasi, Turkey. The mixture of of filler and extender was added into the PF resin, based on the oven-dry weight of PF resin. The dry mixture was prepared from 80 wt%

calcium carbonate and 20 wt% the extender (10 wt% corn powder and 10 wt% corn starch powder)

Table 1: Technical specifications of phenol-formaldehyde (Polifen 47) resin

Technical specifications of PF resin	Method	Result
Density (20 °C, g/cm ³)	TS 1724 ISO 675:1997/T1	1.195-1.205
Solids content (% weight)	TS EN 480-8	47±1
Viscosity (20 °C, cps)	TS 6126 ISO 2555:1998/T1	250-500
pH (20 °C)	TS EN ISO 10523	10.5-13
Free formaldehyde (% weight)	TS EN 1243	max. 1.0

2.1.3. Fire-retardant chemicals

Four powder chemicals were used in the treatments: borax, boric acid, monoammonium phosphate, and diammonium phosphate. The technical grades of the chemicals were supplied from local market in Istanbul, Turkey.

2.2. Treatment of wood veneers

Veneer samples were kept in a conditioning chamber until they reach 7% moisture content. In the next step, the specimens were soaked for 3 h in plexiglass boxes while laid horizontally 4 cm apart from each other in 3% or 6% aqueous solutions of borax (Na₂B₄O₇·10H₂O) or boric acid (H₃BO₃), or in 3% or 11% aqueous solutions of monoammonium phosphate (NH₄H₂PO₄) or, diammonium phosphate ((NH₄)₂HPO₄). The temperature of the various solutions was 60 °C during the treatment process. Each treated veneer sample was then reconditioned to 7% moisture content before plywood panels were manufactured. Before and after treatment process samples were weighted to calculate chemical retention. A total of 20 five-ply plywoods, 4 plywoods for each treatment were manufactured from the veneer with the dimension of 490 mm x 490 mm x 2.20 mm.

2.3. The production of plywood panels

After preparing commercial wood veneers with dimensions of 490 mm x 490 mm x 2.2 mm, 5-layer, the plywood panels were produced under laboratory conditions. Each type of modified UF adhesive was uniformly spread on a single bonding surface of

veneers using a plastic brush at the rate of 200 g/m². After the glue application, individual sheets of the wood veneer were assembled with the same grain directions for all veneers. The plywood mats were hot pressed under 1.2 N/mm² of pressure at a temperature of 140 °C for 12 min in a laboratory type hot press. The densities of plywood panels ranged from 0.69 to 0.71 g/cm³. Plywoods were conditioned at 20 °C and 65% relative humidity until the constant weight before the physical and mechanical tests. The experimental design is given in Table 2.

Table 2: Experimental design

Plywood code	Contentration Fire retardant solution (wt%)	Retention of fire- retardant	The number of panels produce d
Control	-	-	4
Borax	6%	14.54	4
Boric acid	6%	19.37	4
Diammonium phosphate	3%	21.00	4
Monoammonium phosphate	3%	25.57	4



Fig. 2: The plywood sample.

2.4. Test methods

The density, and the mechanical properties such as, bending strenght, modulus of elasticity, internal bond, and bond quality of the specimens were carried out according to EN (European Norm) standards (Table 3). Fire properties such as flame height, and char area of the specimens were evaluated according to DIN (Deutsches Institut für Normung) standard (Fig. 1).

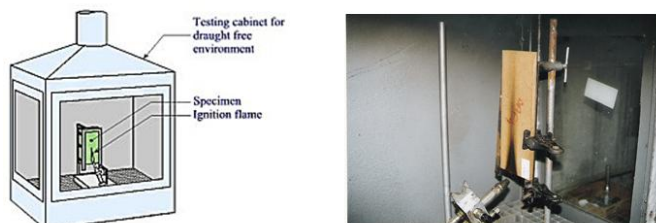


Fig. 1: Fire test according to DIN 4102-1 standard.

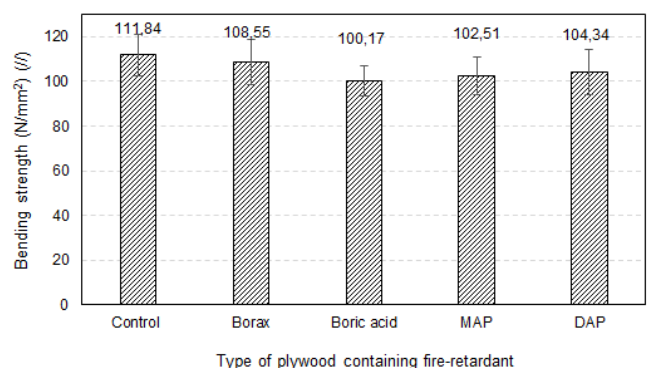
Table 3: Test methods, the number of specimens and their size

Test method	Standard no	Size (mm)	The number of specimens
Density	TS EN 323	50 x 50	30
Thickness swelling (24- h)	TS EN 317	50 x 50	30
Bending strength (//)	TS EN 310	250 x 50	18
Bending strength (⊥)	TS EN 310	250 x 50	18
Bending Modulus (//)	TS EN 310	250 x 50	18
Bending Modulus (⊥)	TS EN 310	250 x 50	18
Tensile-shear strength	TS EN 314	100 x 20	30
Fire resistance	DIN 4102-1	90 x 190	10

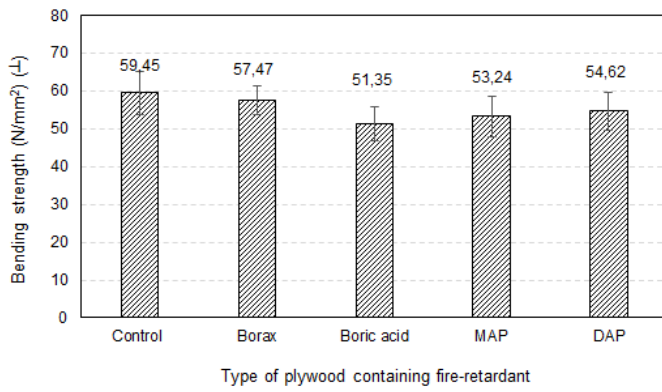
3. Results and Discussion

3.1.. Mechanical properties

The bending strength values of the plywood specimens parallel and perpendicular to the panel surface are presented in Figure 2. The panels treated with borax had highest bending strength, followed by di-ammonium phosphate (DAP), mono-ammonium phosphate (MAP), and, boric acid, respectively. A similar trend was determined for bending modulus (Fig. 4). All the treated panel groups showed lower performance related to mechanical properties when compared to control panels group (Fig 5). The bending strength values of the plywood specimens were compared with to EN 636 (2012) standard. The FR chemical retention values of the each plywood type was different from each other. The FR retention values of plywood specimens produced using the BX, BA, MAP or DAP treated wood veneers were found to be 14.54, 19.37, 21.00, 25.57 kg/m³, respectively. Borax treated specimens showed better mechanical performance than the boric acid treated specimens. Similarly, di-ammonium phosphate treated specimens showed better performance than the mono-ammonium phosphate treated specimens. The bending strength and bending modulus of the plywood specimens parallel to the fiber direction of the surface veneer were considerably higher than the bending strength perpendicular to the fiber direction of surface veneer.

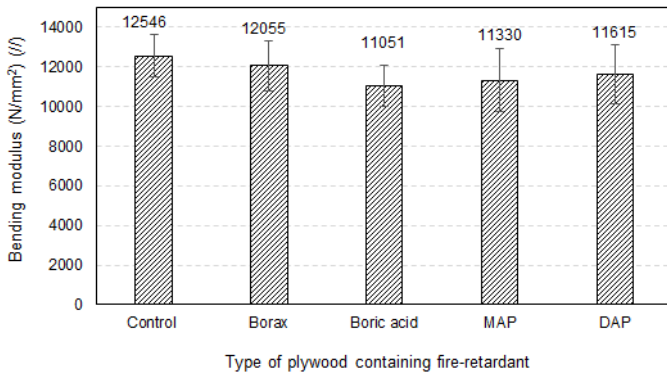


A.

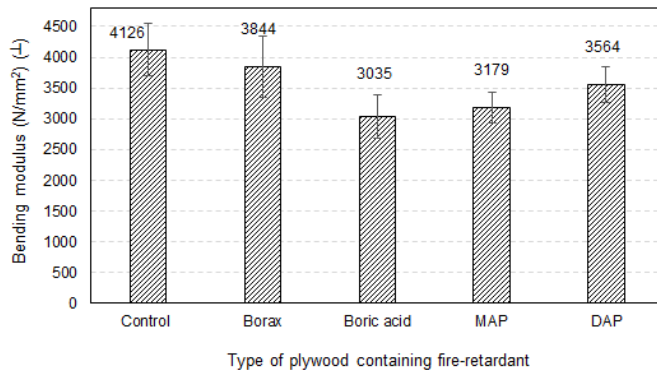


B.

Fig. 2: Bending strength values (A: parallel and B: perpendicular to the panel surface) of plywoods



A.



B.

Fig. 3: Bending modulus values (A: parallel and B: perpendicular to the panel surface) of plywoods.

The tensile shear strength of the plywood specimens shows the bond performance between the wood veneers in the plywood (Fig. 4). The bond performance between the veneers of the plywood specimens showed a similar trend to the bending properties. Although all the plywood produced using modified veneers showed lower tensile shear strength than that of the control group, they complied with the EN 314-2 (2003) standard value (minimum 1 N/mm²). The boric acid and mono-ammonium phosphate showed considerably decreased the bond performance of the plywoods as compared to borax and di-ammonium phosphate treated plywood specimens.

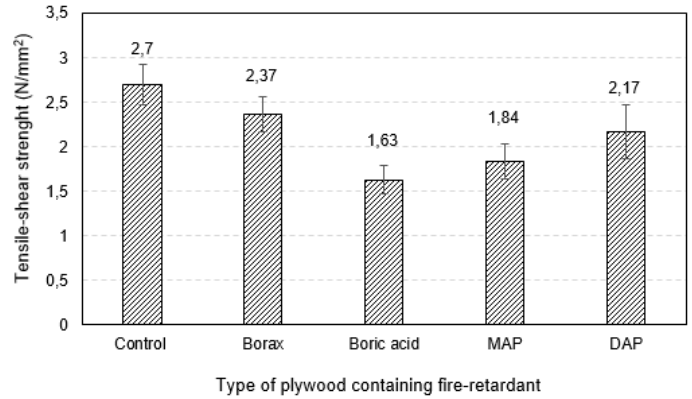
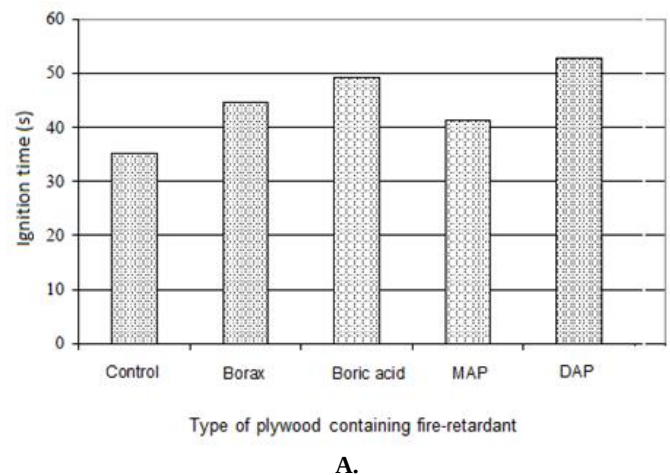


Fig. 4: Tensile-shear strength of plywoods.

The addition of borate to the strands with the PF resin may prevent the curing of PF resin [5]. The use of borate as a fire retardant in wood-based composite panels may cause several problems. The most critical one is related to its adverse effect on the mechanical properties of wood composites bonded with PF resin [4-7]. The main problem is related to the functional methanol groups (CH₂OH) on the PF resin molecules and their interaction with borate ions. In a previous study, Schaeffer et al. [4] determined acidic ammonium salts in both phosphate decrease the pH of the resin to a level much lower than that noted with the alkaline sodium salts. Apparently, the strength reductions in these specimens treated with the acidic fire retardants were probably caused by a combination of accelerated resin cure and thermal decomposition [5].

3.2. Fire resistance

The ignition time and flame length of the plywood specimens are given in Figure 5. The FR chemicals improved the fire resistance of the plywoods. Their effects on the fire resistance of plywood was related to the type of FR chemical. The chemicals showed individually different effects related to improvement of fire resistance of the panels. For example, the OSB panels treated with diammonium phosphate were the latest ignited group (52.8 s) which were followed by the panels treated with boric acid (49.2 s), borax (44.5 s), and monoammonium phosphate (41.2 s), respectively. As compared to the control group (7.5 cm), the plywoods treated with borax (3.6 cm) had the shortest flame length after burner was turned off, followed by diammonium phosphate (4.2 cm), boric acid (5.1 cm), and monoammonium phosphate (5.8 cm).



A.

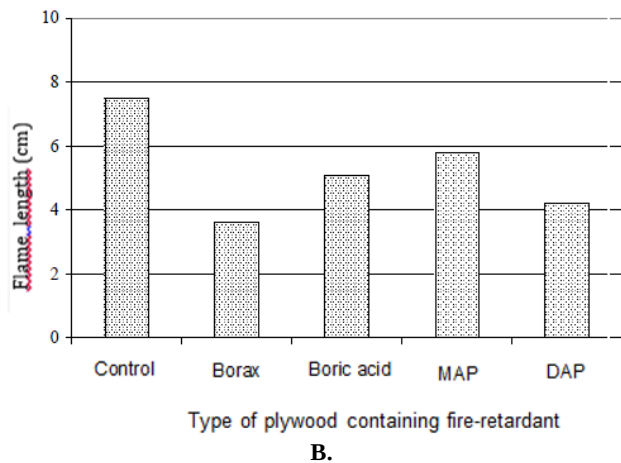


Fig. 5: Ignition time and flame length of the plywood specimens (A: Ignition time. B: flame length)

The main reason for the later ignition time of the plywoods containing diammonium phosphate can be explained by the fact that it more delays the release and amount of flammable gases from plywood as compared to the mono-ammonium phosphate. Furthermore, melting temperature of diammonium phosphate (155 °C) is lower than monoammonium phosphate which is more stable thermally lower than the melting temperature (190 °C) on the sample surface by starting an early reaction. Thus, diammonium phosphate causes carbonization early and the decrease the release of flammable gases from the plywood as compared to the monoammonium phosphate [8].

4. Conclusions

The FR chemicals showed an improvement in the fire resistance of the plywood specimens. However, the mechanical properties were slightly decreased after the treatment. As compared to the boric acid and monoammonium phosphate, borax and diammonium phosphate could be used to improve the fire resistance of the OSB panels because of their relatively little effects on the mechanical properties of the panels. The boric acid and monoammonium phosphate decreased the mechanical properties of the plywood specimens more than borax and diammonium phosphate. The hot water immersion method was used to impregnate the veneers by FR chemicals in this study. If the veneers are treated with FR chemicals using vacuum/pressure method, the fire resistance of the plywood specimens can be more improved.

5. Acknowledgement

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A composite magnetic material with insulating anticorrosive coatings

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Abstract: We have studied electromagnetic and corrosive properties of new soft-magnetic composite materials made from iron powder ASC 100.29 and Atomet 1001HP, surface of which is encapsulated by insulating anticorrosive oxide coating. The results demonstrate that the use of such materials in power supplies, chokes, transformers, stators and rotors of electrical machines and other devices ensures their stable operation under various conditions.

Keywords: SOFT-MAGNETIC COMPOSITE MATERIAL, IRON POWDER, INSULATING COVER, HIGH-FREQUENCY TRANSFORMERS, STATORS AND ROTORS OF ELECTROMACHINES

1. Introduction

Composite materials with the necessary operational properties are widely used in components of various mechanisms and machines in such branches of industry as electrical engineering and electronics. Since the final properties of the products depend on the methods of the starting materials treatment, it is necessary to exactly select the conditions for obtaining composite soft magnetic materials to ensure a controlled chemical composition and structure, which in turn guarantees the required physical and functional properties.

For materials operating in alternating electromagnetic fields, the most important characteristics are magnetic permeability, induction and losses due to remagnetization and eddy currents, corrosion resistance [1-5]. The value of electrical resistivity determines the maximal frequency with which the use of this material is advisable. Currently, a number of firms produce composite soft magnetic materials based on various encapsulated iron powders. The insulating layers prevent iron particles from contacting each other. As a result, the properties of the known composite soft magnetic materials are close to the properties of electrical steel. However, the presence of an insulating magnetically disordered substance between individual particles of metal particles leads to a decrease the magnetic permeability of the material to $\mu_m = 100 - 500$, and the magnitude of the magnetic induction is of the order of $B_m = 1.6 \text{ T}$ [6, 7]. The task is to increase magnetic induction and magnetic permeability, reduce the amount of electromagnetic losses of the material. Essential progress in improvement of magnetic properties of composite materials achieve in the present work due to using in quality isolate coverings various magnetic oxide – ferrites. Thus thickness isolation covering of iron particles have been reduced to some nm. The electromagnetic parameters of the obtained materials depend on the size, morphology of the particles and the purity of the initial powders; the chemical composition and thickness of the insulating coatings, from the atmosphere in which the treatment takes place. Also for practical using of such materials it is important to have a good corrosion resistance.

Metal particles with applied insulating coatings are easily oxidized in a humid environment, but oxides on the metal surface significantly reduce the magnetic properties. Traditionally, various protective coatings are applied to metal surfaces to prevent corrosion. However, over time, the protective coating will deteriorate and the metal has to be reworked in order to protect it from corrosion. In addition, anti-corrosion surface treatment is not always effective, since the presence of defects in parts often leads to internal corrosion, which destroys the latter. The applied special insulating corrosion-resistant layers in the composite material have a dual purpose: reduction of electromagnetic losses and protection against oxidation, since each particle is encapsulated. As a result, parts made of composite materials based on encapsulated powder will be protected from both surface and internal corrosion, and the service life of the parts will be determined only by their mechanical wear.

The aim of this work is to study the influence of the synthesis conditions of composite materials based on particles of iron powders with insulating coatings on its electromagnetic and corrosion characteristics.

2. Experimental part

Based on the requirements for the initial powders the water – atomized iron powder Hoganes ASC100.29 (Sweden) was selected as the main object of studies. On the particles of the material were deposited layers of phosphorus, boron, titan oxides using an optimized technique. Purity of ASC100.29 powder is 99.5%. The chemical composition of the powder is presented in the Table 1.

Table 1: Chemical composition of the water-sprayed iron powder ASC100.29 (Sweden).

Type of iron powder	Fe	Mn	Si	C	P
ASC100.29 (Sweden)	99,5	0,08	0,04	0,08	0,01

From the calculated and experimental data it was found that, depending on the particle size of the initial metal iron powder, the resulting composite materials can be divided into two classes: low-frequency ($f < 1 \text{ kHz}$) and high-frequency ($f > 1 \text{ kHz}$). For subsequent high-frequency applications, powders with a size of less than 100 microns are screened with a separator S49-1000-1, for low-frequency ones with a size > 100 microns. After separation an insulating layer was applied to the surface of the iron particles.

The deposition procedure included the stage of preliminary mixing of the initial metal powders with a given amount of reagent, which included an alcohol solution of orthophosphoric acid in the ratio of 40% H_3PO_4 + 60% ethyl alcohol. Instead of H_3PO_4 , boride or titanium compounds can be added.

In the next step, the prepared powder was placed in an insulation coating reactor. The powders with the reaction additive were treated in the reaction drum at a pressure of 0.1 to 1.0 atm., heated to a temperature of 150 – 200°C during 15 – 30 min. As a result, a complex coating of ferrite compounds and phosphates formed on the surface of iron particles. The chemical composition in case of phosphorus oxide coatings is a complex system of iron oxides FeO , Fe_2O_3 and phosphorus oxide P_2O_5 . A small amount of carbon and silicon are also present. The thickness of the insulating layer on the iron particle depends on the processing time of the powder and the concentration of the alcohol solution of phosphoric acid.

The magnetic permeability of the composites was measured in the frequency range up to 2.0 kHz. To study the features of magnetic properties, cores were made in the form of rings by pressing composite powders under a pressure of 7-8 t/cm². The density of the samples was determined by hydrostatic weighing in distilled water. Measurements of important magnetic characteristics – induction, loss, magnetic permeability – were performed on an express magnetometer. The magnetization dependences of the

obtained samples were recorded, the area of the hysteresis loop in pixels was determined, and losses were calculated. The pixel dimension was determined by measuring the magnetic flux using an F5050 microwebermeter.

The corrosion behavior of composites was investigated by open circuit potential (OCP) and anodic polarization curves (linear and Tafel) using a potentiostat/galvanostat Princeton- PARSTAT 2273 (with a specialized soft "Power Corr") in a 3.5 wt% NaCl aerated solution at a temperature of 25°C. The electrochemical measurements were performed in a glass cell of 50 ml capacity with thermostated jacket, with a conventional three electrode: Ag/AgCl (with KCl 0.3M) as the reference electrode and a platinum plate as counter electrode, both of them of Radiometer production. The working electrodes each had 1 cm² of exposed surface.

3. Results and discussion

On Fig.1 is shown the static magnetization curve of a composite magnetic material on the basis of powder ASC100.29. It is visible from the resulted data, that process of magnetization as against laminated Si-steel is closed to linear at an induction of saturation ~ 2.2 T. For electrotechnical steel the induction of saturation is closed to 1.8 T.

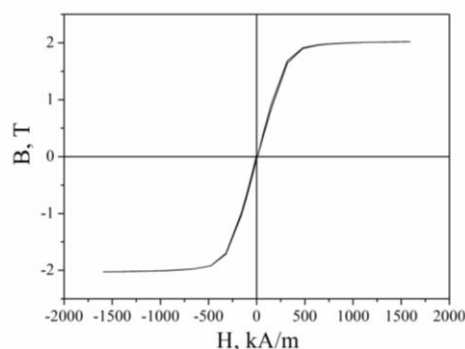


Fig. 1 Static magnetization curves of a composite magnetic material on the basis of powder ASC100.29.

Comparative investigations of electromagnetic characteristics for materials on base of Hoeganes ASC100.29 and such ones from powders of Micrometals and Atomet companies are carried out. On Fig. 2 are shown the magnetization curves of magnetic-soft materials with isolation magnetic oxide of the iron powders ASC100.29 – a curve 1 and known composite materials with dielectric isolation at use of powders High Flux (HF) – a curve 2 (manufactured by Micrometals, USA).

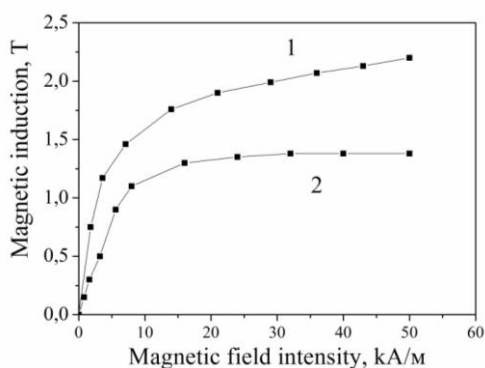


Fig. 2 Magnetization curves of soft magnetic materials with isolation magnetic oxide powders of iron ASC100.29 – a curve 1 and known composite materials with dielectric isolation at use of powders High Flux (HF) – a curve 2 (manufactured by Micrometals, USA).

Presence of isolation backlash between particles of iron in a composite material on the basis of powder ASC100.29 results to

that initial value of magnetic permeability has also the maximal value (Fig. 3).

As against it for powders of iron with a ferrite covering initial permeability $\mu_0 = 80-100$, and the maximal permeability $\mu_m = 800 - 1000$.

Magnetic properties of a composite material essentially depend on pressure of pressing or density of a product. Magnetization curves in a frequency range up to 2000 Hz practically coincide and have identical behavior for a magnetic material on basis ASC100.29.

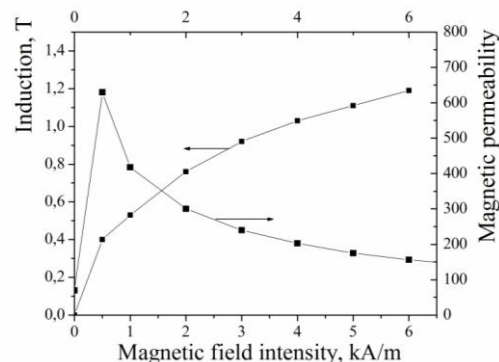


Fig. 3 Field dependencies of induction and magnetic permeability of the soft magnetic material on base of ASC100.29.

Researches of total losses at remagnetization in a frequency range up to 2 kHz and a magnetic induction up to 1.5 T composite materials using as isolator of particles of iron magnetic dielectric material were carried out with use of iron powders Atomet 12001HP and ASC100.29 (Fig. 4). From the results follows, that losses does not exceed 5 % from total losses on remagnetization, and for a material on basis ASC100.29 losses are essentially less.

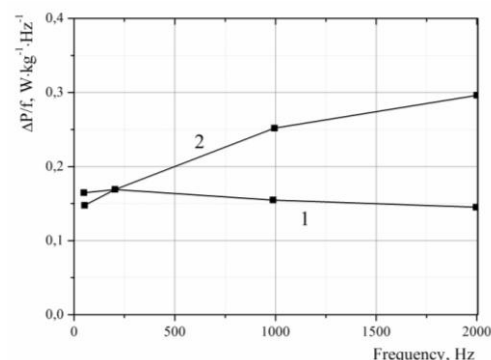


Fig. 4 Total energy losses per cycle as a function of frequency for examined magnetic cores at magnetic induction $B = 1.0$ T (1 – ASC100.29, 2 – Atomet 1001HP).

Frequency dependencies of the inductance and Q-factor of the composite magnetic material (Fig 5) show that in frequencies range 100 Hz ÷ 10 MHz the inductance practically does not change its value. The value of Q-factor reaches its maximum in the range of ~ 20–30 kHz. With use of the developed composite materials on the basis of powders of iron ASC100.29 pre-production models of invertors power supplies up to 10 kW in a frequency range up to 100 kHz are developed, chokes of various purpose, the pre-production model of the electric motor for a frequency range up to 2000 Hz is developed.

Reliability and stability of work in various conditions of power supplies on transformers with the core on base of the composite material, determined by high value of temperature Curie – is higher 800°C and a magnetic induction of saturation 2.1 T, compensates expenses for the additional charge of a copper wire and the losses connected to it for sources with capacity less than 1 kW.

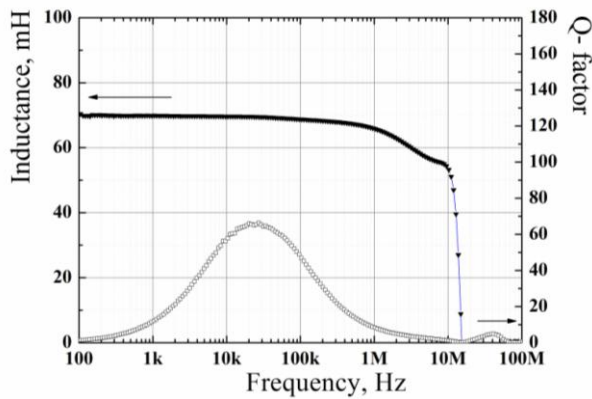


Fig. 5 Frequency dependencies of the inductance and Q-factor of the composite magnetic material on base of ASC100.29.

The results of the study of electrochemical corrosion in the form of the parameters calculated from the linear polarization (LP) and Tafel dependencies are presented in table 2. It follows from the table that for a composite based on a powder with grain over 100 mkm, the corrosion rate is 0.982 mm/year, and for a composite with a grain of 20-100 microns – 0.485 mm/year. This fact can be explained by following. The experimental data on the corrosion of a some of metals and metal alloys, including iron-based ones, indicate that the grain size practically does not affect the corrosion rate. The exception is cases where at the grain boundaries of the metal the conditions are such that corrosion can acquire an intergranular character. The increase in grain size in such alloys creates a great possibility of the appearance of intergranular corrosion and can significantly enhance it: the total length of the boundaries of coarse-grained metal is less than that of fine-grained metal, and, therefore, the intensity of corrosion per unit length of the grain boundary will be greater.

Table 2: Electrochemical corrosion parameters determined from the Tafel curves obtained in 3.5 wt% NaCl at 28°C.

Type of iron powder	E_{OCP} (V)	R_Ω (Ω)	E_{corr} (V)	I_{corr} (A)	CR (mm/year)
composite based on powder with grain over 100 microns	-0,574	88,231	-0,637	$190,9 \times 10^{-6}$	0,982
composite based on powder with grain 20-100 microns	-0,561	59,079	-0,582	$61,23 \times 10^{-6}$	0,485

4. Summary

A method of synthesis of composite materials based on iron powders, the particles of which are coated with a nanoscale layer of phosphides, has been developed, which includes the stage of preliminary mixing of the initial metal powders with a given amount of an alcohol solution of orthophosphoric acid in the ratio 40% H_3PO_4 +60% ethanol. The method makes it possible to reduce the lubricant content to 0.01 – 0.10%, which makes it possible to obtain subsequently a high-quality molded product from a soft magnetic composite material with a density of 7,50 – 7,65 g/cm³ and, as a result, having high electromagnetic characteristics.

The carried out preliminary researches of a composite magnetic material on the basis of powders of iron ASC100.29, surface of which is capsulated by ferrite and phosphides, have shown perspectives of their application in engineering. Unique specific parameters of a soft magnetic composite material – a magnetic induction of saturation 2.1 T, work in a frequency range up to 100 kHz at Curie temperature from above 800°C allow using it in high speed valve and valve-jet electro machines and as chokes and high-frequency transformers. A powder-based composite with a grain size $d > 100$ mkm has less corrosion resistance. The corrosion rate in this case is 2 times higher, due to the fact that in this case there is a manifestation of intergranular corrosion.

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