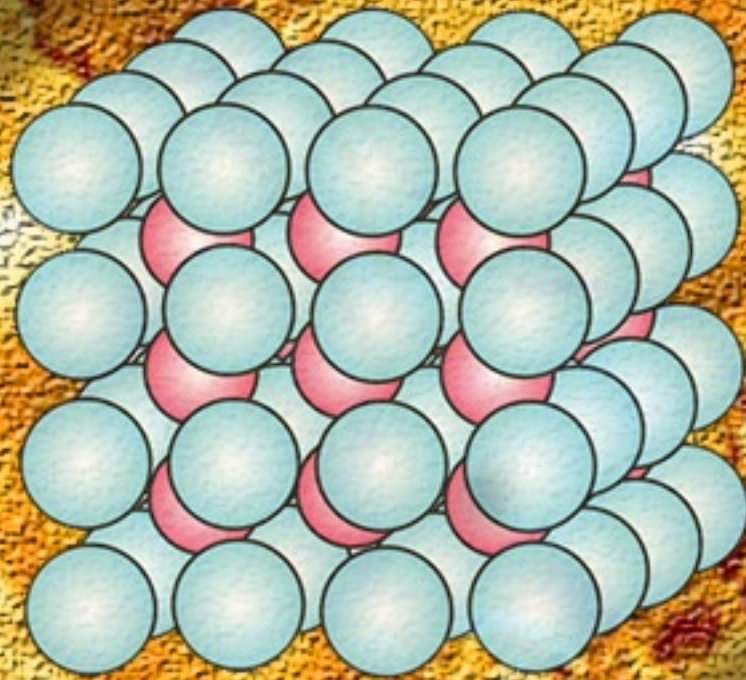


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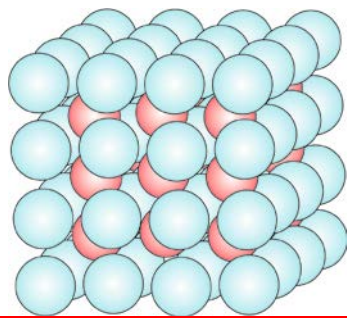
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Combustion synthesis: Towards novel nanomaterials

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Abstract: The combustion synthesis (CS) is an autogenous and strongly exothermic chemical reaction in a powdered mixture of a strong reducer and oxidizer. Such processes, due to short duration and fast quench, can be a source of novel nanomaterials. Here we present (i) the CS synthesis of SiC nanowires (SiCNWs) and (ii) the magnesiothermic reduction of the asbestos waste. The resulting raw and purified products were analyzed with different chemical and physicochemical techniques (XRD, SEM, TGA and Raman spectroscopy) to verify its composition and morphology.

Keywords: COMBUSTION SYNTHESIS, MAGNESIOTHERMIC REDUCTION, SiC NANOWIRES, GRAPHENE, NANOSTRUCTURES, WASTE

1. Introduction

The bottom-up approach of the synthesis of nanomaterials involves the generation of building blocks (ions, atoms, radicals, molecules) via the thermal or plasma activation of starting reactants. Here we propose the combustion synthesis (CS) which is an autogenous and strongly exothermic redox reaction between oxidizer and reducing agents and has been well known and explored for many years now [1]. For example, the thermite reaction has been widely used for connecting rails, in military applications and fireworks while CS has been routinely utilized in the generation of emergency oxygen on board the aircraft. Combustion synthesis has been also successfully used to produce different nanomaterials [2]. The CS is here an adaptation of a simple and easier synthesis option bestowed with time and energy saving prospect. Huczko et al. [3] produced efficiently silicon carbide nanowires (SiCNWs) in the reaction between elemental silicon and halogenated carbon compounds. The CS approach, due to a short reaction duration and fast quench, may be the source of novel nanocarbons, after removal (acid leaching) of side oxides. We tested the magnesiothermic processing of different mixtures including both model carbon-containing compounds and carbon-related commodities [4] to obtain graphene-related nanocarbons. A metallothermic reduction processes have been also patented [5], i.e. a porous silicon-based material comprising porous crystalline elemental silicon formed by reducing silica can be used to construct negative electrode used in lithium ion batteries [6].

Among various 2D nanomaterials, graphene has received extensive research attention in the last 2-3 decades due to its fascinating properties. The multidisciplinary characteristics of graphene provides a platform for a wide range of applications from health to aerospace. As an example, in September 2019 the first in the world photovoltaic power station (power 1.8 MW) was inaugurated in Feliksów (Poland) in which the photovoltaic silicon-based modules were graphene-modified. Tiwari et al. [7] presented recently the review article providing an outline of graphene in terms of fundamental properties, cutting-edge research and applications.

One should also mention here the solution combustion synthesis (SCS) which ensures uniform distribution and atomic level mixing of reactants in liquids, and yields powders with reduced particle size. As an example, Manjunath et al. [8] successfully synthesized zinc oxide nanoparticles using pigeon pea as a fuel. The as-prepared ZnO showed good photocatalytic and antibacterial activities. Recently, the antimicrobial copper-based precipitates were formed during the SCS using L-ascorbic acid as reducing agent but long (24 hours) reaction duration was a clear disadvantage of that approach [9]. Huczko et al. [10] also applied the SCS approach to produce and characterize YAG:Ce³⁺ garnet nanopowders.

We present here the results of two series of combustion runs. The silicon reduction of fluorinated graphite was aimed not only at the production of SiCNWs but it was also expected that the defluorination of CF_x can lead towards the formation of graphene-like carbon nanostructures. The magnesiothermic reduction of asbestos waste can produce fine silica with some specific surface properties this due to the high temperature and fast quench of the combustion products. The resulting raw and purified products were analyzed with XRD, SEM, EDS, TGA and Raman spectroscopy to verify its composition and morphology.

2. Experimental

Table 1 presents the operational parameters of all runs. The starting stoichiometric components were hand-mixed at ambient temperature prior to introduction into the quartz crucible in reactor before performing the combustion synthesis. The combustion was initiated thermally by ohmic heating of a carbon tape immersed in the reactants following the experimental protocol described elsewhere [11]. The reactor was provided with the observation port to record the light emitted from the combustion zone. The starting pressure in the reactor was either 0.1 or 1.0 MPa. The combustion was terminated within ca 1 second and, after cooling period, the solid raw products were collected for the mass balance and the following analyses. The work-up of product mixtures was carried out by wet chemistry to remove non-converted starting reactants and unwanted side-products.

Table 1. Operational parameters of combustion syntheses

Run No.	Starting reactants	Mass of starting reactants, g	Combustion atmosphere	Starting pressure, MPa	Peak pressure, MPa	Mass of raw products, g
I-1	Si + CF _x	4.71	Air	0.1	2.8	3.26
I-2	Si + CF _x	6.63	Air	1.0	7.0	4.53
II-1	Mg + asbestos waste	6.70	Argon	0.1	0.4	6.34
II-2	Mg + asbestos waste	5.48	Argon	1.0	1.4	5.28
II-3	Mg + asbestos waste	5.35	Argon	0.1	1.2	5.32
II-4	Mg + asbestos waste	5.46	Argon	1.0	1.8	5.42

3. Results and Discussion

The exothermal combustion is accompanied by the strong emission of heat and light. The latter one can be a useful source of information about the nature of the reaction and its time. Thus, the Light Signal Diagnostics (LSD) protocol was developed, which enabled the on-line measurement of the reaction duration and characteristics, especially the detailed monitoring of the propagation of the combustion wave and its front. Fig. 1 presents few examples of such results for the selected combustions which confirm the short reaction duration (within ca 1 second) and its susceptibility to even the minor changes in initial operational parameters (such as the pressure and type of gaseous atmosphere). One may also follow the complex time signal trajectory with its oscillations and local combustion wave maxima. They correspond to the kinetics of the process. The light characteristics is reproducible within the same operational conditions. Thus, it can be treated as a reactions fingerprint.

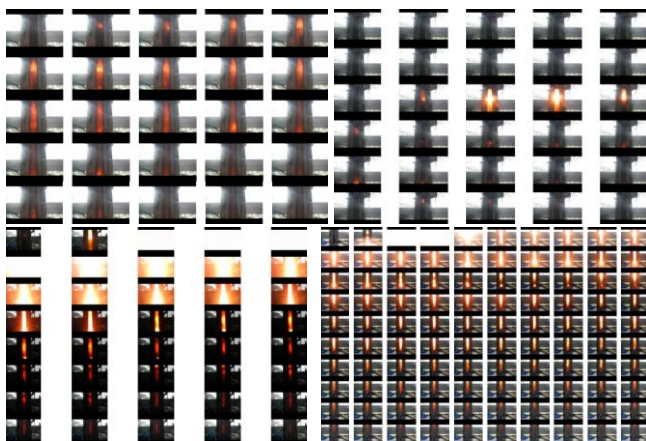


Fig. 1. The in situ mapping of combustion synthesis for different run; A: run II-4; B: run II-3; C: run I-2; D: run II-1

As one can see, the combustion in the Si/CF_x is much more vigorous regarding the emission of a light and heat. Different mixtures of reactants may lead to the designed nanomaterials (Fig. 2). The versatility is a crucial advantage of the combustion synthesis. On the other hand, LSD enables its precise diagnostics and facilitates the optimization.

The morphology of raw products is quite different comparing to the starting mixture (Fig. 2). The raw product from combustions in the Si/CF_x systems is amazingly voluminous this due to the high amount of 1D SiC nanostructures.

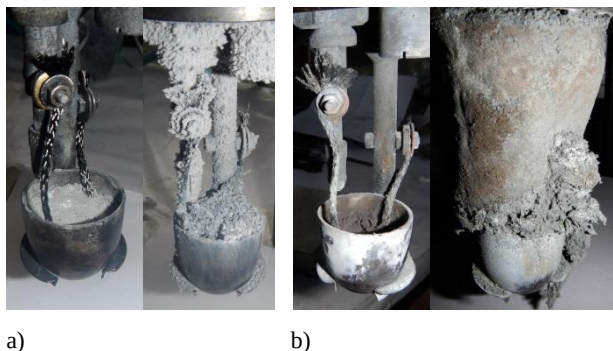
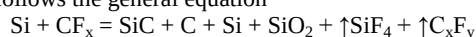


Fig. 2. Reactants before combustion (left) and raw reaction products (right) from runs; a: run II-4; b: run I-2

3.1. Synthesis of silicon carbide nanowires (SiCNWs)

The silicon reduction of the fluorinated graphite CF_x (x = 0.89) in air atmosphere follows the general equation



We showed earlier [12] that the reaction of silicon with halogenated carbons (like TEFLON[®]) proceeds more efficiently under the presence of oxygen this due to vigorous gas phase mass transport of silicon via gaseous SiO molecules. It was expected that the application of the fluorinated graphite as an oxidizer could enable not only the growth of SiCNWs but also the formation of layered graphene-like carbon nanostructures resulting from the silicon extraction of fluorine from layered graphite matrix. To isolate the SiCNWs, the un-reacted Si and silica were leached with boiled 30% KOH why the residual carbon was removed via air oxidation at 600 °C in the following step. The combustion was accompanied by a strong pressure increase (Table 1) this due to the high temperature and formation of gaseous side products (SiF₄ + C_xF_y). The latter one is confirmed by a substantial mass decrease of solid reactants (Table 1). The content of un-reacted Si in a raw product (from wet chemistry analyses) for runs I-1 and I-2 was equal to 5.4 and 3.6 wt%, respectively. Thus, the total conversion of starting silicon was very high, 93.0 % and 95.6 % for runs I-1 and I-2, respectively.

Fig. 3 presents the SEM images of the starting mixture (runs I-1 and I-2) composed of several micron-sized Si crystallites (Fig. 3A) and layered CF_x (Fig. 3B).

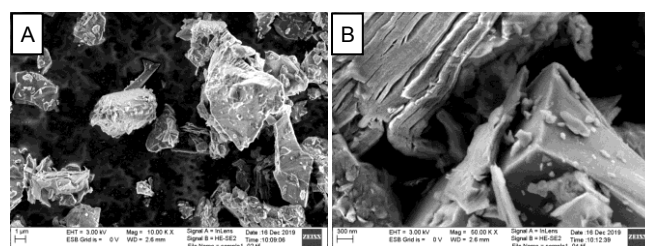


Fig. 3. SEM images of starting mixture (runs I-1 and I-2)

The morphology of the raw product (Fig. 4) does not depend on the starting pressure. The raw product is a non-homogeneous mixture of different nanosized species including SiCNWs, nanoballs (200-400 nm) of SiO₂, spherical (well below 100 nm) soot particles and microcrystallites of SiC.

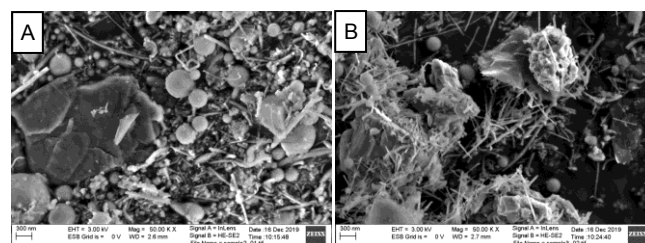


Fig. 4. SEM images of raw product

The purified product (Fig. 5) is composed essentially of SiC nanowires (well below 100 nm) with some SiC cubic microcrystallites.

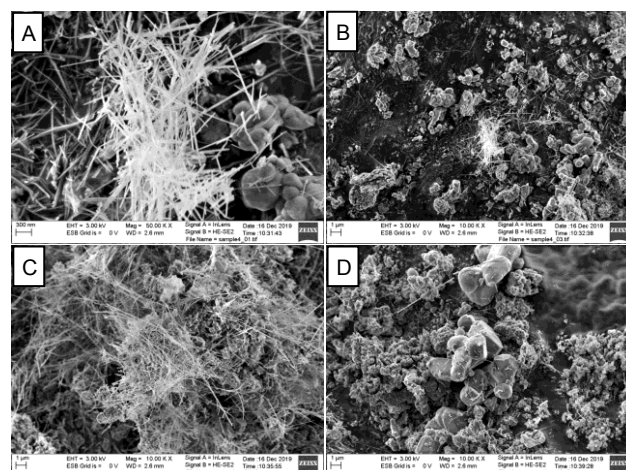


Fig. 5. SEM images of purified product

To confirm the purity of the product the EDS analysis was carried out (Fig. 6) which confirmed the stoichiometry of the formed SiC. The results (Table 2) confirm the content of SiC in a purified product above 90 at.%.

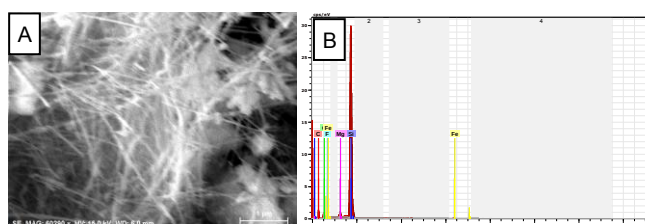


Fig. 6. EDS analysis of purified product

Table 3. EDS analysis of the purified product

Element [wt.%]	Series [wt.%]	unn. C [at.%]	norm. C [wt.%]	Atom. C	Error (1 Sigma)
Carbon	K-series	28.25	30.01	48.14	4.46
Oxygen	K-series	7.23	7.68	9.25	1.23
Silicon	K-series	56.47	59.99	41.15	2.37
Fluorine	K-series	0.16	0.17	0.17	0.10
Magnesium	K-series	1.16	1.24	0.98	0.09
Iron	K-series	0.85	0.90	0.31	0.08

Total: 94.12 100.00 100.00

TGA analysis (Fig. 7) confirmed that conclusion. The purified SiCNWs contain less than 5 wt% of carbon which removal from the final product occurs between 500 and 600 °C.

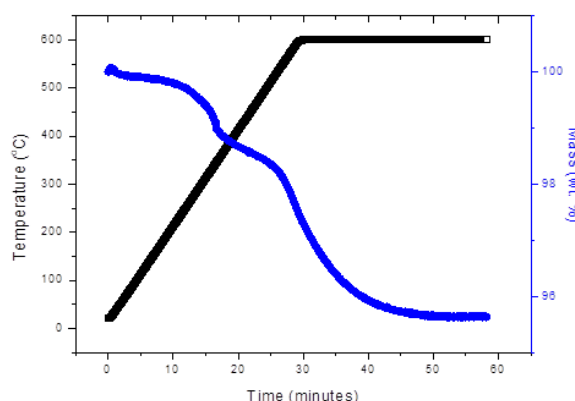


Fig. 7. TGA analysis of purified SiCNWs product

Fig. 8 presents XRD spectra of the reactants. The starting mixture (Fig. 8a) is composed of crystalline Si elemental (with some residual Ge presence) while the CF_x phase seems to be amorphous. The raw product (run I-2, Fig. 8b) contains mostly SiC with some un-reacted silicon while the carbon is evidently in an amorphous form. The purified product (Fig. 8c) is dominated by SiC reflexes.

The results showed that pure SiC nanowires can be efficiently produced via the silicon reduction of the fluorinated graphite. The observations of the product did not reveal, however, the presence of layered carbon nanostructures. Thus, it seems that the extremely strong thermal effect of combustion totally atomizes the carbon (forming the hexagonal network in starting CF_x) which later condenses as amorphous soot.

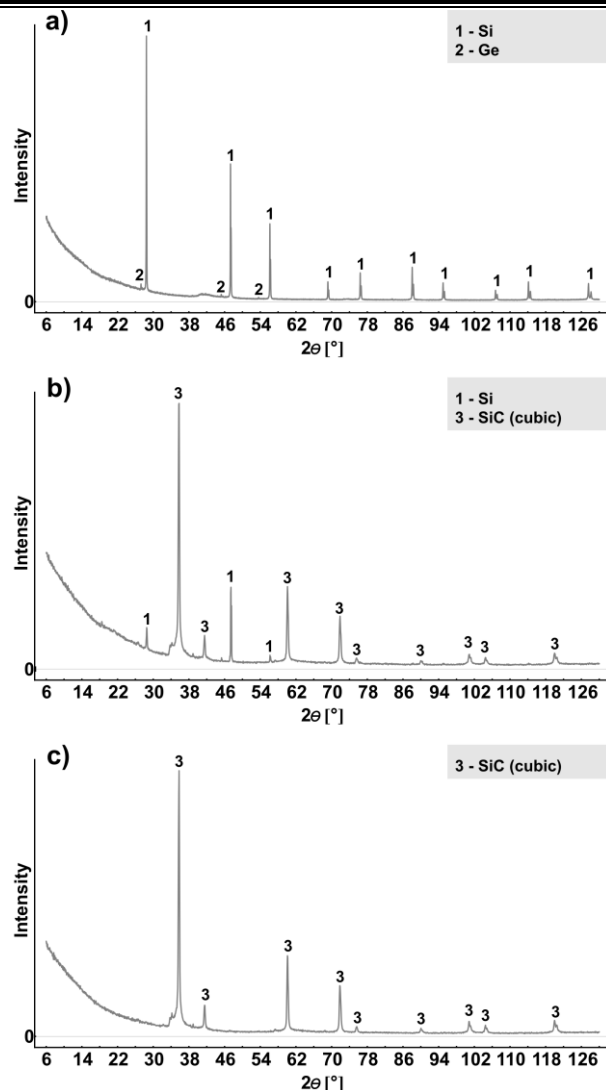
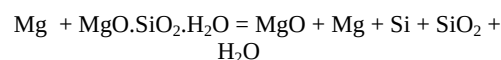


Fig. 8. XRD spectra of selected samples; run I-2: a – starting mixture; b – raw product, c – purified product

3.2. Magnesiothermic reduction of asbestos waste

The magnesiothermic processing of asbestos waste [13] with Mg as a reducing agent follows here the general scheme



Ma et al. [14] earlier produced porous silicon by magnesiothermic reduction of serpentine mineral. It was expected here that the final product, after chemical purification (acid leaching), would contain mostly fine silica (along with Si elemental) with some specific surface properties. As a matter of fact, silica-based amine-grafted sorbents exercised high amine efficiency for CO_2 capture, leading to a record-high CO_2 capacity of $\sim 12 \text{ mmol g}^{-1}$ under simulated flue gas conditions [15].

Fig. 9 presents the micrograph of starting asbestos waste which reveals its particle size well below $5 \mu\text{m}$ and heterogeneous morphology.

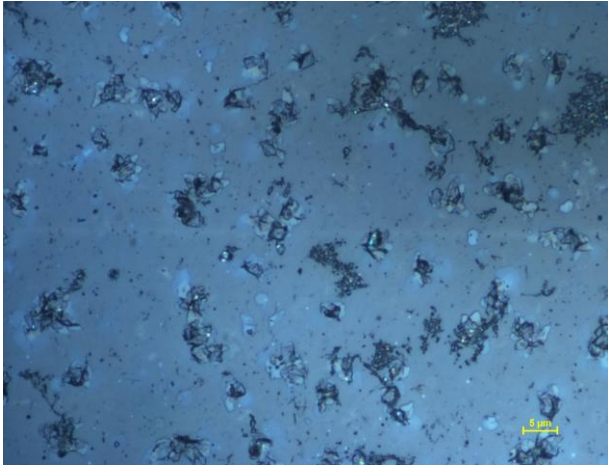


Fig. 9. Micrograph of asbestos waste

The combustions were carried out with a two-fold excess of Mg (runs II-1 and II-2) and with a stoichiometric amount of a reducer (runs II-3 and II-4) – Table 1. The mass of the collected raw product did not differ substantially from the starting mass and the pressure increase was quite moderate this all showing that we dealt entirely with the solid-phase reaction. Fig. 10 presents the SEM images of the starting reactants (runs II-3 and II-4), composed of heterogeneous mixture of Mg particles and waste microcrystallites with some residual asbestos fibers.

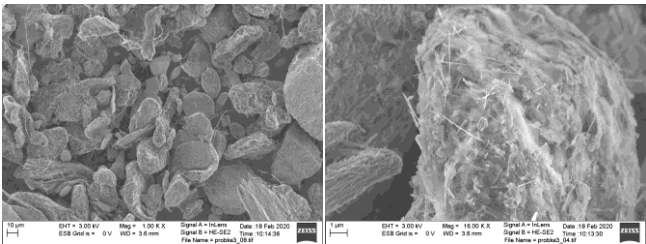


Fig. 10. SEM images of starting mixture (runs II-3 and II-4)

The raw product (Fig. 11) has a quite different morphology. There are only very few of asbestos fibers and the material is dominated by cubic nanocrystallites of MgO.

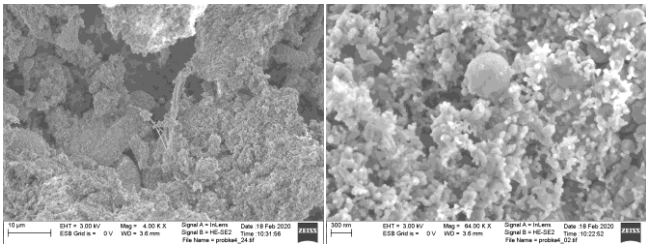


Fig. 11. SEM images of raw product (runs II-3 and II-4)

The purified product (Fig. 12) has a heterogeneous morphology; MgO nanocrystallites are essentially gone while some interesting platelet-like porous nanostructures are easily spotted.

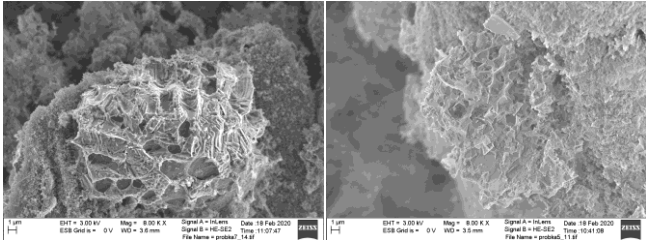


Fig. 12. SEM images of purified product (run II-3 and II-4)

To identify its identity the EDS analysis was carried out (Fig. 13).

Table 3. EDS analysis of the purified product

Spectrum: Acquisition

Element	Series	unn. [wt.%]	C norm. [wt.%]	C Atom. [at.%]	C Error (1 Sigma) [wt.%]
Oxygen	K-series	16.59	17.84	27.83	2.43
Silicon	K-series	74.18	79.74	70.89	3.11
Iron	K-series	1.87	2.01	0.90	0.13
Aluminium	K-series	0.38	0.41	0.38	0.05
Total:		93.03	100.00	100.00	

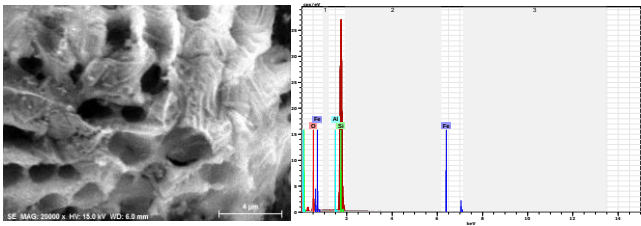


Fig. 13. EDS analysis of purified product (run II-4)

The porous material (in a purified product) is mostly composed of the elemental Si with some residual silica – Table 3.

The XRD spectra of reactants are shown in Fig. 14. The starting mixture (run II-4, Fig. 14a) is dominated by Mg elemental with the waste mineral phase (here denoted as a serpentine). The raw product (run II-4, Fig. 14b) contains mostly MgO with some un-reacted magnesium and serpentine, along with other side products. Surprisingly, the purified product (Fig. 14c) is dominated by the elemental silicon (instead of the expected silica) with some iron silicide and silicon carbide (formed from a residual carbon). That result proves that the sought reaction proceeded much deeply and resulted in a magnesiothermic reduction of silica.

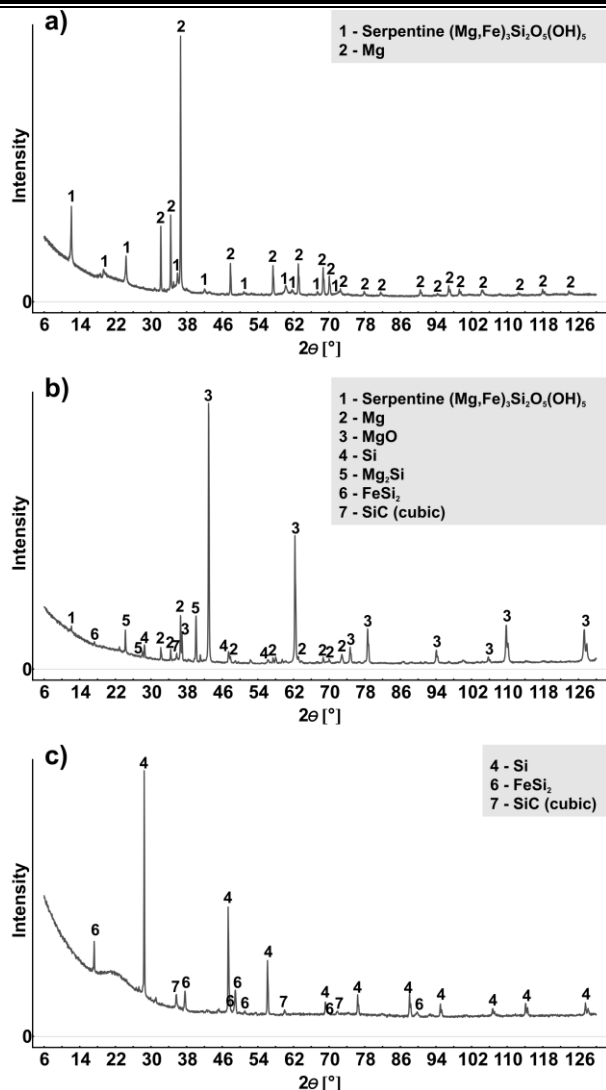


Fig. 14. XRD spectra of selected samples (run II-4): a – starting mixture; b – raw product, c – purified product

The adsorption performance of both raw and purified products was analyzed in the process of 4-chlorophenol removal from aqueous solution. The adsorption of raw product (runs II-3 and II-4) was negligible due to the basicity of the surface. However, the surface of the purified products (after leaching with HCl) does not exhibit basic properties. In these cases the adsorption of 4-chlorophenol was detectable and measurable. However, the highest obtained values of the adsorption capacity were not high, namely 12 mg/g and 18 mg/g for run II-3 and II-4, respectively. The obtained adsorption isotherms (Fig. 15) are typical for S1 isotherms in Giles' classification [16] or for the III type in the IUPAC classification [17]. Both correspond to the weak attraction between solute molecules and the surface of the adsorbent.

4. Conclusions

Combustion synthesis was used to produce SiC nanowires and to reduce the asbestos waste. The silicon defluorination of fluorinated graphite yields 95% pure SiCNWs. However, the residual carbon did not form 2D nanostructures, as expected, but condensed as a soot. The asbestos waste, containing mostly silicon-related compounds, was deeply reduced with Mg elemental, but contrary to expectations, the purified product contained almost 50% of elemental Si along with some residual fine silica.

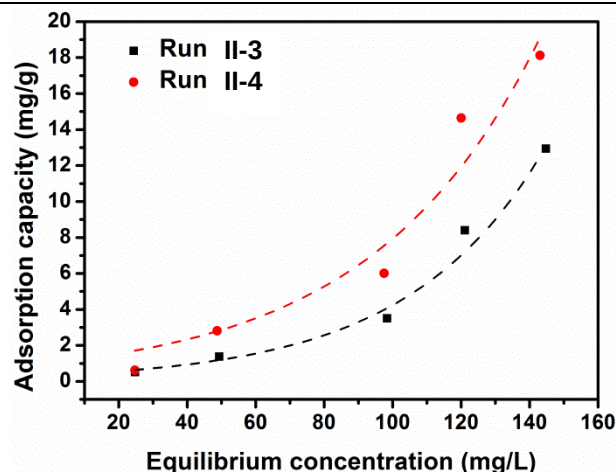


Fig. 15. Adsorption isotherms for purified products of magnesiothermic reduction of asbestos waste

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Current trends in the development of high dielectric permittivity ceramics

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Abstract: The proposed review looks at some aspects concerning ferroelectrics that are characterized by high dielectric constant at/ or near Curie temperature. Particular attention has been paid to the doping of BaTiO₃ with rare earth elements because they prove to be very promising for the production of supercapacitors. It is pointed out that the preparation of ceramic materials with high dielectric permittivity by sol-gel method is of huge interest due to the numerous advantages inherited to this technology.

Keywords: BaTiO₃, CERAMIC MATERIALS, HIGH PERMITTIVITY, RARE EARTH ELEMENTS

1. Introduction

In recent years, interest in the development of new ceramic materials has increased significantly. A directive from the European Union has been introduced to restrict the import and production of lead-containing materials. [1] According to the norms presented, lead should not be contained in dielectric materials that are part of integrated circuits or discrete semiconductor devices. This is how ideas for the creation of high quality lead-free ceramic materials are born. [2]

For a number of simple electronic applications such as ceramic multilayer capacitors (MLCC), they have quite low thermal stability. The dielectric permittivity characteristics of these MLCCs generally meet the temperature specification "Y5V" of the "Electrical Industry Association" (EIA). The 'Y5V' specification for condenser materials operates in the temperature range from - 30°C to + 85°C. Capacity will not increase above 22% and will not decrease below 82% of its nominal value. In the field of electronic components, there is a continuing trend of miniaturization, involving multi-layer capacitors of chips. Therefore, the rapidly expanding market for surface mounted technology chips requires higher and higher compact MLCCs, i.e. greater volume capacity. The required increase in specific capacity is realized in two ways:

- Increasing the relative dielectric permittivity.
- Reducing the thickness of the dielectric layer. [3]

Y5V" dielectric materials typically use the maximum transmittance arising at the Curie point (T_c). The temperature characteristics of "Y5V" materials generally correspond to a simple, wide dielectric close to room temperature. The most commonly used base material for MLCCs is BaTiO₃, showing a T_c of 130°C and a relative dielectric permittivity $\epsilon_r = 2000$. The maximum dielectric constant is shifted to room temperature by chemical modification of the ceramic material.[4]

BaTiO₃ is a well-known ecological material, one of the lead-free materials with a perovskite structure that is widely used in the electronics industry [5,6]. BaTiO₃ pertains to compounds with the general formula ABO₃, where B ions take the place of A and Ti occupy the B places [5,6]. The doping of such ABO₃ ceramics has been studied for many years in order to improve its electrical and dielectric properties.

2. Influence of modifiers

In recent years, particular attention has been paid to the production of high dielectric permittivity (ϵ_r) ceramic materials (ferroelectrics) by doping of BaTiO₃ with ions of various metals in order to apply them as supercapacitors. A significant feature of high dielectric permittivity is also the Curie temperature (T_c) which pertains to the phase transition from ferroelectric to paraelectric state. The combination of high dielectric permittivity with the appropriate Curie temperature (close to room temperature if possible) is crucial for the application of ferroelectric materials to

various technological applications (including as supercapacitors). Therefore, this review pays particular attention to the two mentioned characteristics.

Very high dielectric permittivity is registered for BaTiO₃ doped with trivalent ions of rare earth elements, which induces a significantly increase in the dielectric permittivity [7,8], thus improving the performance of relevant energy storage devices. It has been found that the permittivity depends very strongly on the crystallites sizes and with size decreasing it initially enhances but then diminishes, i.e. a maximum is observed [9]. The permittivity of the rare earth element (RE) doped BaTiO₃ is also determined by the crystal lattice distortion and the presence of point defects in the newly formed perovskite structure. If the radius of the (RE) doping ion is smaller than that of Ba²⁺ and of Ti⁴⁺ the substitution is realized in A sites. This is observed at Nd³⁺, La³⁺, Sm³⁺ and the doping ions improve the dielectric properties of the ferroelectrics. At a larger (RE) radius than Ba²⁺ and Ti⁴⁺ the doping ions substitute in B sites. In the intermediate case, as in Y³⁺ and Er³⁺, both A and B are replaced at the same time. [10] In general, both the Ba and the oxygen-compensating vacancies are formed. [10] Characteristic of all ferroelectrics obtained by doping BaTiO₃ with rare earth elements (except Er) is that the temperature of the ferroelectric - paraelectric phase transition can be lowered to room temperature. [11]

Using the doping of BaTiO₃ with rare earth elements, a number of authors have prepared ferroelectrics with high ϵ_r values. The dielectric permittivity of ferroelectrics obtained by the addition of neodymium to barium titanate has been found to depend very strongly on the size of the crystallites, passing through the maximum. At room temperature (T_c) it reaches a surprisingly high value of $\epsilon_r = 550000$ [10]. The Sm doped BaTiO₃ exhibits dielectric permittivity 6400 at T_c 50°C [9]. A very high $\epsilon_r = 10130$ was registered at T_c equal to 22°C for Ce doped barium titanate. [12] Ferroelectric Ba_{0.95}La_{0.05}TiO_{3-x} with surprisingly high permittivity 800000 room (T_c) has been synthesized by adding La to BaTiO₃ [13] There is evidence in the literature for the preparation of Gd substituted BaTiO₃ by the hydrothermal method and subsequent heating in a nitrogen atmosphere. [14] The material exhibited a high relative dielectric constant of 20000 at room T_c.

High dielectric permittivity ceramic materials have been prepared by doping of BaTiO₃ with elements that do not belong to the rare earths. Thus a ferroelectric with ϵ_r 2500 at room T_c is synthesized by doping of barium titanate with Sr. [15] When Zr is added to BaTiO₃, the resulting BaZr_xTi_{1-x}O₃ ferroelectric exhibit a dielectric permittivity of 10586 at room Curie temperature [16] Another Zr substituted barium titanate with a formula Ba(Ti_{0.7}Zr_{0.3})O₃ has a dielectric permittivity of 5000 at room T_c [17]

The direct metal substitution in BaTiO₃ has been also applied in order to prepare ceramics with high dielectric permittivity. As a rule the synthesis proceeds in a reducing medium. Thus Fe-doped BaTiO₃ ferroelectric with a surprisingly high ϵ_r 66500 at room T_c was synthesized.[18] The codoping of BaTiO₃

with Sm and Mn was also successfully used to synthesize dielectric ceramics with ϵ_r 13,000 at Tc 20.4°C [19]

3. Preparation

A very effective approach for the synthesis of high dielectric permittivity is sol-gel technology. This method belongs to the methods of "soft" chemistry, i.e. the preparation of the materials is carried out at relatively low temperatures and atmospheric pressure, without the need for expensive apparatus (peculiar to the physical methods). Other positive features of this technology are (i) possibility for the production of a very large number of materials and compounds and with complex structure and phase composition (including hybrids, composites); (ii) effective stoichiometry control of the materials obtained, as well as the use of both inorganic and organic precursors [11]. The synthesized samples are distinguished by their homogeneity. The use of sol-gel technology allows the synthesis of high ϵ_r ferroelectrics at significantly lower temperatures than the most commonly used solid phase synthesis. This results in materials with much smaller grain sizes, high homogeneity, and to preparation of high relative dielectric permittivity ceramics at low Curie temperatures and proves to be very effective for the preparation of various ferroelectric materials suitable for high-capacity devices. The sol gel technology was successfully applied to obtain Ce doped BaTiO₃ [12], Sr doped BaTiO₃, [15]

Suitable for the synthesis of ferroelectrics, with surprisingly impressive dielectric permeability is the sol-hydrothermal method applied by Sun et al [13]. It can be considered as a variant of sol-gel technology. The method allows the synthesis of a pure phase composed of nanoparticles with a narrow size distribution, which proves to be extremely favorable for the production of ceramic materials with high dielectric permittivity.

The most commonly applied method for preparation of ferroelectrics with high dielectric permittivity is conventional solid-phase synthesis. Thus, BaTiO₃ is doped with Zr,[16,17] Gd, Y, Yb,[14] Nd,[20,21] Sm and Mn [18] etc. The preparation by solid state reactions requires as a rule higher temperatures in order to obtain doped BaTiO₃ than sol-gel technology.

Recently, the production of dielectric ceramics with high ϵ_r by direct doping of BaTiO₃ with metal has also aroused interest. Fe-doped barium titanate was thus synthesized [19]. The drawback of the method is the compulsory use of a reducing atmosphere.

The synthesis of high dielectric permittivity such as La doped BaTiO₃ [13] has also been accomplished through some physical methods such as spark plasma. Physical methods, however, require expensive and complex apparatus as opposed to the sol-gel method.

4. Conclusions

The dielectric ceramics prepared by rare-earth element(s) doped BaTiO₃ (RE: BaTiO₃) has been considered as one of the most suitable materials for ferroelectric capacitors, because of its high ϵ_r . This high dielectric permittivity of RE: BaTiO₃ is intimately related to the structural distortion and chemical defects surrounding the dopants. The sol-gel method is considered to be very suitable for preparation of high permittivity ferroelectrics due to its advantages: (i) to obtain homogeneous ceramic materials, (ii) the low temperature of synthesis and sintering, (iii) to synthesize materials and compounds with complex structure and phase composition and small grain sizes.

Acknowledgements

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Electrodeposition of copper on cold rolled copper substrate

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Abstract: The microscopic and macroscopic views of copper electrodeposits obtained on plastically deformed copper substrates of different deformation degrees have been investigated. Experiments have been performed under galvanostatic conditions. There appear, depending upon the degree of reduction realized during substrate rolling, three types of deposit: epitaxial, homogenous and texture. Epitaxial growth is observed on unreformed substrate and on the substrates with lesser deformation degree (up to 60 %). With the increase of the substrate reduction degree, heterogeneous type of the deposit appeared and the phenomenon of twinning was stated. On very much deformed substrates, as well as in presence of organic additives, field oriented texture type of the deposit is obtained. On very deformed substrates macroscopic uneven deposits appeared, with the linear structure which follows the direction of substrate rolling. Possible explanations of this phenomenon are given.

KEYWORDS: ELECTROLYSIS, MODELING, DEFORMED COPPER SUBSTRATE, COPPER ELECTRODEPOSITS, DEFORMATION DEGREE, UNDEFORMED AND DEFORMED SUBSTRATE, MICROSTRUCTURE, COLD ROLLING

1. Introduction

The form and structure of metal deposits, which were obtained during electrodeposition, depends, first of all, on overpotential of deposition and desorption of ions and molecules from the solution [1]. According to Fischer [2], there are following types of polycrystalline electrodeposits:

- field orientated isolated crystals type, basis-oriented reproduction type, twinning intermediate type, field oriented texture type, unorientated dispersion type;

This points to a fact that structure of the substrate on which electrodeposition takes place, can also influence the structure of the deposit. In practice, the cases show the tendency that crystallization in the first layer of metal deposit on electrode of the same metal, takes place in the same way in which crystal surfaces of the substrate are oriented (epitaxial growth). This phenomenon also appears during deposition on the substrates made of other metals if crystal lattice parameters don't differ more than 15%. With the increase of deposit thickness there happens discontinuance of the epitaxial growth. Twinned crystals, and, in some cases, texture appears. Pangarov [1] explains these phenomena by the introduction of the principle of minimal energy.

Examining layers of electrolytic alloys obtained on single-crystal substrates, Lagiewka [3] identified three zones, in which the crystallites counting upwards from the substrate, take epitaxial, twin and random orientations. He developed X-ray method for direct determination of the ratio of the epitaxial zone in electrolytic Cu-Cd alloys layers. Epitaxial zone thickness decreases with the increase of the negative potential. Setty and Wilman [4], as well as Bebczuk de Cuzminsky [5, 6] have examined electrodeposition of copper on single-crystal copper substrate under galvanostatic conditions. They have come to a fact that for the stated current density, they get thicker epitaxial layers on the (111) substrates, compared with these on a (110) substrate. The preferred orientation during the thin-film growth appear to be due to low interfacial energies. This has been explained by the influence of the surface density of atoms on those surfaces and the corresponding value of free energy.

Shirokoff and Erb [7] studied the epitaxial silver on silicon single-crystals and concluded that obtained preferred orientations are believed to be due to low interfacial energies. Also, the researches on single crystals [8, 9] have been taken into consideration, as well as the investigation by Maizelis et al. [10].

Cisewski and Allan [11] have done a considerable review of literature dealing with the examination of epitaxial growth of metals on metal substrates by research using field electron emission microscopy. It is especially striking that many cases of metal/metal epitaxy, the dominant factor determining the epitaxial relationship is the alignment of close-packed atomic rows in low-index crystallographic planes of each metal.

In regard to the fact that energetic condition of metal surface is changed during plastic deformation and that crystal lattice deforms also, there has been put an assignment to discover the

influence of the deformation degree of polycrystalline copper substrate on the structure of copper electrodeposit at different current densities both in and without the presence of the neutral organic compounds. Experience about deformed copper base and electrodeposition of copper on copper substrate was basis for our goal here, which was to achieve starting wire dies profile, using reverse drawing process modeling in electrolyte bath with gradual rounding of profiles [12, 13].

2. Experimental technique

The substrate, on which the electrodeposits of copper has been deposited, was a wire made of OFHC (oxygen free high conductivity) copper obtained by dip-forming method which had the initial diameter 15.8 mm. This wire was then rolled on rolling mill as described before [14], stating the realized deformation by the total relative reduction ε being 98.7%. In the table 1 the plan of passes has been shown, which has corresponding relative reduction and obtained hardness of samples in the middle and on the edge. Measuring the hardness, the indenting force of 5 daN has been used. Out of these samples, three groups have been formed:

- on samples 0, 3, 7, 10 and 16 electrodeposition of copper has been carried out from synthetic electrolyte which contained 39 g/L Cu^{2+} as CuSO_4 and 168.5 g/L H_2SO_4 without the addition of organic additives,

- on samples 0, 2, 5, 8, 11 and 14 electrodeposition of copper has been carried out from the electrolyte which is used in cells for obtaining the starting cathode sheets In copper refinery. This electrolyte contains the same concentration of cupric ions and sulphuric acid as well as previous synthetic one, but there are thiourea and gelatin there also in ratio 1:1.

Table 1. Plan of passes with hardness measurements

No. passes	b (mm)	h (mm)	h/h ₀ %	Hardnes (HV)	
				middle	edge
0	Ø15.8	Ø15.8	0	/	/
1	16.9	11.68	26.7	99.7	105
2	16.96	9.82	37.85	110	112
3	17.15	8.7	44.9	110	106
4	17.08	8.03	49.2	103	112
5	17.3	7.23	54.2	122	122
6	17.1	6.5	58.8	123	121
7	17.46	5.8	63.3	114	120
8	17.62	5.03	68.2	115	122
9	17.95	4.25	73.1	126	120
10	18.3	3.5	77.85	122	123
11	18.62	2.8	82.3	127	124
12	19.07	2.1	86.7	135	129
13	19.9	1.35	91.45	134	136
14	20.5	0.72	95.4	127	128
15	21.12	0.33	97.9	126	130
16	21.77	0.2	98.7	132	129

- in the third series of experiments, the substrate was made of parts obtained by cutting a sample wire number 16 (with the

deformation degree being 98.7%). Electrodeposition has been carried out the same like the first series, using the synthetic electrolyte without the addition of the organic compounds, at various current densities.

Before the process of electrodeposition, the samples have been prepared in the following manner:

- on each sample, the constant surface of 2 cm^2 in the middle part has been defined, so that the influence of the effect of the uneven deformation on the sample width has been reduced, and the remnant has been protected by lacquer resistant to carbon-tetrachloride, diluted nitric acid 1:1 and distilled water.
- just before the experiment, the sample has been washed out by carbon-tetrachloride, diluted nitric acid 1:1 and distilled water,
- anodic polishing of the samples has been done by the 50mA current going on for 10 min,
- after anodic polishing, the electrodes were thoroughly washed out by distilled water and sunk in electrolyte, from which electrodeposition of copper has been done and the voltage has been switched on,
- anode is also made of OFHC copper.

After the completed process of electrolytic deposition, the samples were brought out under the voltage from the electrolyte, they were washed out by the distilled water and alcohol and dried in the air. Then, microscopic examination of the texture and metallographic examination of the deposit structure, were done.

Metallographic examination were done transversally to the direction of rolling. The samples were first dipped into polyacrilate mass and then ground on grinding paper, the fineness of which was 3 to 4/0 and polished by alumina. After polishing the structure was "developed" by ferric-chloride.

3. Experimental results

The first group of experiments has been carried out with the constant current density being 50 A/m^2 . As a substrate for electrodeposition the samples marked as 0, 3, 7, 10 and 16 have been used, to which relative reduction of 0%, 44.9%, 63.3%, 77.85% and 98.7% correspond, respectively. In figures 1 to 5 microstructure of the obtained electrodeposits being magnified 500 times, is shown.

In Figure 1 it is given the microphotography of the substrate made of undeformed wire and grains of the deposit which succeed the substrate growth. The deposit is distinctly massive-grained, so partly it has been separated from the substrate during metallographic preparation. Also on the substrate which had 44.9% deformation degree, massive-grained, clearly defined layer of the deposit has been obtained (Figure 2), which has a distinct epitaxial growth as well as on the undeformed substrate.

The grains of the substrate with the 63.3% deformation degree are elongated (Figure 3). The limits of deposits grains are determined by the elongated grains of the substrate, while the grain growth of the deposit is defined by the direction of the electric field.

In Figure 4 the deformed substrate, $\epsilon=77.85\%$, has very elongated grains and transitive type of deposit. Some substrate grains keep on epitaxial growth, while the growth of other grains is under the influence of the electric field direction. It is here that clear twinning of some crystals appears.



Fig. 1. Optical micrograph of copper deposit obtained from pure sulphate electrolyte on undeformed copper substrate, $j=5 \text{ mA/cm}^2$

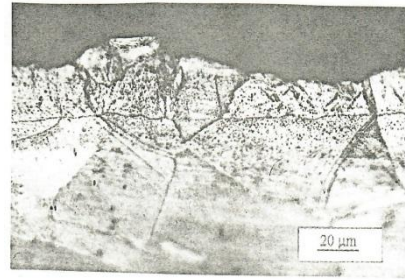


Fig. 2. Optical micrograph of copper deposit obtained from pure sulphate electrolyte on cold rolled copper substrate, $\epsilon=44.9\%$, $j=5 \text{ mA/cm}^2$

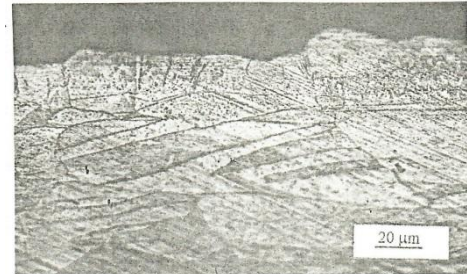


Fig. 3. Optical micrograph of copper deposit obtained from pure sulphate electrolyte on cold rolled copper substrate, $\epsilon=63.3\%$, $j=5 \text{ mA/cm}^2$

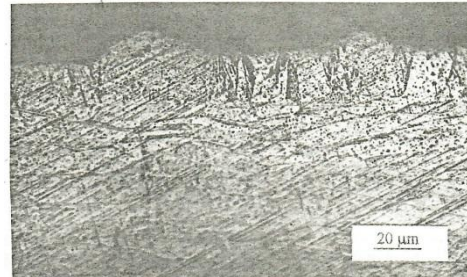


Fig. 4. Optical micrograph of copper deposit obtained from pure sulphate electrolyte on cold rolled copper substrate, $\epsilon=77.85\%$, $j=5 \text{ mA/cm}^2$

Figure 5 shows microstructure of copper electrodeposit obtained on the sample of wire number 16 with relative reduction of 98.7%. The grains of the substrate are so deformed that can be seen only as fibers. The deposit is clearly defined with periodical exchange of somewhat larger grains and grouped dendrites. The growth is totally defined by the direction of electric field. Macrostructure of this deposit in form of longitudinal rows with fine structure (Fig. 6), clearly marks the direction of sample rolling.

This series of experiments which were carried out by the use of synthetic electrolyte without the addition of the organic additives, has shown that epitaxial growth of electrodeposits is getting weaker with growth of the substrate deformation degree. With the considerable degrees of deformation, conditions are fulfilled for the appearance of crystal twinning, and microstructure is no longer homogenous, but linear with rows which follow the direction of rolling.

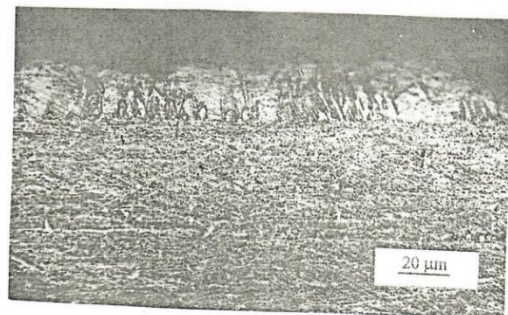


Fig. 5. Optical micrograph of copper deposit obtained from pure sulphate electrolyte on cold rolled copper substrate, $\epsilon=98.7\%$, $j=5 \text{ mA/cm}^2$

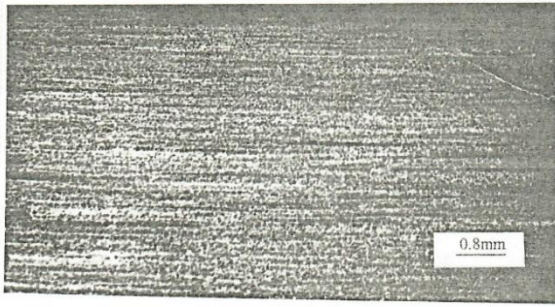


Fig. 6. Macrolook of the electrodeposit shown on Fig. 5.

On undeformed polycrystalline substrate, its influence on the orientation of the deposit is strongest and disappears last. The factors which can earlier end the substrate influence on the form of the deposit are the existence of more concentrated defects, adsorptions etc. With plastically deformed substrates there appears proportional growth of the number of defects, so that epitaxial growth is observed on the undeformed substrate and on the substrates with lesser deformation degree (up to about 60%) and when the number of defects per surface unit gets to a certain value, transitional (heterogeneous) type of crystal growth appears. On surfaces with the biggest deformation degree the quantity of defects is so big that epitaxial growth is completely omitted. However, macroscopic uneven deposit appears, with the linear structure which follows the direction of substrate rolling. Since it is known that plastic deformation always gets to the formation of relief (traces of gliding both on grain edges and inside the grains themselves), the possible explanation of this phenomenon is that defects (which represent the centers of nucleation) haven't been arranged evenly on the surface of the substrate, but they have been concentrated alongside certain lines parallel to the deformation direction.

The next possible cause is the fact that surfaces are different at certain grains on the surface of the sample. The grains are very much elongated by the plastic deformation, and the rate of the deposition growth is biggest on surfaces with the greatest Millers index values, so the deposit can look as in Fig. 6.

Also, the interesting phenomenon is the appearance of the twins in the deposits obtained on substrates with bigger relative reduction. The phenomenon of twinning in initial stadiums of electrocrystallization of copper on neutral substrates has been described in detail by Mamontov et al. [15, 16]. Sulphate electrolyte and current densities of 1 to 10 A/m² have been used. The deposit consisted of spheroids while their nucleus becomes first, an then in the next stage of growth the periphery of spheroids appears. The defects which result in twinning, appear together with the becoming of embryo.

The appearance of twins in electrodeposit is shown here, also happens at the very beginning of the process. Twin crystals become narrower with the growth (in the direction of electric field) and they end in the form of pyramids, so that they are present in the part of the deposit which is right next to the substrate, while, first of all, the conditions for total epitaxy must be eliminated. This was also noted in literature which treats electrodeposition on single-crystal substrates.

With spheroids, twins appeared on their periphery also. By this analogy, they could be expected in later layers of electrodeposit over epitaxial layer on less deformed substrates.

II group of experiments

In Figure 7 it is shown the microstructure of electrodeposit obtained on the substrate which had relative reduction of 54.2% by the use of electrolytes which contain the organic additives. This deposit looks typically like all electrodeposits obtained under the same condition on the substrates with relative reduction of 37.85 to 95.4%. Starting from the least deformed substrates already, what dominates is the growth of crystals in the direction of the electric field normally to the basic structure – the deposit shows the

characteristic texture, so that the typical example of field-oriented texture type of the deposit was obtained. Macrostructure of the deposit is smooth, which is, also, the result of the presence of gelatin and thiocarbamide in electrolyte. It was observed that the number of crystals are so much more tiny as the degree of substrate deformation is bigger.

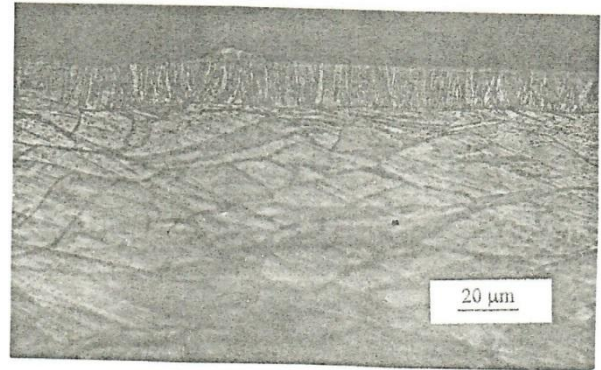


Fig. 7. Microstructure of copper deposit obtained from sulphate electrolyte containing thiourea and gelatin in ratio 1/1, on cold rolled copper substrate, $\epsilon=54.2\%$, $j=10 \text{ mA/cm}^2$

III group of experiments

The third group of experiments has been carried out on the substrate which had reduction degree of 98.7%. The same electrolyte has been used as in the first group (so, there were no organic additives). The current density varied from 5 to 25 mA/cm². The experiment with 5 mA/cm² belongs to the first series also, and is shown in Fig. 5. In all experiments of the third series, field oriented texture type of the deposit was obtained. The deposit is uneven. In Fig. 8 microstructure is shown, and in Fig. 8a macrolook of the deposit obtained by the current density of 10 mA/cm². In Figs. 9 and 9a, micro and macrostructure of the deposit obtained by the current density of 15 mA/cm² is shown. The deposit has more tiny, the orientation of the grain growth in the direction of electric field is clearer. Somewhat bigger grains of rectangular form alternate with pillar-like crystals. Macrostructure has two layers visually. The layer next to very deformed substrate is defined longitudinally while that layer extends to the layer of considerably rougher grains in the form of notches, little stars and irregular circles. Deposits are grouped in the form of bands – thicker in the middle of the band than on the edge. Twins appear.

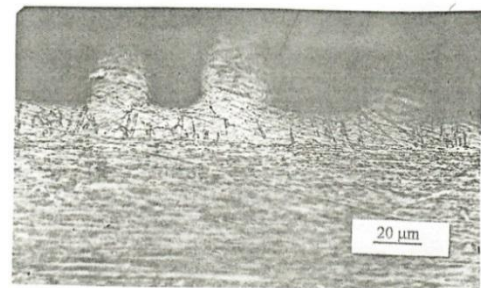


Fig. 8. Optical micrograph of copper deposit obtained from pure sulphate electrolyte on cold rolled copper substrate, $\epsilon=98.7\%$, $j=10 \text{ mA/cm}^2$



Fig. 8a. Macrolook of the electrodeposit shown on Fig. 8.

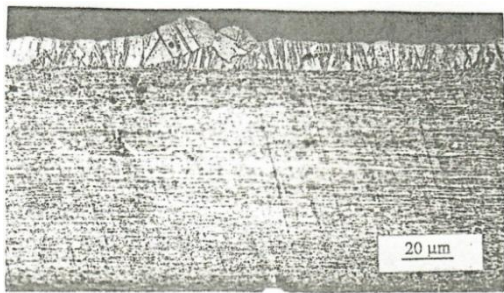


Fig. 9. Optical micrograph of copper deposit obtained from pure sulphate electrolyte on cold rolled copper substrate, $\varepsilon=98.7\%$, $j=15 \text{ mA/cm}^2$

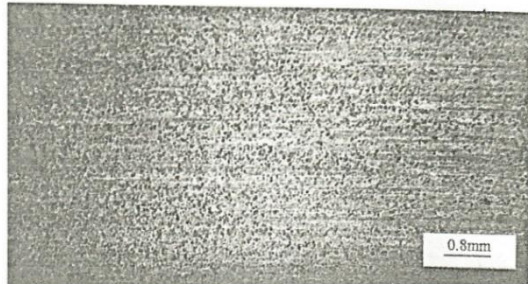


Fig. 9a. Macrolook of the electrodeposit shown on Fig. 9.

The structure of the deposit obtained with 20 and 25 mA/cm^2 is similar and has the form of pseudo-double layer. The growth of grains is determined by electric field.

4. Conclusion

During electrodeposition of copper from electrolytes which do not contain neutral organic additives on cold deformed copper substrate there appear, depending upon the degree of reduction realized during substrate rolling, three types of deposit: epitaxial, homogenous and texture.

Epitaxial growth is mostly noticeable on least deformed substrates. With the increase of the substrate reduction degree, there becomes heterogeneous type of the deposit, when it was stated a phenomenon of twining, which become narrower with the growth of the deposit. On very much deformed substrates texture type of the deposit appear.

Macrostructure of the deposit which is obtained on very deformed substrates ($\varepsilon=98.7\%$) is considerably linear and follows the direction of substrate rolling.

In the presence of organic additives, fields oriented texture type is obtained and tiny-grain structure of the electrodeposit, not depending on the degree of substrate deformation.

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Enhancement of corrosion resistance of steel, coated with various coatings on the base of SiO_2 , TiO_2 , ZrO_2 and CeO_2

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Abstract: Different corrosion-resistant coatings based on various SiO_2 , TiO_2 , ZrO_2 and CeO_2 oxides have been applied to various steels by the sol-gel method and spray pyrolysis. The obtained experimental coatings were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and weight loss measurements in 3.5% NaCl medium. $\text{TiO}_2/\text{SiO}_2$ and $\text{CeO}_2/\text{SiO}_2$ coatings treated at lower temperatures (500°C) have been shown to exhibit higher corrosion resistance than $\text{ZrO}_2/\text{SiO}_2$ samples. Increasing the treatment temperature decreases the protective properties of the investigated coatings. The enhanced protective properties of $\text{TiO}_2/\text{SiO}_2$ are probably due to their low crystallized fine grained structure and relatively dense surface without visible cracks.

Keywords: SOL-GEL SPRAY PYROLYSIS, CORROSION RESISTANT COATINGS

1. Introduction

The high hardness, corrosion stability, high temperature strength and oxidation resistance make stainless steel an ideal material, but unfortunately, in the presence of aggressive environments (for instance halide ions) proceeds excessive corrosion attack on the steels surfaces. [1] Corrosion of the marine equipments (i.e. crude oil tankers, oil platforms and gas extraction) is very serious problem, because in salt water, which is a conductor of electricity, the potential difference between adjacent metals cause electrons to flow from one metal to the other, causing galvanic corrosion. The eventual corrosion destruction of shipping facilities could lead to spills and other environmental disasters, damaging ecosystems and environmental pollution, which not only results in material losses, but it is dangerous for human life. Inorganic substances especially arsenic and chromium salts are often used to prevent steel corrosion, but they are highly toxic for human health and environment and have to be replaced. Many other strategies are applied - one of most effective is the deposition of non-toxic oxides coating as barrier layers, such as CeO_2 , ZrO_2 , TiO_2 , hybrid coatings etc. [2]. The effect of the change of various technological parameters such as the type of precursor, heat treatment, introduction of various dopants, etc. are investigated on the crystalline structure, the density and hydrophobicity of the coatings and hence their corrosion protective properties. Several types of mono component and bicomponent oxide coatings have been synthesized using the sol gel method. The aim of this study is to obtain corrosion resistant coatings of various inorganic oxides (pure and composite) TiO_2 , CeO_2 and ZrO_2 deposited on SiO_2 by sol gel method. The selected sol gel method have advantages such as low cost of equipment, the ability to apply larger size pads that give potential for industrial application[3].

2. Experimental

AISI 316 stainless steel, 7.5x 2.5 cm in size, was ultrasonically cleaned in ethanol and acetone as substrates. The SiO_2 layers were applied from a solution of tetraethoxysilane (TEOS) in a mixture of ethanol, water and hydrochloric acid as a catalyst and stirred for 2 hours to form a 0.5M solution. The molar ratio of H_2O : TEOS is 3.7. The solution is aged for 7 days to form bonds in them. The metal pads are immersed in the solution and drawn at a constant speed of 3 cm / min and then dried successively at 60°C and at 90°C and 300°C. These steps are repeated 2 times.

The coatings are characterized by a set of physicochemical methods such as X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectric spectroscopy (XPS), energy dispersive analysis (DDA) analysis, EDA), infrared spectroscopy (IR), and more.

Corrosion resistance was assessed by two techniques: weight analysis after residence in NaCl salt fog.

3. Results and Discussion

Multilayer coatings of $\text{ZrO}_2/\text{SiO}_2$, $\text{TiO}_2/\text{SiO}_2$ and $\text{CeO}_2/\text{SiO}_2$ incl.

3.1 Multilayer coatings of ZrO_2 deposited on SiO_2 support by sol-gel method with immersion technique.

3.2 Multilayer coatings of CeO_2 deposited on SiO_2 by sol-gel method with immersion technique.

3.3 Multilayer coatings of TiO_2 deposited on SiO_2 support by sol-gel method with immersion technique.

In connection with 3.1, three layers of ZrO_2 from the solution obtained as follows are applied to the specimens. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ dissolved in ethanol to 0.4M solution was used as a precursor. 0.016 mol of acetylacetone is added as a complexing agent of droplets and a few drops of nitric acid to prevent hydrolysis. Substitutes of silica deposited are immersed in the solution and drawn at a constant speed of 3 cm/min and then dried successively at 300°C for 80 min. at a heating rate of 3°C/min for some of the specimens, while for others the above technology is repeated as the final heat treatment is carried out at 700°C for 1 hour in air.

Initially, 2 layers of silicon dioxide were applied in accordance with 3.2 using the above-described technology, after which 3 layers of CeO_2 were applied. $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ dissolved in isopropanol to 0.4M solution was used as a precursor. Substitutes of silica deposited were immersed in the solution and withdrawn at a constant speed of 3 cm / min and then sequentially dried at 300°C for 80 min. These steps were repeated 3 times, finally finishing at 500°C for 1 hour in air at a heating rate of 3°C/min.

The initial 2 layers of silica were applied in accordance with 3.3 according to the above technology, after which 3 layers of TiO_2 were applied and titanium isopropoxide (TTIP) was used as a precursor; $\text{Ti}(\text{OC}_3\text{H}_7)_4$ (98% purity) which was dissolved in a mixture of ethanol (EtOH) and butanol (ButOH). The reaction of complex formation is exothermic. After vigorous stirring at room temperature, a mixed solution of distilled water and ethanol was added drop wise to the above solution with stirring. Hydrochloric acid is added drop wise as a catalyst. The molar ratio of the components is TTIP: EtOH: ButOH: H_2O : HCl = 1: 19: 1: 1: 0.03. The silicon-coated substrates were immersed in the solution and drawn at a constant speed of 3 cm / min and then dried successively at 300°C for 80 min. These steps were repeated 3 times, finally finishing at 500°C for 1 hour air with a heating rate of 3°C / min, while in others the above technology is repeated, with the final heat treatment being carried out at 700°C for 1 hour of air.

The XRD of samples slightly crystallized the anatase TiO_2 phase. A similar result was reported by Cheng and co-authors for sol-gel layers of titanium dioxide doped with SiO_2 . They demonstrate that the anatase phase peaks attenuate with increasing silicon dioxide concentration, as for the doped with 0% SiO_2 the titanium dioxide layer is amorphous [4] Another group of researchers also showed that the introduction of SiO_2 into TiO_2

nanoparticles slows the crystallization of the anatase phase. Figures 1 and 2 show the results of the XRD performed on the obtained experimental coatings.

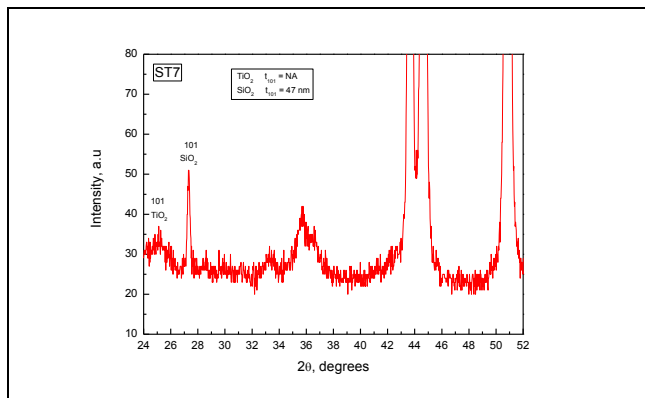


Fig. 1. XRD of the TiO_2 deposited on SiO_2 coatings

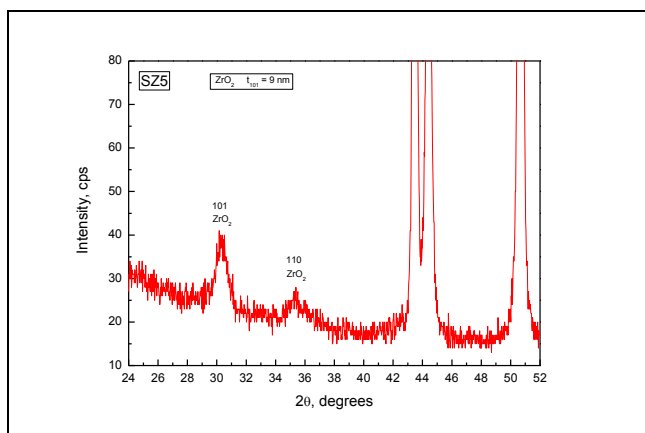


Fig. 2. XRD of the ZrO_2 deposited on SiO_2 coatings.

Legend:

SC5 - CeO_2 on SiO_2 , treated at 500°C
 SC7 - CeO_2 on SiO_2 , treated at 700°C
 ST5 - TiO_2 on SiO_2 , treated at 500°C
 ST7 - TiO_2 on SiO_2 , treated at 700°C
 SZ5 - ZrO_2 on SiO_2 , treated at 500°C
 SZ7 - ZrO_2 on SiO_2 , treated at 700°C

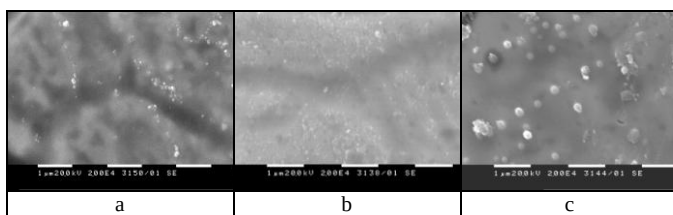


Fig 3. Morphology of coatings – SZ5 (a), SC5(b) and ST5(c).

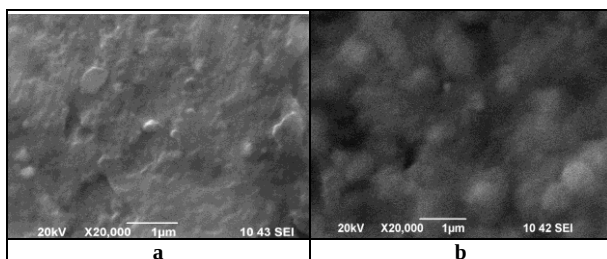


Fig 4. Morphology of coatings – SC5 (a) and ST5(b) after corrosion test.

Figures 3 and 4 show the morphology of coatings. The multilayer coatings of $\text{CeO}_2/\text{SiO}_2$ after corrosion attack have a preserved surface, without craters and cracks, which proves their high corrosion stability (Fig. 4 a). In contrast, the surface of $\text{ZrO}_2/\text{SiO}_2$ coatings is much more rough with many craters and pits, and these corrosion effects are exacerbated by samples treated at higher temperature (SZ7) (not shown). $\text{TiO}_2/\text{SiO}_2$ coatings after the corrosion test slightly increase their roughness but retain their characteristic grain structure, without exhibiting corrosion effects such as cracks, pores and other defects (Fig. 4b).

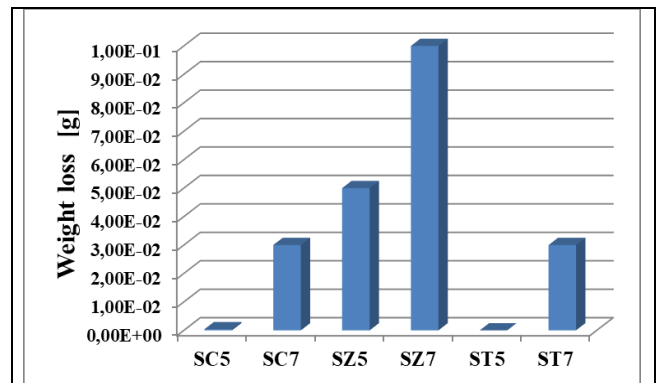


Fig. 5. Weight loss of $\text{SiO}_2/\text{CeO}_2$, $\text{SiO}_2/\text{ZrO}_2$, and $\text{SiO}_2/\text{TiO}_2$ multilayer coatings after corrosion attack..

$\text{TiO}_2/\text{SiO}_2$ and $\text{CeO}_2/\text{SiO}_2$ coatings treated at a lower temperature exhibit higher corrosion resistance than $\text{ZrO}_2/\text{SiO}_2$ samples (Fig.5), as evidenced by the weight loss test in NaCl medium and the studies of morphology. Increasing the processing temperature impairs the protective properties of the two types of coatings. The better protective properties of $\text{TiO}_2/\text{SiO}_2$ heated at 500°C may be due to their very weak crystalline structure and relatively dense surface. In contrast, the other 2 types of coatings exhibit weaker barrier properties, which is probably due to the increased crystallization and the type of surface morphology.

The new $\text{TiO}_2/\text{SiO}_2$ multilayer structures obtained are promising with a view to increasing the corrosion resistance of the steel.

4. Conclusions

It was proved that $\text{TiO}_2/\text{SiO}_2$ and $\text{CeO}_2/\text{SiO}_2$ coatings treated at a lower temperature exhibit higher corrosion resistance than $\text{ZrO}_2/\text{SiO}_2$ samples, as evidenced by the NaCl medium weight loss test and morphology studies. It has been found that decreased treatment temperature (up to 500°C) enhances the protective properties of the two types of coatings. The better protective properties of $\text{TiO}_2/\text{SiO}_2$ treated at 500°C are due to their lower degree of crystallinity and relatively dense surface. In contrast, the other two types of coatings exhibit slightly lower barrier properties.

The new $\text{TiO}_2/\text{SiO}_2$ multilayer structures obtained are promising approach for increasing the corrosion resistance of the steel.

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Effect of silicon content on the resistance of ductile iron to high-temperature oxidation

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Abstract: This paper analyses the oxidation resistance of ductile irons containing 2.11, 3, 4.28, 4.49 and 4.81 wt.% Si that were held at 850 °C for 32 hours. A scale was formed on all the samples and their weight increased. The scale thickness and increase in weight were decreased with increase of the silicon content, especially when the silicon content > 4 wt.%. The compactness of the scale on the sample surface is significantly higher at higher silicon contents. The results obtained indicate that the resistance of ductile iron to high-temperature oxidation increases with increasing silicon content.

Keywords: DUCTILE IRON, SILICON, HIGH-TEMPERATURE OXIDATION

1. Introduction

Ductile iron is a kind of cast iron containing graphite particles in a microstructure [1 – 3]. Since the graphite particles have a spherical shape, ductile iron has significantly different properties than gray and compacted graphite iron. Through variations in chemical composition and microstructure, different properties can be achieved. Because of this, ductile iron castings are widely used, even at low and high temperatures. Certainly the most famous high-temperature applications are exhaust manifolds and turbocharger housings of the internal combustion engines.

Long exposure of iron to air at high temperatures results in oxidation [4 – 11]. Because of that, a scale (oxide layer) is formed on the surface consisting of three oxides: the outer layer is Fe₂O₃, the middle layer is Fe₃O₄, and the inner layer (layer to base material) is FeO. The rate of oxidation, i.e. penetration into the material, depends on the diffusion of oxygen through the oxide layer. An oxide layer which is compact and tightly connected to the base material acts as a protective barrier, resulting in a decrease in the rate of oxidation. On the other hand, an oxide layer that is porous and contains cracks and is not firmly bonded to the base material will not act as a barrier to oxygen diffusion. As a result, oxidation continues and the thickness of the oxide layer increases, which becomes prone to cracking and to spallation.

The resistance of graphitic cast irons to high-temperature oxidation also depends on the shape of the graphite particles. Oxidation mainly progresses along the graphite phase. Therefore, the oxidation rate in the ductile iron is lower than in the gray and compacted graphite iron [12].

Silicon is the most significant and economically most suitable element to improve the resistance of cast iron to high-temperature oxidation. When the silicon content is > 4 wt.%, β -SiO₂ barrier layer is formed at the oxide/base material interface [12]. SiO₂ is significantly more compact than Fe-oxides. Therefore, the transport of oxidizing substances to the interior of the material is reduced, which ultimately results in a decrease in the rate of oxidation. The scale (oxide layer), observed from the surface towards the interior of the silicon alloyed ductile iron, consists of Fe₂O₃, Fe₃O₄, FeO + Fe₂SiO₄ and finally β -SiO₂ separating the oxide layer from the base material [13].

This paper analyses the influence of silicon content on the resistance of the ductile iron to oxidation at 850 °C.

2. Experimental

The five ductile iron (DI) melts was made with the following targeted silicon content: 2.1 wt.%, 3 wt.%, 4.2 wt.%, 4.5 wt.% and 4.8 wt.%. A 25 mm thick Y-shaped sample (type II according to EN 1563:2012) was cast from each melt. The moulds are made by sodium silicate/CO₂ process. High-temperature oxidation resistance test specimens were cut from Y-shaped samples and then placed in porcelain bowls that were annealed to constant mass at 850 °C. The heating of the samples was carried out in a furnace in an oxidizing atmosphere. Samples were held for 32 hours at 850 °C. Weighing the samples together with porcelain bowls was carried out on a digital scale before and after heating in the furnace. Scale (oxide

layer) on the surface of the samples after heating was analysed using light metallographic microscope with a digital camera.

3. Results and discussion

The chemical composition of the analysed ductile irons is shown in Table 1. The scale on the surface of the samples is shown in Figures 1 and 2. The effect of silicon on the change in samples weight and scale thickness is shown in Figures 3 and 4.

Table 1: Chemical composition of ductile irons.

	Element content, wt.%				
	DI 1	DI 2	DI 3	DI 4	DI 5
C	3.61	3.56	3.32	3.15	3.05
Si	2.11	3	4.28	4.49	4.81
Mn	0.1	0.14	0.11	0.11	0.11
P	0.034	0.028	0.032	0.03	0.029
S	0.013	0.011	0.012	0.012	0.009
Mg	0.052	0.048	0.066	0.065	0.045
Cu	0.019	0.015	0.02	0.02	0.02
Cr	0.032	0.038	0.04	0.04	0.04
Mo	0.002	0.009	0.63	0.63	0.61
Ni	0.014	0.019	0.02	0.01	0.02
Nb	0.003	0.001	0.002	0.001	0.002
V	0.01	0.007	0.009	0.009	0.009
Sn	0.0044	0.0052	0.007	0.006	0.007
Al	0.011	0.008	0.009	0.009	0.012
Ti	0.016	0.009	0.01	0.01	0.01

In Figure 1 it can be seen that all the samples oxidized during heating. However, it is clearly seen that the thickness of the scale (oxide layer) is greatest on DI 1 which has the lowest content of silicon (2.11 wt.% Si).

Figure 2 shows that the oxide layer on the surface of all the analysed ductile irons consists of two parts. The inner part of the oxide layer on DI 3, DI 4 and DI 5 is compact and tightly connected with the ductile iron, which hinders the penetration of oxygen into the material. With increasing silicon content in the DI 3, DI 4 and DI 5 the thickness of the inner part of the oxide layer increases. The outer part of the oxide layer is less compact, but does not separate from the inner part. The outer part of the oxide layer on DI 3, DI 4 and DI 5 is much more compact than the outer part of the oxide layer on DI 1 and DI 2.

The inner part of the oxide layer on DI 1 is not compact. It is significantly porous and not firmly bonded to ductile iron. The outer part of the oxide layer is also non-compact and separates from the inner part of the oxide layer. Such an oxide layer structure does not represent a significant barrier to oxygen penetration into the interior of the material. It is obvious that low-silicon ductile iron castings are not suitable for high-temperature applications.

DI 2 has higher silicon content than DI 1. For this reason, DI 2 has a different resistance to high-temperature oxidation. The inner part of the oxide layer on DI 2 is more compact than the inner part of the oxide layer on DI 1 and is more firmly connected with the ductile iron. However, its compactness and connection with ductile iron is lower than in DI 3, DI 4 and DI 5. According to the characteristics, the outer part of the oxide layer on DI 1 and DI 2 are similar. Taking all this into consideration, DI 2 has better resistance

to high-temperature oxidation than DI 1, but less than DI 3, DI 4 and DI 5.

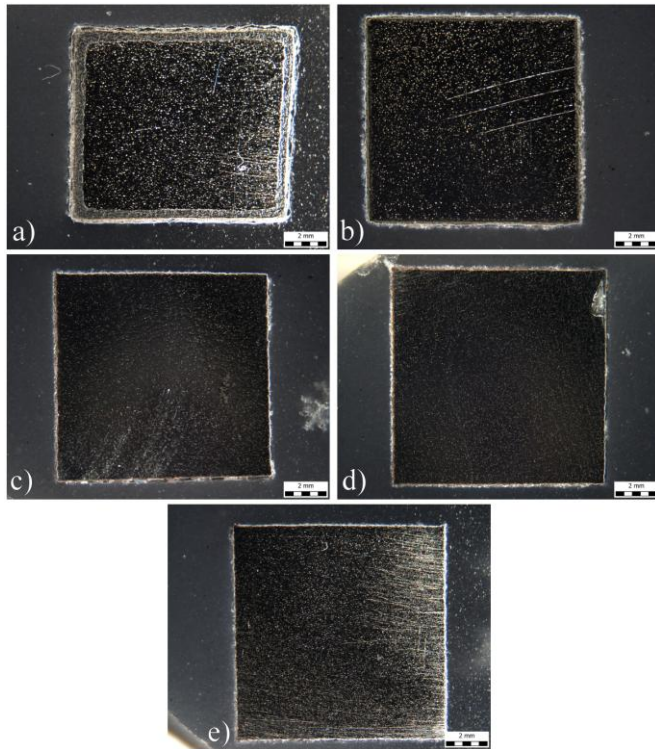


Fig. 1 Macrostructures of the samples after 32 hour of heating at 850 °C: a) DI 1 (2.11 wt.% Si), b) DI 2 (3 wt.% Si), c) DI 3 (4.28 wt.% Si), d) DI 4 (4.49 wt.% Si), e) DI 5 (4.81 wt.% Si).

The obtained results show that during heating the weight of all samples increased due to oxidation, i.e. formation of an oxide layer (scale) on the surface. However, it can be seen from Figure 3 that the increase in weight decreases with increasing silicon content. This shows that the resistance of ductile iron to high-temperature oxidation increases with increasing silicon content.

It can be seen from Figures 2 and 4 that the thickness of the scale is much smaller on ductile irons containing > 4 wt.% Si (DI 3, DI 4 and DI 5) than on DI 1 and DI 2 which have lower silicon contents. The thickness of the oxide layer is greatest on DI 1 which has the lowest silicon content (2.11 wt.%). The oxide layer is the thinnest on DI 5 which has the highest silicon content (4.81 wt.%). This shows that the thickness of the scale on the ductile iron decreases with increasing silicon content.

4. Conclusion

The results obtained show that the ductile iron oxidizes during prolonged exposure to high temperatures, resulting in an increase in its weight and the formation of a scale on the surface. However, with an increase in silicon content, especially > 4wt.%, the increase in weight and thickness of the scale are significantly reduced. In addition, the scale on the surface of high-silicon ductile irons is largely compact, which hinders the penetration of oxygen in the ductile iron and the progress of oxidation. It can be concluded that silicon greatly increases the resistance of ductile iron to high-temperature oxidation.

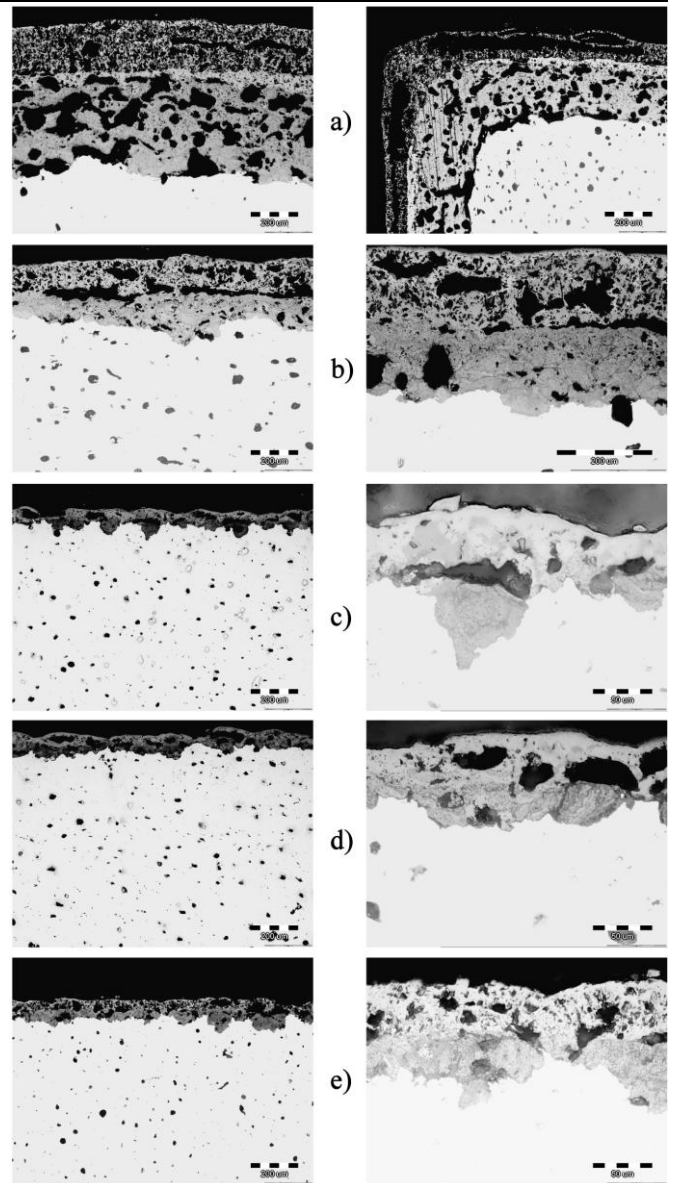


Fig. 2 Microstructures of the surface part of the samples after 32 hours of heating at 850 °C (non-etched): a) DI 1 (2.11 wt.% Si), b) DI 2 (3 wt.% Si), c) DI 3 (4.28 wt.% Si), d) DI 4 (4.49 wt.% Si), e) DI 5 (4.81 wt.% Si).

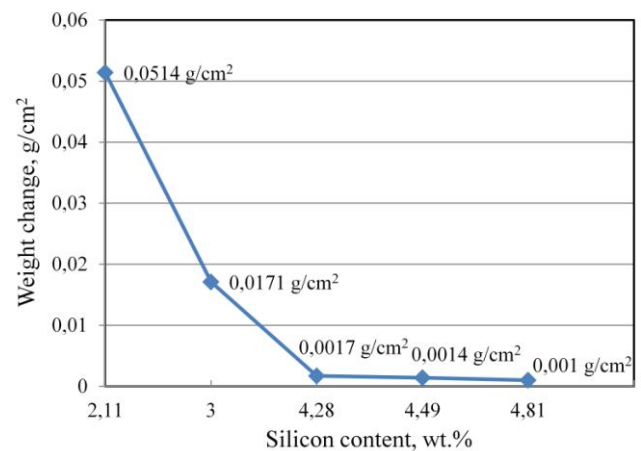


Fig. 3 Influence of silicon content in the analysed ductile irons on the change in weight of the samples after 32 hours of heating at 850 °C.

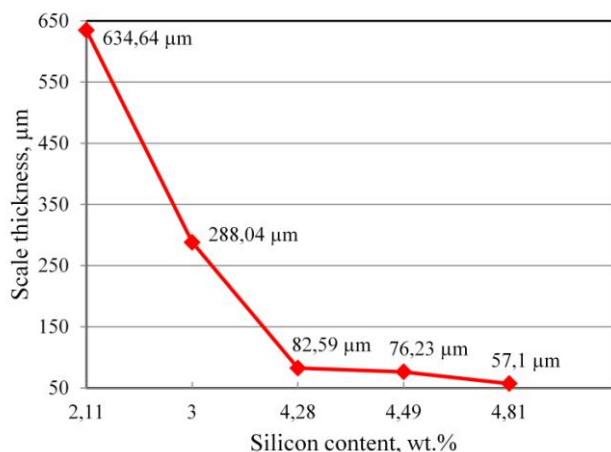


Fig. 4 Influence of silicon content in the analysed ductile irons on the scale thickness formed during 32 hours of heating at 850 °C.

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Conditions for obtaining and characteristics of lead-free passive elements for high energy impact

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Abstracts: Compression was carried out of modified copper powder workpieces at a pre-determined value of the pressure. High temperature sintering of the workpieces in a neutral medium at a temperature of 1,000°C was performed. A high density metal-ceramic composite material was obtained. Its structure and physico-chemical parameters were determined. Lead-free prototypes were created, corresponding to the weight and dimensions of the reference standard lead passive elements for high energy impact.

KEYWORDS: PRESSING, HIGH TEMPERATURE SINTERING, HIGH ENERGY IMPACT

1. INTRODUCTION

The use of lead in many products and devices such as piezoelectric elements, passive high energy impact elements and others poses certain risks to the human health and the environment. This calls for seeking alternatives and creating lead-free prototypes that perform the same functions. As of 1 June 2006, restrictions on the production and import of electronic components and other articles containing lead, as well as of equipment containing lead, have been introduced in the European Union. The requirements are set out in a series of EU documents (RoHS directives). In 2013, the Council of Ministers of the Republic of Bulgaria adopted a Decree on the conditions and procedure for equipment marketing in line with the restrictions on the use of certain hazardous substances (Decree of the Council of Ministers No 55/06.03.2013, published in the State Gazette No 24 of 12.03.2013).

According to the norms stated, as of 21.07.2016, no lead should be contained in ceramic, dielectric, metal-ceramic and composite materials which are part of integrated circuits, discrete semiconductors or high energy impact elements [1].

As is known, Directive 2017/2102 of the European Parliament and of the Council of 15.11.2017 amends Directive 2011/65/EU concerning the restriction of the use of certain hazardous substances.

Lead is prohibited in water pipes and as an additive in motor fuels and paints. It is also prohibited for use in hunting ammunition and as fishing tackle in most of Europe. The European Union with its Directive 2012/65/EU has also banned its use in balancing tires, as well as in electrical and electronic equipment.

Increasingly, regulatory burdens, processing costs and the costs of atmospheric discharges are also affecting the use of lead, including in the automotive, aerospace and nuclear energy industries and in consumer and sports goods, for medical purposes and more. [2, 3, 4, 5]

In the present study, experiments and studies have been carried out and a metal-ceramic composite has been created based on a modified copper powder, with a sediment composition of less than 100 microns, which complies with EC No 231-159-6. The chemical composition of the powder comprises the following chemical elements in weight %: Cu 99.5%; Ag 0.005%; Ag 0.005%; As 0.0002%; Fe 0.005%; Mn 0.002%; Pb 0.05%; Sb 0.005%; Sn 0.005%.

Workpieces were obtained whose density, hardness, microhardness, compressive strength and structure are equivalent to those of a standard lead sample. The new material from which the samples are made does not pose a toxic or environmental threat and can be successfully recycled after first use or at the end of the useful life of the product.

2. EXPERIMENTS

From the modified copper powder and using the powder metallurgy method, 10 pieces of sample bodies were compressed by bilateral pressing in a small matrix - Figure 1, [6].



Figure 1. Photo of the matrix for molding workpieces of passive elements

The measured density ρ of 6 sample bodies is shown in Table 1, and a plot of the change in their density as a function of the applied force P is shown in Figure 2. Using the $P - \rho$ curve of Figure 2, the optimal force $P = 8,000$ kg is determined, for which the density ρ corresponds to that of the reference lead samples.

Table 1. Density ρ of copper based sample bodies

No	P [ton]	d [mm]	H [mm]	V [cm ³]	G [g]	ρ [g/cm ³]
1	2	10	14.40	1.13	6.88	6.08
2	4	10	11.30	0.89	6.30	7.10
3	6	10	10.50	0.82	6.40	7.77
4	8	10	11.00	0.86	6.90	7.98
5	9	10	9.98	0.80	6.40	8.17
6	11	10	9.80	0.77	6.50	8.15

These experimental results were preliminary, as changes in the samples were expected to occur at their high temperature sintering at 1,000°C, with a retention time of $\tau = 60$ min. Indeed, the curve showing the dependence of the density after sintering ρ on the force P undergoes modification, as shown in Table 2 and Figure 3, and the compression pressure required for the final useful and correct density changes.

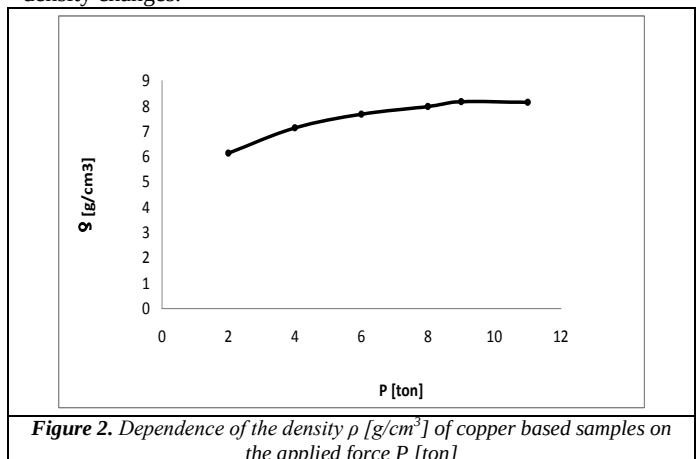


Figure 2. Dependence of the density ρ [g/cm³] of copper based samples on the applied force P [ton]

Figure 3 shows that a force of 5.5 tons must be applied to achieve a value of the density $\rho \approx 8 \text{ g/cm}^3$ after sintering.

Table 2. Density of copper based samples after heat treatment

No	P [ton]	d [mm]	H[mm]	V [cm ³]	G [g]	ρ [g/cm ³]
1	2	9.0	13.00	0.82	6.70	8.11
2	4	9.8	11.60	0.77	6.20	8.05
3	6	10.2	12.60	1.03	6.50	6.50
4	8	10.3	12.98	1.08	6.70	6.20
5	9	10.0	13.20	1.03	6.30	6.11
6	11	10.28	12.0	1.00	6.50	6.53

7	5.5	13.90	25.52	3.87	30.96	8.00
8	5.5	13.70	24.98	3.68	29.48	8.01
9	5.5	13.90	25.98	3.94	31.48	7.99
10	5.5	13.30	28.01	3.89	31.12	8.00

The prototypes were made using a cutting machine, a conventional lathe, a semi-automatic lathe CNC 500SAN-Lynx/220 LM, and a programmable automatic 5-axis CNC machining center Hurco VMX - 30U for the milling.



Figure 4. Photo of the obtained passive elements

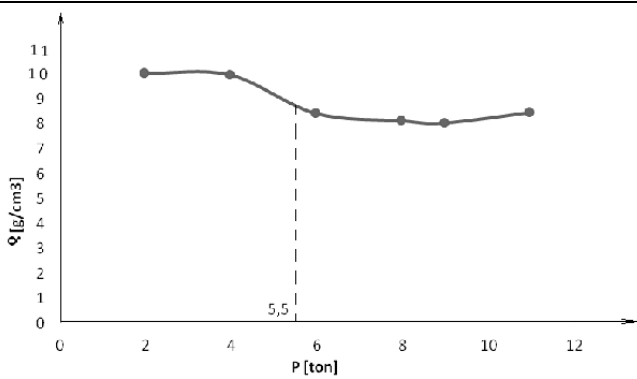


Figure 3. Dependence of the density ρ [g/cm³] of copper based samples on the applied force P [ton] after heat treatment

10 workpieces were molded in working matrices with diameters roughly between 14.73 mm and 14.80 mm under the above mentioned conditions: force of 5.5 ton, sintering temperature of 1,000°C and isothermal retention time of 60 min. The parameters of the workpieces after pressing are shown in Table 3, and the parameters after high-temperature sintering are shown in Table 4.

Table 3. Density of copper specimens pressed with force $P = 5.5 \text{ ton}$

No	P [ton]	d [mm]	H[mm]	V [cm ³]	G [g]	ρ [g/cm ³]
1	5.5	14.78	29.60	5.90	31.00	5.25
2	5.5	14.73	31.11	5.31	34.58	6.52
3	5.5	14.80	27.90	4.80	31.13	6.48
4	5.5	14.80	25.00	4.30	27.90	6.49
5	5.5	14.80	25.35	4.36	28.47	6.54
6	5.5	14.80	27.80	4.78	30.92	6.40
7	5.5	14.80	27.20	4.67	30.46	6.53
8	5.5	14.80	27.50	4.73	29.67	6.17
9	5.5	14.80	27.70	4.76	31.30	6.57
10	5.5	14.80	29.90	5.14	32.12	6.25

From the workpieces were produced 10 prototype samples of passive elements for high energy impact, equivalent not only in structure and physic-chemical properties, but also in size to the standard lead samples, as shown in Figure 4.

Table 4. Density of copper based specimens pressed with force $P = 5.5 \text{ ton}$, temperature $T = 1,000^\circ\text{C}$ and retention time $\tau = 60 \text{ min}$

№	P [ton]	d [mm]	H[mm]	V [cm ³]	G [g]	ρ [g/cm ³]
1	5.5	13.50	27.55	3.82	30.40	7.96
2	5.5	13.50	29.77	4.26	33.99	7.98
3	5.5	13.50	26.42	3.78	30.16	7.98
4	5.5	13.90	25.23	3.58	28.53	7.97
5	5.5	14.00	23.92	3.68	29.26	7.95
6	5.5	13.80	26.02	3.89	31.08	7.99

In Table 5 are shown the physico-mechanical parameters of the composite material from which the prototypes were made.

Table 5. Production parameters and physico-mechanical characteristics of a passive element for high energy impact

1	Force P , [kg]	5,500
2	Average density after pressing ρ , [g/cm ³]	5.25 – 6.57
3	Density after high temperature sintering ρ , [g/cm ³]	7.44 – 7.95
4	Compressive strength, [kg/cm ²]	4,800 – 5,480
5	Microhardness, [MPa]	925 - 517

It should be noted that the table shows the average microhardness obtained at five points for each sample.

3. ANALYSIS OF THE MICROSTRUCTURE OF A SAMPLE OF SINTERED COPPER POWDER

Of interest is the structure of the obtained metal-ceramic composite material – see Figures 5 - 8.

Subjected to metallographic analysis was a sample of sintered Cu powder with the following composition: Cu 99.5%; Ag 0.005%; As 0.0002%; Fe 0.005%; Mn 0.002%; Pb 0.05%; Sb 0.005%; Sn 0.005%. To prepare it for analysis of the microstructure, the specimen underwent the standard procedure - embedding in acrylic resin, grinding using glass-paper of grade up to 2,400, mechanical polishing with diamond paste and etching with a solution of 5 ml FeCl₃, 30 ml HCl and 100 ml H₂O.

The metallographic analysis was performed using a Reichert-Jung Polyvar Met optical microscope coupled to a ProgRes CT3 digital camera using ProgRes CapturePro image processing software.

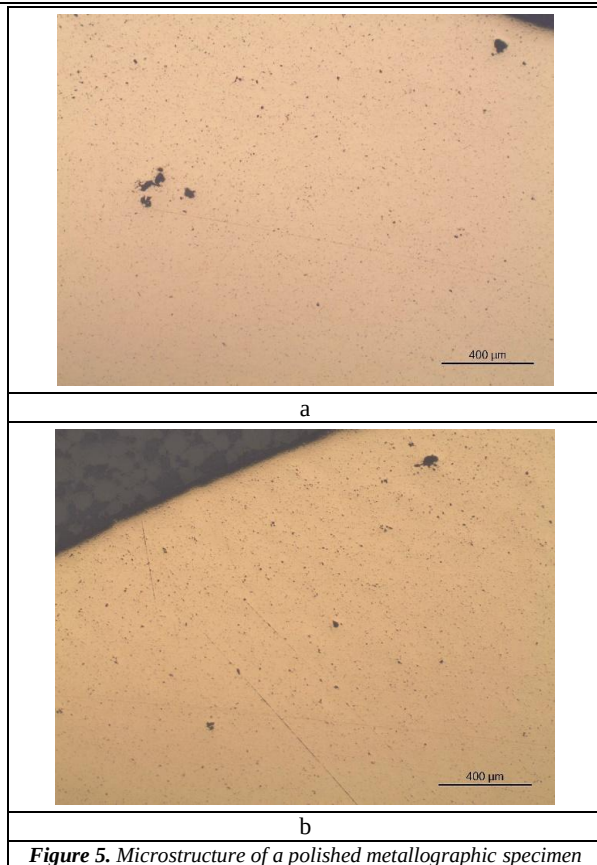


Figure 5. Microstructure of a polished metallographic specimen

The microhardness was measured using a MicroDuromat 4000 microhardness meter with a load of 20 gf, a loading time of 10 s and a retention time of 10 s.

Figure 5 shows the microstructure of a polished metallographic specimen. Imperfections in the microstructure are observed in the form of small air cell segments, most of which are located at the periphery of the specimen.

The measured microhardness HV0.02/10/10 of the samples varies from 94.3 kgf/mm² (925 MPa) at the periphery of the sample to 52.7 kgf/mm² (517 MPa) in its central part. Figure 6 shows the imprints from the measurement of the microhardness at the periphery (Figure 6a) and in the central part (Figure 6b) of the sample.

In a part along the periphery of the specimen (less than ¼ of its circumference), a dark coating layer is observed (Figure 7), with a maximum measured coating thickness of about 93 µm.

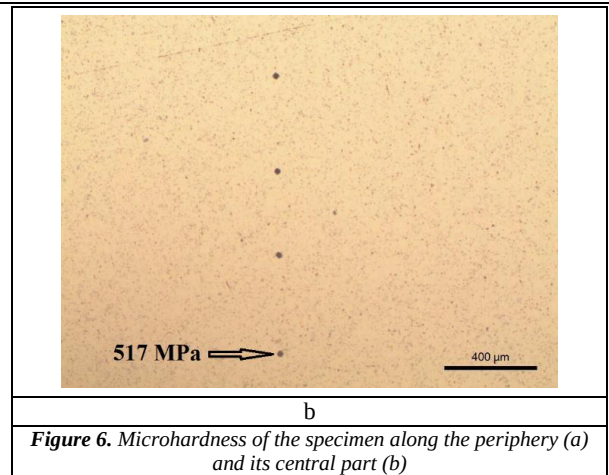
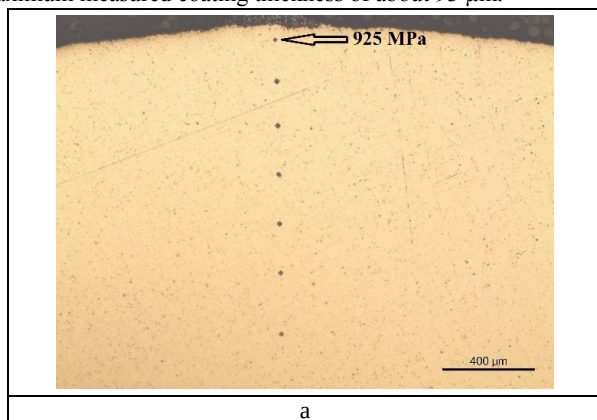


Figure 6. Microhardness of the specimen along the periphery (a) and its central part (b)

The measured microhardness of the coating (layer) is 199.5 kgf/mm² (1,956 MPa). In machining, this coating layer is removed and the real prototype is obtained only from the inner layer.

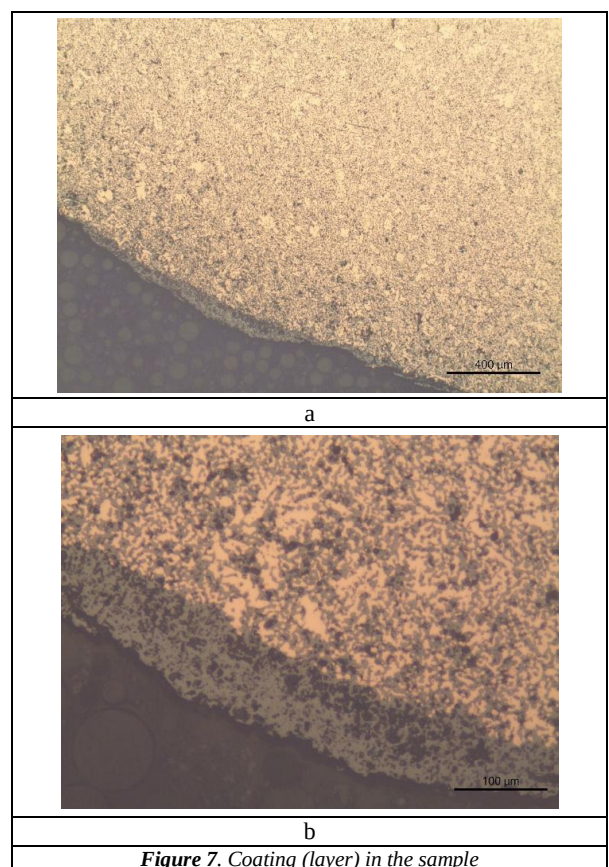
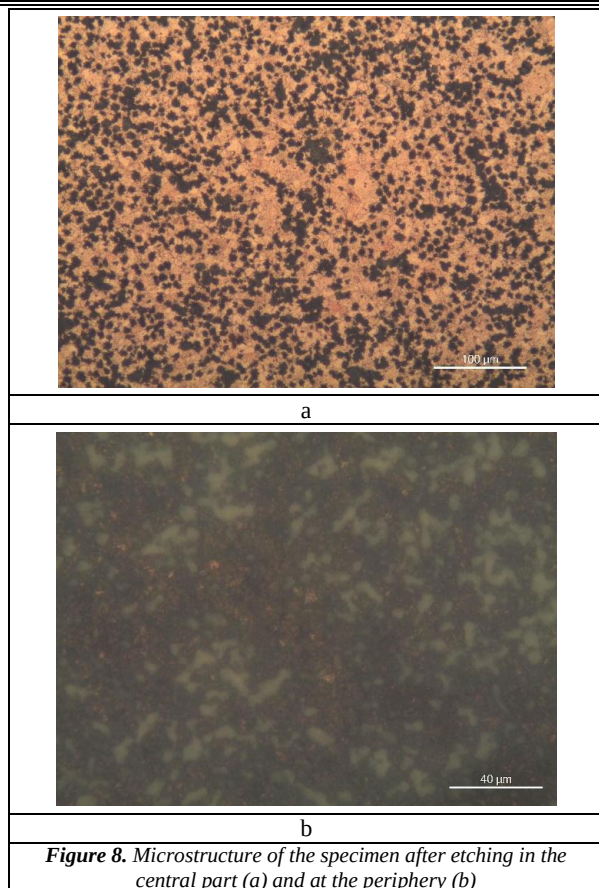


Figure 7. Coating (layer) in the sample

Figure 8 shows the microstructure of the sample after etching. A correlation was observed between the measured microhardness in the individual zones and the microstructure. It was observed that it is more pronounced along the periphery (Figure 8b) than in the central part (Figure 8a). Dark areas are observed, which are gray and more densely located along the periphery (Figure 8b) and black in the central part (Figure 8a), where Cu grains with twins can be noticed below the latter.



4. CONCLUSIONS

1. The ability to control the density of the obtained non-toxic composite metal ceramics in order to meet the customer's needs, thereby replacing the metal material – in this case toxic lead – is the most important attribute of the obtained material.
2. The ability to formulate and produce this composite material with acceptable physical properties at a sufficiently high relative weight is a challenge that has been overcome.
3. The high density $8 \text{ g/cm}^3 \pm 1\%$ composite metal-ceramic material is capable of providing optimum sample weight.
4. The new non-toxic, high density composite material is available to engineers and designers for use in applications requiring weight adjustment, balancing, damping, crushing or breaking in sport shooting.
5. The non-toxic material can replace lead and other traditional metallic materials in a more cost-effective way by offering improved physical properties and workability with conventional equipment.

5. REFERENCES

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First order phase transition in 3D printer – numerical experiments

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Abstract: A methodology for analyzing and evaluating macroscopic level of first-order phase transition in 3D printer technology is proposed. A classic Stefan-Schwarz task was used. A 3D mathematical model of the Stefan-Schwarz problem is made. The finite element method for numerical solution is applied.

A numerical experiment was evaluated. A geometric drop (flow) model in 3D printer technology is proposed. The idea of filling a "flow" drop by smaller droplets than a "flow" has been investigated numerically. The temperature field at filling in the flow as hereditary was investigated.

Keywords: PHASE TRANSITION OF EIRST ORDER, 3D PRINTER, STEFAN-SCHWARZ TASK, NUMERICAL EXPERIMENTS.

1. Introduction – macroscopic description of first order phase transition in 3D printer

First order phase transition $\text{LIQUID} \xrightarrow{\text{TRANSITION}} \text{SOLID}$ we describe only of macro-level in the frame of mathematical heat conductivity theory by Stefan-Schwarz task [4, 5] in Foundry is:

- Open thermodynamic system in foundry (OTSF):

$$V_{SYS} = (V_{CL} \cup S_{Font} \cup V_{CS}) \cup B_{WS} \cup (V_M \cup B_M), \text{ (OTSF)}$$

- Equation of the heat conductivity:

$$(c + S_F Q_m) \rho \frac{\partial T}{\partial t} = \lambda \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) \text{ in } V_{SYS}, \quad (1, 1)$$

- Stefan's boundary condition (S_F):

$$-\lambda_L \nabla T|_{L|S_F} = \rho_S R Q_m - \lambda_S \nabla T|_{S|S_F}, \quad (1, 2)$$

or

$$R = [\lambda_L \nabla T|_{L|S_F} - \lambda_S \nabla T|_{S|S_F}] / \rho_S Q_m, \quad (1, 2, 1)$$

- Boundary condition at the mold's work surface (B_{WS}):

$$-\lambda_C \nabla T|_{C|B_{WS}} = \alpha_{B_{WS}} (T_{C|B_{WS}} - T_{M|B_{WS}}) = -\lambda_M \nabla T|_{M|B_M}, \quad (1, 3)$$

- Boundary condition mold-environment (B_M):

$$-\lambda_M \nabla T|_{M|B_M} = \alpha_{B_M} (T_{M|B_M} - T_{En}), \quad (1, 4)$$

- Initial conditions at $t = 0$:

$$T_L(x, y, z, t) = \text{const}_L, T_M(x, y, z, t) = \text{const}_M, \quad (1, 5)$$

where T is the temperature with indexes for the cast (C) liquid (L) and solid (S) phases and mold (M); the thermophysical coefficients of the (OTSF) are: thermal conductivity (λ), thermal capacity (c), density (ρ); S_F is function of the heat source, Q_m is latent heat of the melting at the melting temperature T_m .

Methodology of the first order phase transition $\text{L} \xrightarrow{\text{transition}} \text{S}$ (see Fig.1): 1. Finite Elements Method (FEM); 2.1 Min volume: $1 \mu\text{m}^3$ or min Sum of $8 \mu\text{m}^3$ of (FE); 2.2 Max volumes: of the Cast is $64 \mu\text{m}^3$ and the Substrate (Mold) is $24 \mu\text{m}^3$. The first order phase transition is cold crystallization (or solidification) [1-3, 7 and 8] on the base of the velocity of moving and the geometry of the isothermal surface in the Stefan's boundary eq.(1, 2) or eq.(1, 2, 1). On the Fig. 1 we introduce geometry of (OTSF) for numerical investigation of the first order phase transition in the droplet of the 3D printer.

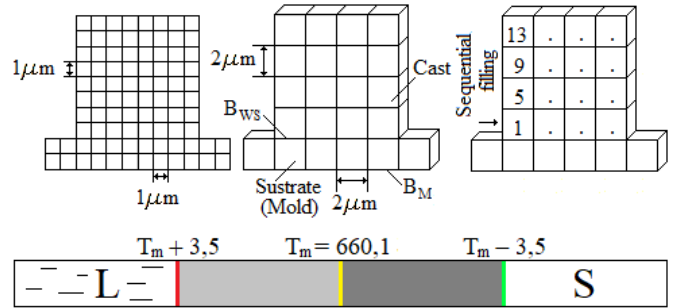
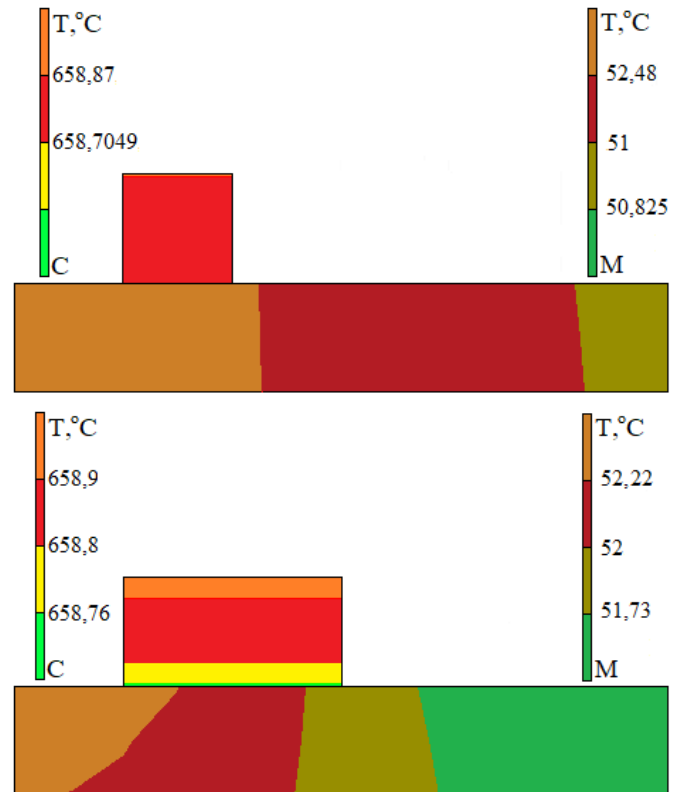


Fig. 1 Open thermodynamics system of foundry Cast and Mold (Substrate): the finite element grid is the cubes with a volume of $1 \mu\text{m}^3$; B_{WS} is the work surface contact Cast/(Substrate or Mold); B_M is the boundary surface mold/environment i.e. (OTS)/environment; Sequential filling by droplets with volume of $8 \mu\text{m}^3$; Temperature interval of first order phase transition is $[T_m \pm 3,5]^\circ \text{C}$, where $T_m = 660,1^\circ \text{C}$ is temperature of melt, between liquid phase (L) and solid phase (S).

An initial and roughly orientated numerical experiment is presented in Fig. 2 - non-stationary temperature field of a first-order phase transition when filling the "cast" through droplets of $8 \mu\text{m}^3$:



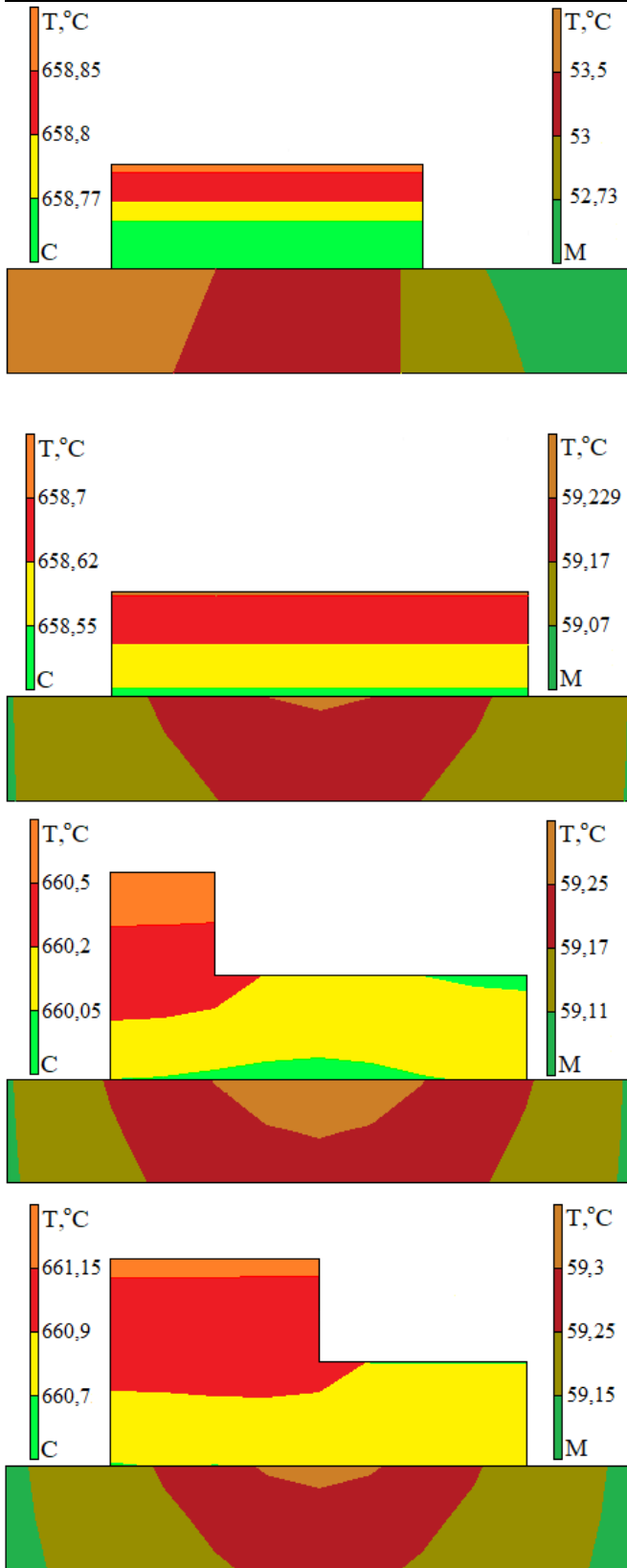


Fig. 2 Hereditary temperature field when filled in the "cast" with a slight change in the hereditary temperature field of the substrate.

The calculation data for the Stefan-Schwartz task (1) are: $T_L = \text{const}_L = 690,5^\circ \text{C}$; $T_M = \text{const}_M = 50^\circ \text{C}$; temperature of melting $T_m = 660,1^\circ \text{C}$ with interval of transition $\pm 3,5^\circ \text{C}$; $Q_m = 401819 \text{ J/kg}$; $\alpha_{BWS} = 56000 \text{ W/m}^2\text{Ks}$, $\alpha_{BM} = 56000 \text{ W/m}^2\text{Ks}$; cast: $\lambda_L = 104,675 \text{ W/mKs}$, $c_L = 1088,23 \text{ J/kgK}$, $\rho_L = 2380 \text{ kg/m}^3$, $\lambda_S = 209,275 \text{ W/m}^2\text{Ks}$, $c_S = 1130,085 \text{ J/kgK}$, $\rho_S = 2540 \text{ kg/m}^3$; $\lambda_M = 385 \text{ W/m}^2\text{Ks}$, $c_M = 1090 \text{ J/kgK}$, $\rho_M = 8930 \text{ kg/m}^3$. The aim of this work is to estimate the non-stationary temperature field of 1-st order phase transition upon filling by adding a $4 \mu\text{m}^3$ droplet.

2. Numerical Experiments

We assume that the continuously added material flowing from the 3D printer has some flow, which for us is already physically a droplet (Fig. 1 and Fig. 2). It is apparent from Figure 2 that the possibility of evaluating the thickness (volume) flow rate of the printer is considered one of the basics. It follows: what is the temperature of the "old" drop and the effect of the "fresh" drop, which creates the flow called by us the "big drop $64 \mu\text{m}^3$ " i.e. a major question about the "inherited temperature field" in the 3D printer and substrate flow rate.

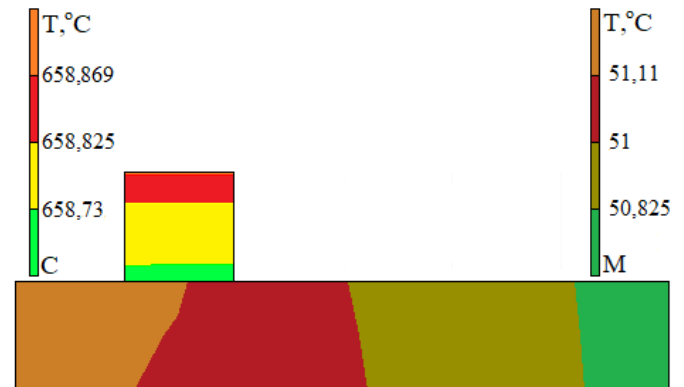
The residence time of the $8 \mu\text{m}^3$ droplet of Fig. 1 is up to ~ 3 (4) μs and the thermodynamic state of the former is determined!

The methodology and its geometric appearance is shown in FIG. 1: 1. The first row of drops that are in contact with the substrate (shape) is filled and the first row consists of drop 1 to drop 4; 2. The second row is filled from drop 5 to drop 8 and lies on the first row; 3. The third row is filled with drops from 9 to 12; 4. The fourth line consists of drops from 13 to the last 16 drops.

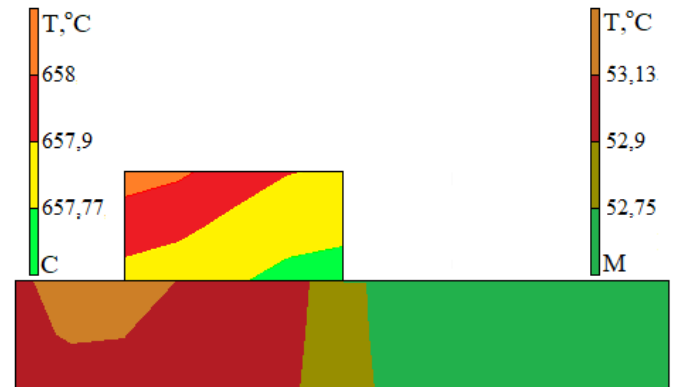
The state of the system changes with each fresh drop: The beginning of the process is the first drop with its initial temperature and substrate with its initial temperature. The system is cooled down to the next drop, etc. The temperature field of the system immediately before each drop is called a "hereditary temperature field".

Initial state of the system: the droplet temperature is 690°C and the substrate is 50°C . In Fig. 3 shows the hereditary temperature field as follows: The hereditary temperature field is represented by two scales, one for the cast, marked "C", the other for the substrate and marked "M"

1-st "hereditary temperature field"

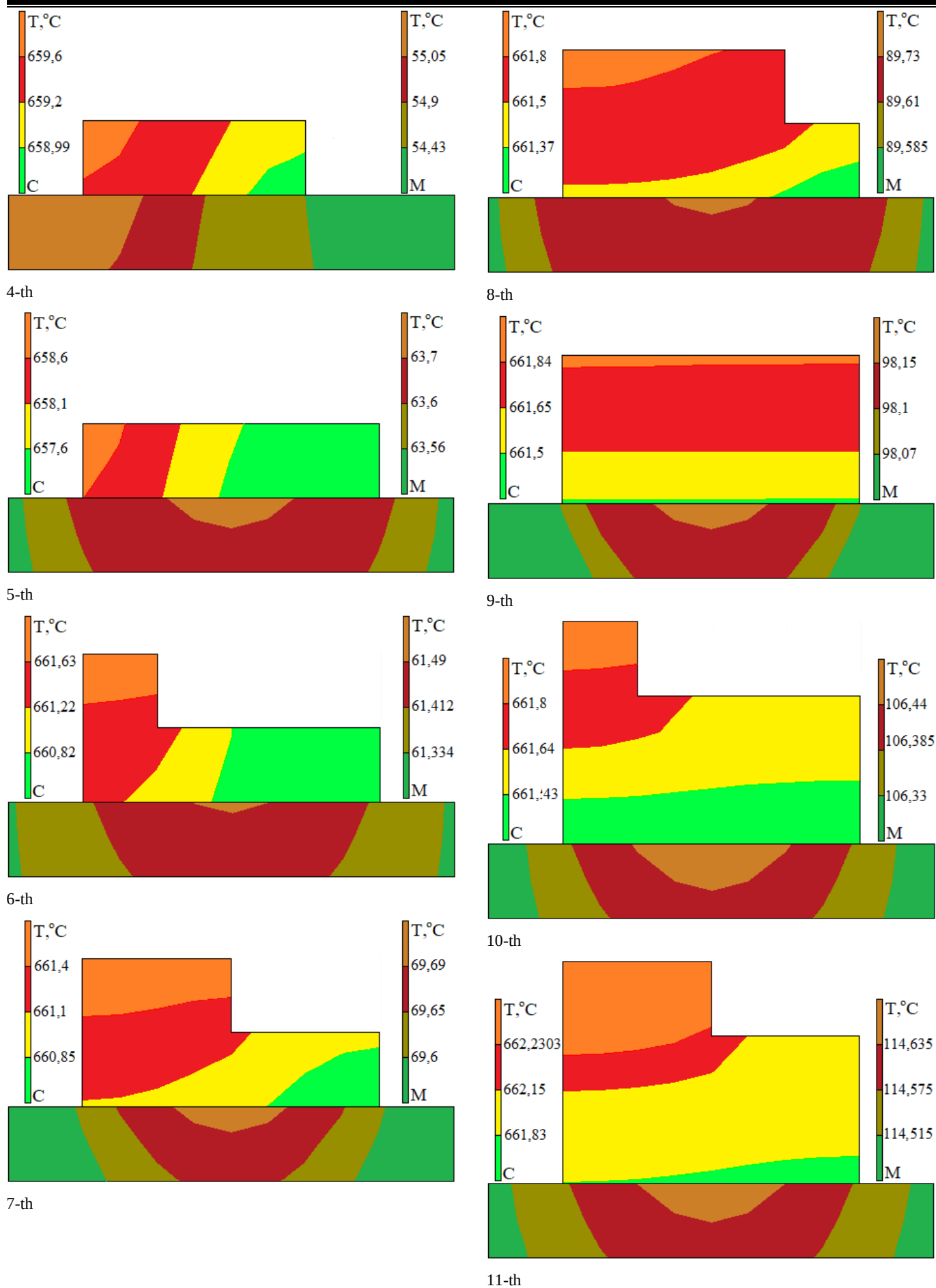


2-nd "hereditary temperature field"



reduction of the melt temperature

3-rd



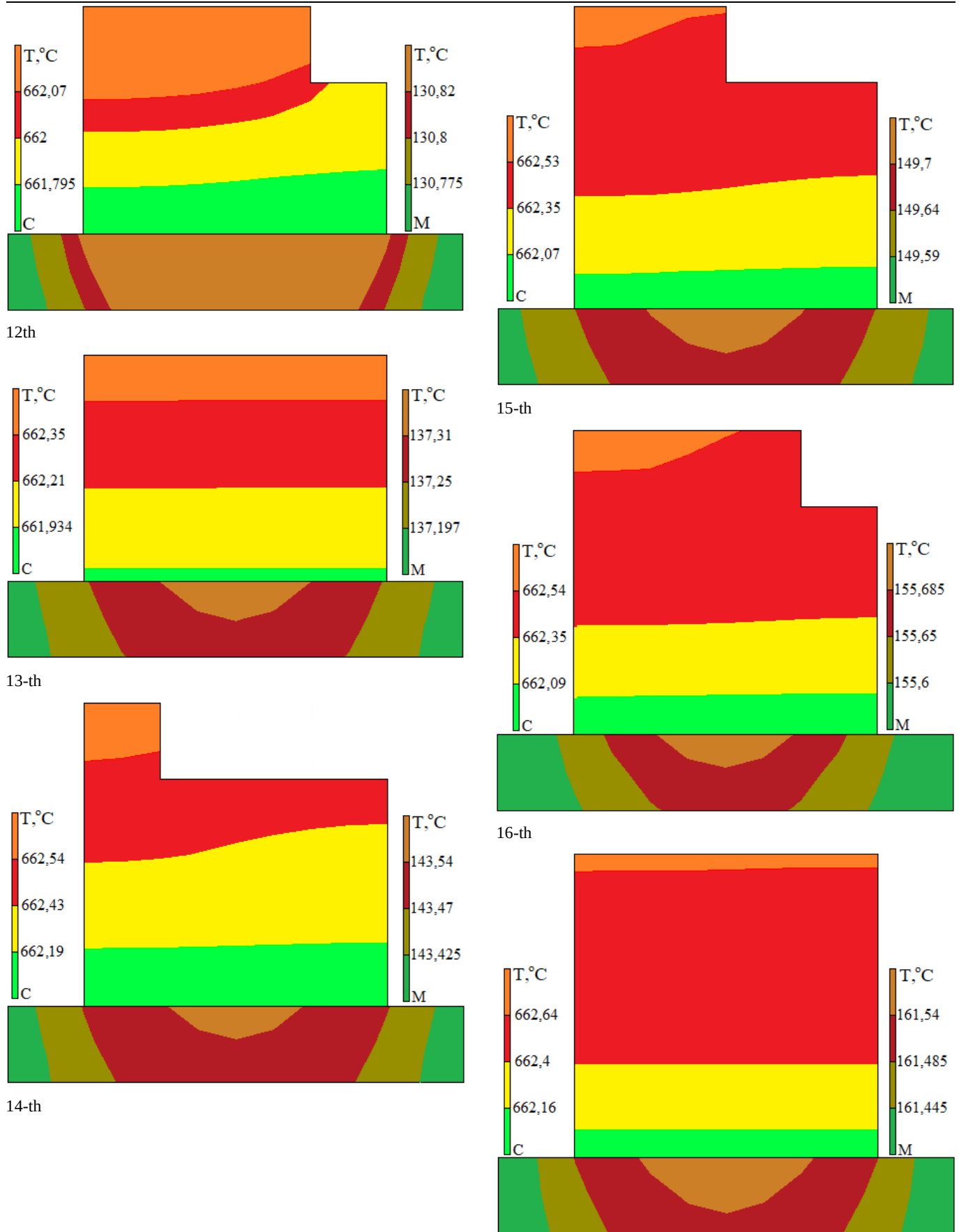


Fig. 3 Working principle of the 3D printer: with a hereditary temperature field of the droplet/substrate system

The introduction of fresh drops in the adopted methodology indicates that the storage of the liquid phase state is ahead of the starting point for phase conversion.

The phase transition temperature range is ($T_m + 3.5$, $T_m - 3.5$) $\equiv$ (660.1 + 3.5, 660.1 - 3.5). It has been learned from previous experiments that even with this maximum heat exchange, curing conditions can be found that relate to future potentialities. The next last numerical experiment is to represent the process of solidifying a large drop equivalent to a flow rate. In FIG. 4 presents the process for solidifying the large drop (flow):

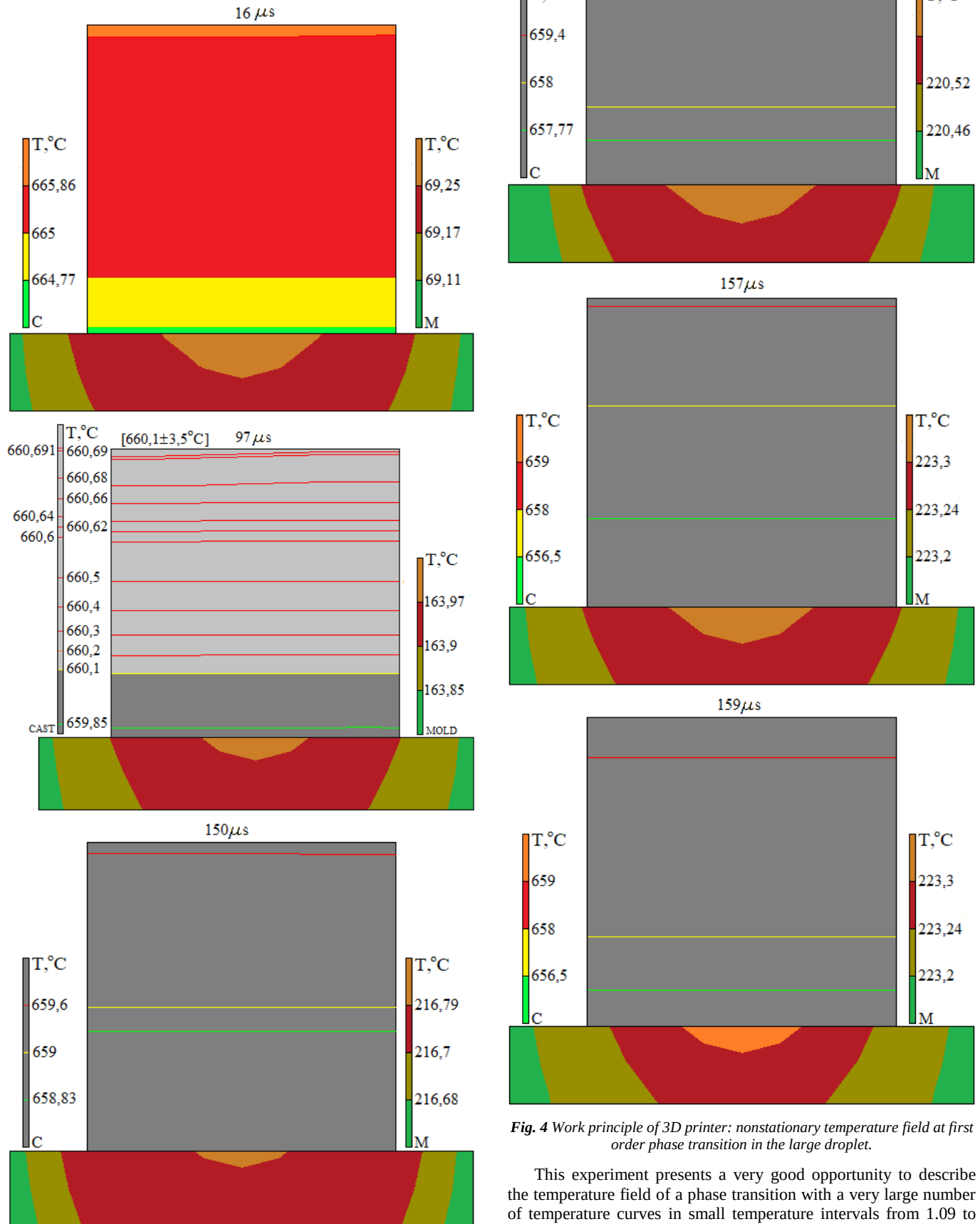


Fig. 4 Work principle of 3D printer; nonstationary temperature field at first order phase transition in the large droplet.

This experiment presents a very good opportunity to describe the temperature field of a phase transition with a very large number of temperature curves in small temperature intervals from 1.09 to 2.5°C.

3. Analysis

The works of J. Stefan [4] and C. Schwarz [5] are the mathematical foundation of the theory of casting. These tasks [4 and 5] are an important section in the mathematical theory of thermal conductivity. Along with classical crystallization theory, theoretical and applied thermodynamics are at the heart of theoretical material science.

Phase transitions of the first and second order are fundamental processes of material science because they are in the nature of the formation of structures of pure metals, alloys and composite materials [1, 2, and 3]. It is known that in the foundry, in addition to crystallization, the term solidification is used [1, 2]. There is a fundamental connection between these two concepts through the solidification front according to [3]:

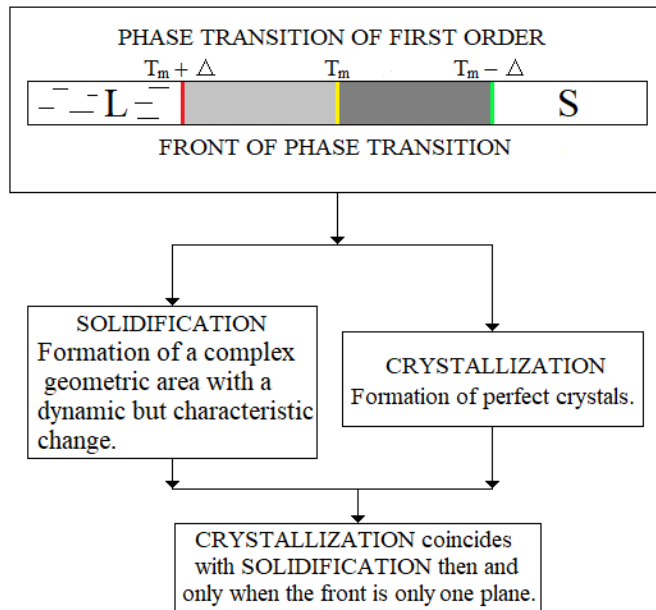


Fig. 5 Phase transition of first order: solidification and crystallization.

The interest in the tasks [4 and 5], but always presented in their classic type. Tasks [4 and 5] are used in various experimental techniques [1, 3, 8 and 10] or are the basis of mathematical studies [7, 11, 12, and 13]. The mathematical models of foundry are based on [4 and 5] for example work [8]. The use of tasks has long been a common mathematical basis for the study of first- and second-order phase transitions. The mathematical model (1) used here is the Stefan-Schwarz joint problem from the first half of the 20th century.

Numerical experiments have clearly shown that the presented methodology can be used in 3D printer technology. At least by numerical experiment it is possible to make estimates for the **crystallization front** [3]. Numerical experiments in this pure type are "easy", but taking into account real contact and the need to use mathematical methods in solid state physics [6, 2] requires many high-level knowledge resources: for example, huge computational resources, mathematics, mathematical physics, computational mathematics and physics, high resolution for quantum level observation.

Numerical experiments draw our attention to the notion of crystallization front as an important common criterion for evaluating heat transfer and droplet size in 3D printer technology. The achievement of high technological characteristics of products made using a 3D printer raise the question of optimization and control.

4. Conclusion

The basic mathematical methodology for creating and optimizing 3D printer technology is Stefan-Schwarz's task.

The crystallization front is an important general control criterion in 3D printer technology as well.

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