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Applications of collaborative industrial robots

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Abstract: Collaborative robots, or cobots, are increasingly being taken out from behind the cages and being used alongside human beings to automate a variety of tasks, including quality inspection, pick-and-place. Collaborative industrial robots are harmless to the human worker, affordable, and easy to use and program. This paper studies applications of collaborative industrial robots in industry.

Keywords: collaborative robots, cobots, industrial robots

1. Introduction

The term "collaborative robot" is often a misnomer. Although a collaborative robot is designed to work alongside humans, the device itself is not necessarily forced limited. This means that the robotic cell is monitored, is safe for human co-workers, and relies on at least one of the 4 collaborative modes. The term "collaborative robot" is unique in that it describes the fact that humans and robots work with each other, not whether the robots are force limited.

"Cobot" is a slang term used to describe a collaborative robot. Cobots are designed to be used within a defined collaborative workspace with human workers, and typically have some built-in safety mechanisms to support this use. Cobots typically fulfill repetitive or injury-prone tasks such as machine tending or palletizing while the human worker performs higher-value upstream or downstream manual tasks. Cobots mimic human actions and carry out tasks at similar or slower speeds, with payload and reach that is also similar to a human's.

The International Federation of Robotics defines two types of robots designed for collaborative use. One group covers robots designed for collaborative use that comply with the International Organization for Standards norm 10218-1 which specifies requirements and guidelines for the inherent safe design, protective measures, and information for use of industrial robots. The other group covers robots designed for collaborative use that do not satisfy the requirements of ISO 10218-1. This does not imply that these robots are unsafe. They may follow different safety standards, for example, national or in-house standards.

Human-industrial robot collaboration can range from a shared workspace with no direct human-robot contact or task synchronization, to a robot that adjusts its motion in real-time to the motion of an individual human worker (Fig. 1).

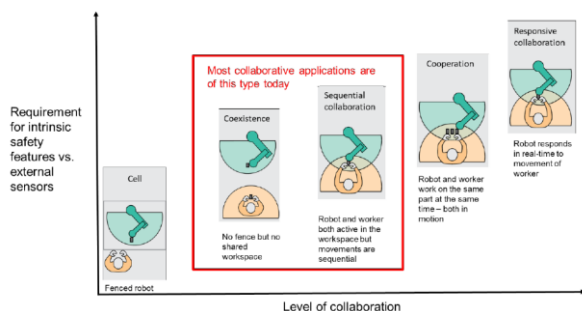


Fig. 1 Types of Human-Industrial Robot Collaboration [1]

Applications in which the robot responds in real-time to the motion of a worker (altering the angle of the gripper to match the angle at which a worker presents apart, for example) are the most technically challenging. Since the robot needs to adjust to the motion of the worker, its movements are not completely predictable and therefore the end-user must be sure that the full parameters of

its potential scope of motion meet safety requirements. Examples of responsive collaboration in industrial settings are unlikely to appear soon in most manufacturing sectors, which rely on precision and repeatability to achieve productivity gains.

2. Applications of collaborative robots

Over the last few years, automation has gained immense popularity in various industries. And the manufacturing industry sits on the cutting edge of automation technology, ahead of other industries. With automation, manufacturing companies have revolutionized the way activities were once performed. With autonomous systems coming into the picture, human participation and involvement have reduced significantly. As a result, work gets done faster and more importantly, with greater precision.

Though automation changes the nature of employment, it has brought in huge profit opportunities to the manufacturing industry. One of the most extensively used types of automation machines is a collaborative robot. Robots programmed to operate 24x7 in almost any situation to help manufacturing companies achieve greater productivity, higher throughput, and greater revenue gains. Besides, robots in manufacturing now have the cognitive abilities to take decisions independently. As the underlying technologies mature, collaborative robots in manufacturing can be made more versatile to take up more creative tasks.

Areas of application collaborative robots in manufacturing are:

- Picking, packing and palletizing,
- Welding,
- Assembling items,
- Handling materials,
- Inspecting products for quality

2.1. Picking, packing, and palletizing

Picking, packing, and palletizing are activities that need to be accurately performed. Manually performing these tasks can be mind-numbing, labor-intensive, and also time-consuming. Expecting humans to work with endless energy levels is unreasonable. Besides, humans can make errors while performing tasks. Collaborative robots (cobots), programmed to work alongside and share the human workload, have a very interesting role to play in a manufacturing company. One of the most important advantages of deploying collaborative robots is speed. Having the potential to function around the clock, these robots can work for long hours and even days (unlike humans). Robots can pick different items (which are required in constructing a product), pack them in different cartons, and palletize them. With the advantage of speed, manufacturing companies can achieve their production goals at a faster rate. Besides, there will be no room for error with collaborative robots. As a result, the time taken for the completion of manufacturing processes will be saved tremendously [2].

Bin picking comes in many shapes and sizes, from high payload automotive and heavy equipment manufacturing applications, to pick and drop e-commerce order fulfillment and part sortation applications (Fig.2)



Fig. 2 Bin-picking cobot

The packaging is a wonderful application for collaborative robots. First, it's a vital but non-value-added task—perfect for cobots (Fig. 3). Moreover, today's industries have an ever-increasing need for packaging. Nine out of ten packaging companies are now using robots. According to one report, the cobot market has an estimated 57 percent Compound Annual Growth Rate (CAGR) between now and 2023.

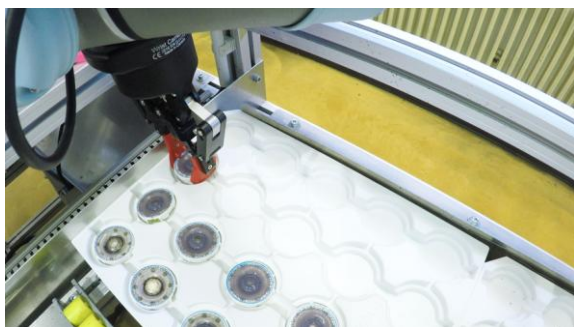


Fig. 3 Packing cobot

Using manual palletizers can take a toll on the workers and the rate of production. They are slow, they need constant monitoring and their payload is not much. Introducing cobot palletizers improves the working conditions of the workers as they can leave most of the heavy duties to the cobots and attend to other easier tasks (see Fig. 4). Cobots do not require too much monitoring and as long as their sensors and programs are in place, then they carry out their tasks effectively. They can also handle heavier payloads with better speeds per minute.



Fig. 4 Palletizing cobot

Cobot palletizers come with an easy to use technology that does not require a permanent trained robotic expert to keep monitoring it. This saves you the costs of hiring technicians and operators.

2.2. Welding

Manufacturing companies try to produce goods according to customer expectations while keeping the prices low. In their quest to accomplish these goals, these companies leverage new-age technologies. And collaborative robots can be one of these technologies. One of the most cumbersome tasks in a manufacturing plant is welding and soldering (Fig. 5). Humans can definitely perform these activities, but for how long? It is no surprise that workers can't be expected to work all day long. Sensors and computer vision systems increase collaborative robot sensing capabilities. With this potential, robots can sense catastrophic environments and notify workers about the same. This way, collaborative robots can work alongside humans, preventing accidents and loss of lives too [3].

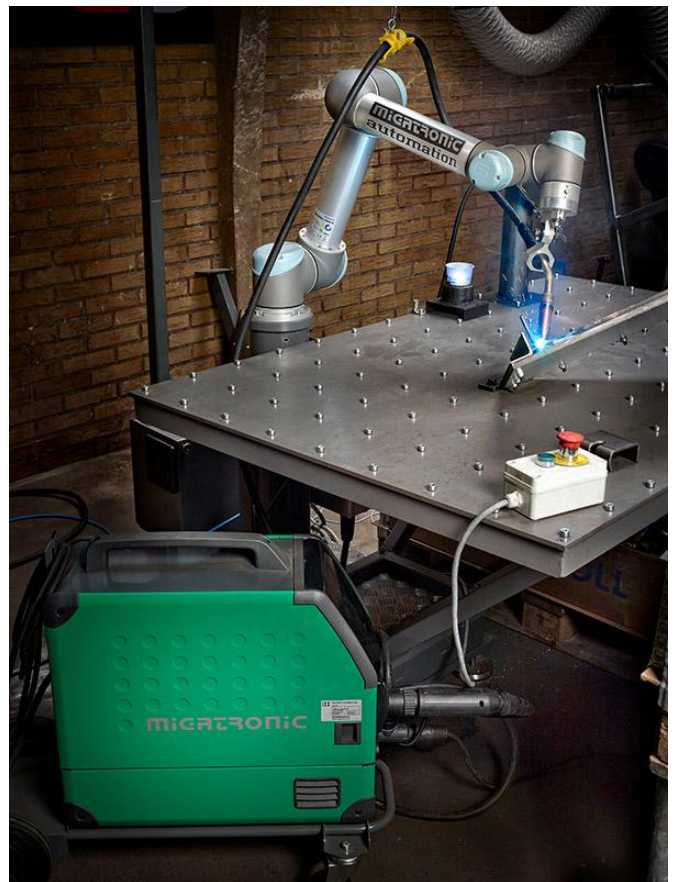


Fig. 5 Welding cobot

With collaborative robots, manufacturing companies will see: an increased rate in their production rate, no errors that are otherwise seen in their human counterparts, and improved work quality with high-level uniformity, and a reduction in wastage.

2.3. Assembling items

Assembly tasks are becoming more and more automated. With the introduction of robots that can work alongside workers, human-robot collaboration is truly a step up. It is now easier, less risky, and a lot faster to use a robot for your assembly line [4]. A collaborative robot general term used to describe the power and force limited robots, robots that can be used without safety guarding or that has incorporated other safety features. This means it can be put

beside a machine or a person and set to perform a certain task without needing to be fenced off from the surrounding environment. That being said, to introduce a cobot to an assembly line and program it to load and unload parts is not as simple as it sounds (Fig. 6).



Fig. 6 Assembly cobot

Advantages of collaborative robots for assembly applications

- Increased quality, consistency, and production speed
- Easy programming for fast redeployment to new assembly configurations
- Space-saving, lightweight design for exceptional manufacturing flexibility
- Ability to adapt assembly output to meet peak seasons and changing consumer demands
- Fast payback with none of the traditional robotic costs for programming, set-up, and dedicated work cells

2.5. Handling

Moving materials inside a manufacturing unit, around a factory floor, is a tedious process for humans. To ensure that production meets customer expectations, companies have to automate repetitive tasks like material handling. One of the best ways to deal with this concern is by bringing collaborative robots to the factory aisle. Collaborative robots can easily understand work requirements and move materials to the desired location at faster speeds. Besides, collaborative robots can help in providing a hazard-free work environment by taking care of harmful raw materials automatically.



Fig. 7 Handling cobot

By using collaborative robots for material handling, manufacturing companies can witness:

- increased worker health and safety,
- reduced costs,
- faster production cycles, and
- reduced downtime.

2.6. Inspecting products for quality

Making quality inspection quick and easy with the help of a collaborative robot arm ensures that you have the flexibility to automate almost any manual task. This is especially useful when dealing with small batches or having to switch quickly from task to task. A cobot can reuse programs for repetitive tasks [5].

Quality inspection is a suitable task for the cobot. If you use a vision system together with a cobot, it is possible to check products for quality and immediately remove defective products from the production line. With the camera, you can identify and remove defective parts before they are packaged or shipped.

Precision and consistency are the qualifications of a cobot that are most important for quality inspection. A robot arm consistently and repeatedly follows precise processes with minimal deviations; much more precise than a human.

Examples of quality inspection by the cobot

- Inspecting aircraft engines
- Inspecting car doors
- Inspecting central heating boilers
- Inspecting parts of X-ray equipment
- Inspecting welds
- Checking the correct shape/dimensions of fruit and vegetables
- Repeatedly opening and closing drawers with a specific force set

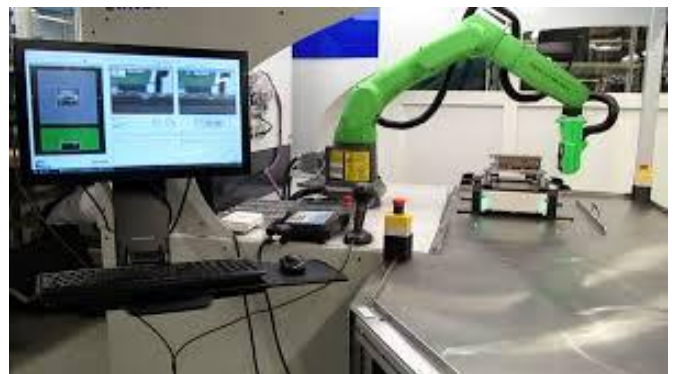


Fig. 8 Inspecting cobot

Benefits of quality inspection by the cobot

- Prevent employees from getting injured (or bored) due to repetitive work during quality inspection

- Reduce operating costs
- Consistent quality

3. Conclusion

The market for collaborative robots is still in its infancy. End-users and systems integrators are still gaining experience in what works and don't in the design and implementation of collaborative applications. Technology developments in sensors and grippers hold promise for expanding the range of actions that the robot end-effector can perform. Programming interfaces will continue to become more intuitive, not just for cobots, but also for traditional industrial robots.

4. References

1. Bauer, Wilhelm (Ed.); Bender, Manfred; Braun, Martin; Rally, Peter und Scholtz, Oliver (2016): Lightweight Robots in Manual Assembly – Best to Start Simply. Examining Companies' Initial Experiences with Lightweight Robots. Fraunhofer Institute for Industrial Engineering IAO, Stuttgart.
2. [Robotiq 2016] Robotiq, Collaborative robots e-book [online] Available from <http://robotiq.com/resource-center/ebooks/>
3. <https://weldingproductivity.com/article/i-cobot/>
4. <https://www.collaborativerobotarm.com/robot-assembly-line>
5. <https://www.controleng.com/articles/safety-and-control-in-collaborative-robotics/>

Plastic gears: State-of-the-art design and technology (review)

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Abstract. A review of the retrospective and modern state in the field of theory and practice of plastic gears is presented. Various aspects of such gears design, technology and applications are discussed. It is noted that corresponding problems are under consideration permanently on the last common engineering meetings and specialized ones. The analysis of the papers allows to conclude that main trends in plastic gears are the following once: comparison the experimental results with VDI 2736 and JIS 1759 normative paper data; development of the methods of accelerated tests; investigation on fatigue bending strength, pitting and wear resistance; improvement of the noise, vibration and harshness behaviors; analysis and optimization of reinforced composite materials structure; application of additive technologies; fabrication of high precise plastic gears and development of computer-aided design methodology.

1 Introduction

Design, technology and application of the plastic and polymer composite gears are remaining a subject of intensive investigation. Modern state and the last results in this field permanently discussed on the common engineering and especially topical conferences on gearing are discussed.

From the rest ones it should be mentioned the followings:

- International Conference on Gears (Garching near Munich, Germany) (ICG) 2005, 2010, 2015, 2017, 2018, 2019.
- The 10th and 11th International ASME Power Transmission Conference (Las Vegas, Nevada, USA) (PTC) 2007, 2011.
- International Conference "Theory and Practice of Gearing" (Izhevsk, Russia) (TPG) 2014, 2017.
- International Gear Conference (IGC) (Lyon, Villeurbanne, France) 2014, 2018.
- International Conference on High Performance Plastic Gears (Garching near Munich, Germany) (HPPG) 2015, 2017, 2019.
- International Conference "Machine and Industrial Design in Mechanical Engineering" (2010, Palic, Serbia; 2012, Balatonfüred, Hungary; 2018, Novi Sad, Serbia) (KOD).
- International Conference "Problems of Quality and Lifetime of Gears and Power Transmissions" (GPT) (the last ones: 2013, Sevastopol; 2014, Odessa, Ukraine).
- International BAPT Conference (BAPT) – 2019.
- Belarussian National Congress on Theoretical and Applied Mechanics (Minsk, Belarus) (CTAM), 2013, 2016, 2019.

It should be noted in general the crossover from the separate lectures (ICG, TRG, KOD, GPT, CTAM) to the special conference sessions (PTC, IGC) and even to the special purpose conferences (HPPG). More detailed distribution IGC, PTG and HPPG plastic gear topic papers is showed below.

IGC-2014: Session 1: Worm gears – 1; Session 4: Plastic gears – 3; Session 29: Monitoring detection of failures – 1; Poster session – 2.

IGC-2018: Sessions 26 and 30: Plastic gears – 7.

PTG-2007: Session: PTG-08: Design and analysis (DET C 2007 – 34155; 34170; 34057; 34470; 34093) – 5.

PTG-2011: Session: Plastic gears (DET C 2011 – 47426; 47501; 47554; 48372) – 4.

HPPG-2015: Sessions:

- Possibility and potentials of plastics in gear application – 4.
- Plastic materials and tribology – 4.
- Typical and future materials – 3.
- Limits and changer of shape and form – 4.
- Plastic gears – prediction and calculation of endurance and lifetime – 3.
- Plastic gears – experimental and analytical determination of load carrying capacity – 4.

HPPG-2017: Sessions:

- Possibilities and potentials of plastic gear application – 4.
- Tribology of plastic gears – 4.
- NVH of plastic gears – 6.

- Comparison of typical and future materials – 4.
- Load carrying capacity of plastic gears – 4
- HPPG-2019: Proceeding divisions (pp. 1267-1495):
- Strength evaluation – 10.
- Tooth flank load capacity – 4.
- NVH/condition monitoring – 3.
- Application – 4.

General share of polymeric gear topic papers in the total amount of conference papers is shown in Table 1. In connection with frequent mentions of aforesaid conferences in references we shall use its abbreviations.

Table 1. Share of conference polymeric gear topic papers in the total amount ones.

Conference denomination, year	Total conference paper number / Polymeric gear topic paper
ICG-2015	112/3
-2010	26/3
-2015	71/-
-2017	134/-
-2019	104/-
PTG-2007	116/5
-2011	70/4
TPG-2014	80/4
-2015	–
-2017	39/1
IGC-2014	125/7
-2018	144/7
HPPG-2015	22/22
-2017	22/22
-2019	21/21
KOD-2010	70/-
-2012	107/-
-2018	167/1
GPT-2012	60/2
-2013	62/1
-2014	57/1
BAPT-2019	83/2
CTAM*-2013	39/-
-2016	28/1
-2019	12/1

*The paper numbers of the conference session "Reliability, dynamics, strength of machines and constructions" are indicated.

The goal of paper is to extant and to present in a structural fashion information presented in above conference papers.

2 Comparison of experimental results with standardized document VDI 2736 and Japanese Standard JIS B 1759

One of the main topic discussed at above mentioned conferences is analysis of standardized documents VDI2736 [1–4] and JISB1759 [5] regulating approach to design and calculation of plastic gear load-carrying capacity. Document VDI 2736 represents renewed version VDI 2545 [6], complemented by new information, presumptive modern state in the theory and practice of gears made of thermoplastic polymers. In given division the review of this topic is represents [7-15, 17-22]. It is stated in [7] that measured data according to the VDI 2736-4 [4] should be converted correctly to become usable for strength calculation according to the VDI 2736-2 [1]. Software tool was developed and the extrapolate method for plastic gear lifetime determination is briefly discussed too. Overview on the state of art in plastic gear material data for plastic gear calculation is considered and influence of the wear coefficient as a function of contact temperature, pairing, surface roughness and lubrication is discussed [8].

Calculation method [9] includes, by extending an approach based on VDI 2736 [2] the effects of load-induced deflection as well as dynamic tooth forces and further more allows maintaining the known bending fatigue strength according to [2].

It is overviewed [10] in the whole the new VDI 27636 [1-4] standard. In [11] the overall performance comparison of different material mechanical, thermal and wear properties is given, in [12] – according to the VDI 2736 [1] temperature calculation and comparison with measurement are presented. Comparison of the first version of analogous standard VDI 2545 [6] with the new one for PA/POM gears is discussed in [13]. General test results and the problems of material selection for customer different applications are the contents of point [14]. In [15] the wear of the POM/Steel and PBT/Steel gear pairs (wear coefficient $K_w = 1.8 \div 2.5 \cdot 10^{-6} \text{ mm}^3/\text{Nm}$) is compared with magnitude of wear according to VDI 2637 [12] ($3.4 \cdot 10^{-6} \text{ mm}^3/\text{Nm}$) and KISSoft prediction ($2.8 \cdot 10^{-6} \text{ mm}^3/\text{Nm}$) [16]. It is shown that in spite of certain difference between wear magnitudes, LTCA analysis from KISSoft could be used to determine K_w with the use of worn profile and iterative calculations.

Problems of wear resistance, equal as influence of other failure types (pitting damage, creep resistance, melting, tooth root fracture, deformation etc.) at gear carrying capacity are discussed in [17-19], in particular on plastic gears, manufactured from the PA 66, PEEK [17], Delrin 100, 100P, 311DP, 511P [18], PEEK, POM [19].

In [19] the permissible tooth bending stress of POM gears was calculated in accordance with JISB 1759, using operating tests results.

Authors [20-22] present results of analysis of differences between normative document VDI 2736 and Japanese Standard JISB 1759. It is established, that VDI 2736 based on DIN 3990 (C method), JIS 1759 – on ISO 6336 (B method).

In [20] the different parameters of both documents are compared: methods of the bonding stress and permissible bending stress calculation; test rig setup and standard test condition; test gears and reach to conclusion that both equal in effectiveness. In [21] the deficiency of data for material properties is established. In [22] the example of calculating tooth bending strength from results of operating tests with POM gear pair according to the JISB 1759.

3 Accelerated tests

In [7, 8, 12] the necessity of renovation of thermoplastics nomenclature is discussed. In this context beside of standard long-term fatigue tests accelerated ones are carried out at variation of mating pairs of different materials which does not include in VDI 2736-1 [1].

Along with accelerated fatigue gear tests (usually until $10^5 \div 10^7$ cycles) the extrapolation is fulfilled used either Corten/Dolan plus Haibach approach [7, 12] nor tensile strength results [8].

It is remarked in [7, 12] that to make load spectrum calculation possible, measured data should be extrapolated according to some principles and they are proposing a combination of Corten/Dolan

approach extrapolation (from 10^7 cycles to 10^{10} cycles) and Haibach approach one (from 10^{10} to 10^{15} ones).

To minimize the influence of wear and speed up on test results of the curve S-N generation, a hybrid method is proposed [8], consisting in that, when a few gear tests are performed below or equal 10^5 cycles to define the temperature dependency of the material and avoid gear and remaining parts of the curves then extrapolated or competed with tensile fatigue tests.

Techniques for accelerated tribological, quasistatic and fatigue mechanical tests of engineering polymer composites for gears are presented in [23-25]. It is proposed complex of interrelated databases for the system of automated design, pre-operating and production assimilation of drive system components (among them databases of gears, gearings, other components polymer composite properties construction, technologies, techniques and design tools, test results, etc. [25]).

4 Study of gear lifetime

Gears of different plastics and polymer composite materials are studied on the object of gear life time [26-30, 32, 33]: fatigue bending strength; pitting; wear, creep and temperature resistance, other failure modes.

Separate fragments of the topics are below. Authors [26] compare the composite flow molding gears (FMG) and milled gears made of composite plate materials (GP) (composite material is 45% PEEK reinforced with 55% endless carbon fibers). It is noted that higher GP gear quality (8f) in comparison of FMG one (10e) according to DIN 58405 is very convenient in conditions of very high torque moments, high temperatures and rather slow motion. The tests were provided according to VDI 2736-2 [2] and test results were evaluated according to VDI 2736-4 [4].

The fatigue strength of plastic gears with taking into account material, design, operation conditions and environment is determined in [27]. For 4 values of temperature (60, 80, 100, 120°C), 4 values of humidity (10, 65, 90%) and 2 modes of loading (pulsating and alternating) the formula for (let us cite [27]) “realistic service life fatigue strength calculation on the basis of a load, temperature and humidity spectrum” is presented.

Among the diverse combination of gear pair ($m = 1.0 \text{ mm}$, $z_1 = z_2 = 20$, $\alpha_w = 20^\circ$) polymer materials (PA 66, POM reinforced with glass fibers, glass spheres, aramid fibers, PTFE) [29], the combination of POM (grade KAOOM) and PA 66 (Zytel 103 HSL NC010) demonstrates best performance.

The main topic of [4] is comparison and clarification of gear wear coefficient k_w equal to $3.4 \cdot 10^{-6} \text{ mm}^3/\text{N} \cdot \text{m}$ in accordance with VDI-2736-2 [2] with values obtained by authors [30] in pin-on-disc tests ($15 \div 21 \cdot 10^{-6} \text{ mm}^3/\text{N} \cdot \text{m}$ and gear ones ($m = 0.8 \text{ mm}$, $z_1 = 17$, $z_2 = 22$, $\alpha_w = 20^\circ$, $b_1 = 8 \text{ mm}$, $b_2 = 16 \text{ mm}$, POM-Delrin 500P) tests ($1.8 \div 2.8 \cdot 10^{-6} \text{ mm}^3/\text{N} \cdot \text{m}$). It is noted that combination of loaded tooth contact analysis (LTC A), iterative wear calculation method of KISSoft [30] and gear worn profile value it is possible to determine wear coefficient of a polymer gears.

Overview of the different wear resisting compounds and fillers Alcom® WP [31] is based on different thermoplastic matrix (PA, POM, PBT, PC, PPS). The example of improving the linear wear rate and coefficient of sliding friction for the unmodified and modified PA 66 is presented in [32].

The result of oil-lubricated PEEK spur gears ($m = 3 \text{ mm}$, $z_1 = 24$, $z_2 = 36$, $\alpha = 20^\circ$, $b_1 = 22 \text{ mm}$, $b_2 = 20 \text{ mm}$) tests aimed to definition an adequate failure criterion for discrimination progressive and non-progressive pitting growth are presented in [32].

According to experimental data for Delrin 311DP gears, the methodology of lifetime prognosis of plastic gear systems is developed in [33], including some factors that can affect to fatigue life of plastic gears, i.e. creep, surface **finish**, humidity, aging, self-heating and frequency.

5 Polymer materials and composites

Different versions of polymer gears and gear engagement (steel-polymer, polymer-polymer) it is presented in above conference papers. It is discussed not only using traditional plastics gears [34-39], but also gears made of disperse filled polymer composites [40-46] reinforced with particles and short fibers of glass, carbon, Fe_2O_3 and so on. The most often used matrix materials are the polyoximethelene POM (Delrin 100, Delrin 100P [34, 38], Tecaform AH [37]), polyamide PA66 (Tecamid 66 [37]) and polyetheretherketone (PEEK) such as Victrex 450 [35].

The wear and fatigue behavior of polymer gears (SS steel driving pinion – POM driven gear wheel pair, $m = 1.0$ mm, $b = 6$ mm, $z_1/z_2 = 17/20$, $\alpha = 20^\circ$, $x_1, x_2 = 0$) under controlled temperature conditions is discussed [38].

The results confirm the important effect of the temperature on the fatigue life of POM gears – at low of temperature 30°C the fatigue life of POM gears is greatly improved while life time was down to four times at 70°C and down to two times at 50°C , as compared to 30°C .

Step loading tests at the speed 1000 rpm significant differences in failure modes and performance have been observed for the five polymer gear materials [40] – high density polyethylene (HDPE), polycarbonate (PC), acetal (Delrin 500), Nylon (PA 46) and polyetheretherketone ($m = 2$ mm, $z = 30$, $\alpha = 20^\circ$, $b = 17$ mm, $\epsilon_a = 1.67$).

For example, fracture failure for PC gears, thermal wear for Delrin 500 gears, progressive wear for the Nylon 46 and PEEK 650 gears were noticed. The best performance was achieved with acetal as a driver and PEEK as a driven gear. Significant performance improvement is reached for 28% glass fiber reinforced acetal gears. The lubricated PEEK gears against of nonlubricated PEEK gears load capacity has been increased over 40%.

Authors [41] used for experimental samples (co-rotating discs and gears ($m = 1.0$ mm, $z_{1,2} = 30$, $b = 6$ mm, $h^* = 2.25$) polymer composite on the base Polyamide 4.6 matrix (PA 4.6) of two grades DSM Stangl® – TW241F10 (50% Glass fiber GF) and TW271F6910 (30% GF + PTFE). It was attempt, using FEM analysis, to link wear rates experimentally obtained from a co-rotating discs' experiment to the wear of gear. In [42] two grades of composite are used for experiments – PEEK-1 (reinforced by carbon fibers) and PEEK-2 (carbon fibers + graphite + titanium dioxide + zink sulfide). Samples (10x4x4 mm) were tested by means of sliding friction in dry sliding conditions. Anisotropic thermal conductivities of above materials are calculated using analytical and numerical homogenization. The results are compared to experimentally determined values.

The methods and results of disperse filled composite gear design are described in [43-46]. The optimization procedure based on iterative calculating stress-strain state and prediction of wear resistance of disperse-filled composite joints, including gears, by the effective two-level method [44]. The method allows to determine the parameters of stress-strain state, elastic compliance, strength and wear resistance of gears, as well as to find an optimum composition of the material in terms of technical requirements.

The effectiveness of the proposed two-level method for gears consists of a rational combination of analytical micromechanical approach of the elasticity theory and numerical macromechanical techniques (first of all, finite element approximation) of machine part strength analysis. Due to the first level it is suitable to describe the deforming process of essentially heterogeneous composite materials and due to the second one – to determine the parameters of the stress-strain state of intricate in shape parts, i.e., the gear.

Some experimental results are presented in [44, 45] (carbon-filled antifriction composite material "Fluvis", MPRI NASB), detailed description of methodology and results of composite gear design – in [46].

An experimental study of the wear resistance of two dispersion-filled composite materials based on polyamide used in metal-polymer gear drives with a 30% volume content of short glass or carbon fibers was performed and described in [47, 48]. As a result of tribotests in the "pin-disk" scheme, the mass wear of these composites was determined under dry friction conditions for steel 45 at room temperature in the range of contact pressures of 10-40

MPa, as well as the kinetics of the coefficient of sliding friction and the contact temperature of the tribosystem elements.

It was established that polyamide strengthened by carbon fibers has almost four times higher wear resistance in comparison with a polyamide filled with glass fibers. The wear resistance characteristics are calculated, using the durability of the straight spur metal-polymer gear drive on the basis of the original calculation method [47, 48]. It was established that gear drive durability with a pinion or a wheel reinforced with carbon fibers is more than eight times the durability of gear drive with gear wheels from polyamide filled with glass fibers. The gear drive durability with the steel pinion and the composite gear wheel increases in proportion to the gear ratio as compared to the gear drive with the composite pinion and the steel wheel.

6 Multi-criteria computer-aided design optimization and quality improvement of plastic gears

As is known, there is many universal CAD/CAM/CAE systems (for example Pro/Engineer, Solid Works, Compas 3D, AutoCAD and others), which have special modules for computing various types of gear trains. Ones of them intend for plastic gears PC-aided design, for example, KISS Soft [49], StarGear [50], "Plastic Gearing" [51] and so on.

Computer program Opti Tooth 10.0 for spur and helical polymer gears, described in [52], enables to select and to optimize, step by step, the optimum geometry of gear pairs takes into account the criteria of root and flank stress, gear temperature, wear, tooth deformation, and allowed load level for the selected material.

Another PC-aided software offered by authors [53] allows to calculate nominal dimensions and geometrical parameters of gear wheels; accuracy grade and backlash norms; quality of engagement, animated visual control over the gear wheel meshing process; full calculation protocol; data for drawings; contact and bending strength. Calculation of gear forming mould dies is performed which results are used as the data for their manufacturing by CNC machines. Nominal dimensions of cylindrical gear drive and gear wheels are calculated as per GOST 16532-83. The tolerances are selected automatically in accordance with the accepted grades of accuracy as per norms of kinematic accuracy, smoothness of operation, teeth contact, type of gear mating and backlash tolerance based on GOST 1643-81 at $m > 1$ and GOST 9178-81 at $m < 1$.

The procedure of strength calculations (including the design and verification calculations) meets GOST 21354-85 requirements. Strength design uses the basic calculation dependencies to determine contact strength of the active tooth flanks and teeth bending strength as specified in standard (some specialities see in [54, 55]).

Software [53] has module which promote to rise of plastic gear accuracy by means of female die dimensions' correction after measuring the experimental gear batch with simplest measuring technique and to compute clarified mold shrinkage of tip circle diameter, base circle diameter and angle tooth thickness on the base circle.

Example of increasing plastic gear accuracy of electro mincing machine drive is presented in the Table 2.

Table 2. Increasing plastic gear accuracy of electro-mincing machine drive by correction of mould die specified dimensions [56].

Parameter		Parameter numerical value					
Module m , mm		1.5		2.0		2.5	
Tooth number, z		12	36	15	32	15	33
Nominal tip diameter d_a , mm		21.9	56.1	35.2	66.8	44.0	86.0
Probability $P(d_a)$	Before	0.370	0.297	0	0	0	0
	After	0.941	0.990	0.684	0.776	0.335	0.999
Measurement over pins, M_p , mm		22.189	57.641	35.532	70.254	47.648	90.046
Probability $P(M_p)$	Before	0	0	0.390	0.144	0.492	0
	After	0.937	0.998	0.973	0.949	0.905	0.999

7 Additive manufacturing technologies

Trends in the development of modern technical objects and their generation in many ways reflect the ideology of Industry 4.0 (i4.0), in which the key role is prominent in the creation of sensor base, intellectualization of machines and materials, generation of Digital Twins (DT), Internet of Things etc [57, 58]. The fundamental concept of i4.0 is a "cyber-physical system" (CPS), which is characterized by physical object and its DT – i.e. computer realization of mathematical model (model complex), simulating behaviors of the physical object [57, 58].

Significant element of DT process for gears of polymer and composite materials is additive technologies substantially accelerating preproduction of that style of products. DT of physical object acts here as a CAD-model, which it is necessary as of yet to adapt for the concrete 3D-printer. Authors [46, 59-64] was developing above CPS by way of elaboration of hardware environment, computer software (CSW) and consumable materials for 3D-printers, as well as in implementation of additive technologies in gear train and transmission production.

Key elements of 3D-printing in that event are the gradient materials and issues manufacturing as well as CSW [59, 64]. Using 3D printing for polymer materials, which should provide simultaneously of high mechanical and antifrictional properties has significant benefits in comparison with traditional technologies. Controlled and relatively rapid process of gear manufacturing is realized desired form of article and optimal material property gradient. It is significant to note that material composition necessary to optimize by known methods of mechanics of composites (in simplest case that is rule of additivity), what permits to create CAD-models for 3D-printing polymer composite gears from gradient materials, optimized with volume distribution of its mechanical characteristics [59, 64].

Computer software for 3D-printing is elaborate by the companies USG, IBM, Autodesk, Solid Works, Siemens PLM Software and others and overlap the whole circuit on control with life time of goods and control of technological processes, as well to simulate the items as to make analysis of completed model taking into account features of manufacturing and used materials. 3D-printing design possibilities unobtainable with other technologies the planetary gear train is demonstrated (Figure) where any and all gears are herringbone ones. Prototype is printed on 3D-printer "Engineer V2-K", which design is described in [62]. Some peculiarities of CSW for 3D-printing are described in [60].



Fig. Model of the planetary gear train with the herringbone gears, manufactured with additive technology. (The specimens and their photographs have been rendered by V. Dubrovskii).

Authors [65] on the example of planetary train ("Backlash Drive") consider possibilities of the novel design to integrate the gears into either fully or mostly additively manufactured gear boxes. Realization of technology is carried out with step by step generation from the half tooth profile points through the full tooth – 2D – representation of gear to the 3D point cloud. There is reference [66] to algorithm for different profiles (involute, cycloid), variations of tooth systems (helical, herringbone and spiral), some types of gears (spur, bevel, internal, ones and cylindrical worms). It is noted [65] that additive manufacturing of gears offers potential in the fast drafting and design of arbitrary gear boxes, leading to accelerated testing of mechanisms and prototypes.

8 Gear train noise, vibration and harshness (NVH) improvement with plastic gears

Some paper topics of the last scientific conferences dedicate to NVH problem study [67-70]. It is noted [67] that the PEEK gear solution provides up to 45% reduction of the gear rattle emission and did exhibit an in overage 70% reduction of gear whine emission (gear whine noise) of the first three gear orders.

The influence of different motor speed on the change the meshing frequencies is studied [68] with the change the motor pinions with a lower tooth number (7 instead of 9) and higher tooth number (13 instead of 9). It is established, that a damping of the transfer parts shows the best results, followed by the macrogeometry of the teeth and the quality of the parts. A combination of all measure can lead to an even higher reduction.

Some examples of gears with symmetric and asymmetric teeth are discussed [69] and it is showed, that due to a well applied profile modification the operating characteristics (lifetime and noise) could be significantly improved. For sinter/POM pairing (symmetric teeth and tip relief value 30 μm) reduction of differences between effective contact ratio and theoretical one indicates on improvement of the NVH behavior; for asymmetric teeth tip relief modification value of 30 μm for both gears shows the smallest transmission error (reduction by 35%) and low wear (reduction by 25%). Compared to the symmetric design results of asymmetric one show much lower wear and transmission error. It is concluded – NVH properties in order to improve profile modification should be applying.

Comparative results of testing PEEK-Victrex 450 GTM gears and steel ones on NVH behaviors are presented in [70].

Therefore, the benefits of polymer gear solution compared of metal ones are consisted of up to 3dB (50%) improvement in NVH, up to 68% weight reduction, which is resulting in 70% reduction of the moment of inertia and therefore requiring 9% less torque to operate to a cast iron gear set.

9 Conclusions

The main trends of the last investigation topics in the field of polymer material and composite gears are discussed. It is established that the dominant subjects of the papers are the outstanding normative papers VDI 2736 and JISB 1759, regulating the main aspects of thermoplastic gears – polymer material properties and selection, production methods, tolerances and accuracy, design, load-carrying capacity calculation of cylindrical gears and helical ones [7-22].

A part of publications [7, 8, 12] dedicates to the different techniques of the accelerated tests, consisted of as directly gear durability tests as well fatigue tensile strength tests. The accelerated tests for determining the polymer material and composite fatigue properties (strength and friction ones) in the context of gears are carried out too [23-25].

The other paper topics are the following: the gear lifetime study, namely the failure modes with fatigue bending strength; pitting; wear, creep and temperature resistance [26-30, 32, 33]; comparison of gear carrying capacity of different gear pairing (steel-polymer, polymer-polymer) and influence of different operating factors (temperature, humidity, lubricants etc.) [34-46]; computer-aided software and quality improvement of plastic gears [52-56]; additive technologies as an important element of the Industry 4.0 concept [57-66]; plastic gears for improvement of noise, vibration and hardness characteristics of gearboxes [67-70].

In the whole it is obeyed to acknowledge, that majority publications touch upon subject of gear bending and surface strength wear resistance, PC-aided gear design and their accuracy, study of polymer gear load-capacity.

Abbreviation

PA – polyamide (nylon)
 POM – polyoxymethylene (acetal)
 PBT – polybutadiene terephthalate
 PEEK – polyetheretherketone
 PC – polycarbonate

PPS – polyphenylene sulfide
HDPE – high density polyethylene
GF – glass fillers

References

1. VDI 2736. Thermoplastische Zahnäder Werkstoffe, Werkstoffauswahl, Herstellverfahren, Herstellgenauigkeit. VDI-RICHTLINIEN. Entwurf. **1** (2016)
2. VDI 2736. Thermoplastische Zahnäder Stirnradgetriebe Tragfähigkeitsberechnung. VDI-RICHTLINIEN. Entwurf. **2** (2013)
3. VDI 2736. Thermoplastische Zahnäder Stirnradgetriebe Paarung Zylinderschnecke Schrägstirnrad Tragfähigkeitsberechnung. VDI-RICHTLINIEN. Entwurf. **3** (2012)
4. VDI 2736. Thermoplastische Zahnäder Ermittlung von Tragfähigkeitskennwerten an Zahnädern. VDI-RICHTLINIEN. Entwurf. **4** (2016)
5. JIS B 1759 Estimation of tooth bending strength of cylindrical plastic gears (2013)
6. VDI 2545. Zahnäder aus Thermoplastischen Kunststoffen. Dusseldorf (1981)
7. A. Pogačnik, S. Beermann, *Intern. Conf. on HPPG*. 145-2294 (2017)
8. J. Cathelin, R. Janssen, *Intern. Conf. on HPPG*. 146-2294 (2017)
9. C. Hasl, P. Oster, T. Tobie, K. Stahl, *Intern. Conf. on HPPG*. 155-2294 (2017)
10. S. Oberle, *Intern. Conf. on HPPG* (www.vdi.de/plasticgears) (2015)
11. D. Merken, *Intern. Conf. on HPPG* (www.vdi.de/plasticgears) (2015)
12. A. Pogačnik, *Intern. Conf. on HPPG* (www.vdi.de/plasticgears) (2015)
13. S. Beermann, *Intern. Conf. on HPPG* (www.vdi.de/plasticgears) (2015)
14. W. Schmidt, *Intern. Conf. on HPPG* (www.vdi.de/plasticgears) (2015)
15. S. Matkovič, A. Pogačnik, M. Kalin, *Proc. of the Int. Conf. on HPPG*, 1311-1322 (2019)
16. U. Kissling, S. Hauri, IGCC (2015)
17. C.M. Illenberger, T. Tobie, S. Stahl, *Proc. of the Int. Conf. on HPPG*, 1379-1390 (2019)
18. R. Ratnagiri, M. Kato, H. Kuchelka, *Proc. of the Int. Conf. on HPPG*, 1357-1366 (2019)
19. H.-J. Dennig, A. Vademager, *Proc. of the Int. Conf. on HPPG*, 1279-1290 (2019)
20. I. Bae, U. Kissling, *Proc. of the Int. Conf. on HPPG*, 1267-1278 (2019)
21. Ju. Gathelin, *Proc. of the Int. Conf. on HPPG*, 1335-1344 (2019)
22. I. Moriwaki, A. Ueda, M. Nakamura, K. Itoneda, D. Iba, *Proc. of the IGC* (Lyon, Villeurbanne, France, 2014) 1172-1178 (2014)
23. V.L. Basinyuk, V.E. Starzhinsky, E.I. Mardosevich, M.P. Lobkova, *Proc. of the Int. Symposium TRG* 521-528 (Sc. Ed. V.I. Goldfarb, Izhevsk: IzhSTU 2014) (in Russian)
24. V.L. Basinyuk, V.E. Starzhinsky, E.I. Mardosevich, M.P. Lobkova, *Proc. of the Int. Symposium TRG* 529-534 (Sc. Ed. V.I. Goldfarb, Izhevsk: IzhSTU 2014) (in Russian)
25. V.L. Basinyuk, V.E. Starzhinsky, A.A. Kalina, A.V. Kuleshova, *Coll. of Sci. papers «Actual problems of Machine Science»* (CTAM) (Minsk: JIME of NASB) **2** 334-338 (2013) (in Russian)
26. N.-J. Dennig, S. Monn, A. Wodermayer, *Proc. of the 3th Int. Conf. on HPPG*, 1279-1290 (2019)
27. K. Humm, M.-S. Wirth, A. Linnemann, T. Schalk, *Proc. of the 3th Int. Conf. on HPPG*, 12791-1298 (2019)
28. G. Hlebanja, M. Hriberšek, M. Erjavec, S. Kulovec, *Proc. of the 6th Int. Conf. BAPT* (2019)
29. S. Matkovič, A. Pogačnik, M. Kalin, *Proc. of Int. Conf. on HPPG*, 1311-1321 (2019)
30. K. Smrczkova, *Proc. of Int. Conf. on HPPG*, 1345-1356 (2019)
31. PIP Alcom® WP – Wear Protect, Company Publication, ALBIS Plastic, GmbH, Hamburg (2018)
32. C.M. Illenberger, T. Tobie, K. Stahl, *Proc. of Int. Conf. on HPPG*, 1379-1390 (2019)
33. R. Ratnagiri, M. Kato, H. Kuchelka, *Proc. of Int. Conf. on HPPG*, 1357-1366 (2019)
34. A. Pogačnik, S. Beermann, *Int. Conf. on HPPG*. 145-2294 (2017)
35. R. Weidig, *Proc. of the Int. Conf. on HPPG*. 142-2294 (2017)
36. M. Baar, P. Oster, T. Tobie, K. Stahl, *Int. Conf. on HPPG*, 151-2294 (2017)
37. B. Cerne, D. Zorko, J. Duhovnik, *Int. Conf. on HPPG* (2017)
38. M. Kalin, A. Kuper, *Int. Conf. on HPPG*, 154-2294 (2017)
39. C. Hasl, P. Oster, T. Tobie, K. Stahe, *Int. Conf. on HPPG*, 155-2294 (2017)
40. K. Mao, V. Goodship, N. Madhov, R. Ramakrishna, P. Langlois, *Int. Conf. on HPPG*. 153-2294 (2017)
41. M. Kanters, B. Wissen, R. Nickel, *Int. Conf. on HPPG* 142-2294 (2017)
42. N.S. Ecke, A.K. Schearb, H. Holler, J. Wiedermeyer, P. Klein, *Proc. of the 3th Int. Conf. on HPPG*, 1411-1420 (2019)
43. S.V. Shil'ko, V.E. Starzhinsky, E.M. Petrokovets, D.A. Chernous, *J. of Friction and Wear. Part 2*, **35**, 1 40-47 (2014)
44. S.V. Shil'ko, V.E. Starzhinsky // *Proc. of the 26th Working Meeting on Standardization of Terminology* (WMST – Bucharest: Politehnica Press) 57-64 (2016)
45. S.V. Shil'ko, V.E. Starzhinsky, E.M. Petrokovets, T.V. Ryabchenko, *Coll. of Sci. Works «Actual Problems of Machine Science»* (CTAM-2016). (Minsk: JIME NASB), 233-236 (2016) (in Russian)
46. S.V. Shil'ko, V.E. Starzhinsky, E.M. Petrokovets, *Theory and Practice of Gearing and Transmissions* (Eds.: V. Goldfarb, N. Barmina, Springer, 2016)
47. M.V. Chernets, S.V. Shil'ko, M.I. Pashechko, M. Barshch, *J. of Friction and Wear*. **39**, 5 361-364 (2018)
48. M. Chernets, S. Shil'ko, M. Pashechko, *Tribologia*, **3** 19-23 (2018)
49. KISSsoft. URL: (www.kisssoft.ag)
50. Star Gear. URL: (http://www.stargear.com)
51. Plastics Gearing Technology, Inc. URL: (www.abapgt.com)
52. J. Tavčar, J. Kos, D. Zorko, J. Duhovnik, *Proc. of Int. Conf. on HPPG*, 1473-1484 (2019)
53. V.E. Starzhinsky, RB Certificate **370** (2011)
54. V.E. Starzhinsky, S.V. Shil'ko, E.M. Petrokovets, V.V. Supin, E.V. Shalobaev, Ye.I. Gutman, *KOD 2018 IOP Publ. Conf. Series: Mat. Sci. and Eng.* 393 (2018)
55. V.E. Starzhinsky, S.V. Shil'ko, E.V. Shalobaev, M. Rackov, *Col. of Sci. Works «Actual Problems of Machine Science»*, (CTAM-2019) (Minsk: JIME NASB) **8** 195-198 (2019)
56. V.E. Starzhinsky, Yu.L. Soliterman, A.M. Goman, *Monograph «Machine Design»* (Un. of Novi Sad, Fac. of Tech. Sci., Novi Sad) 237-242 (2008)
57. V.B. Algin, S.N. Paddubko, V.E. Starzhinsky, S.V. Shil'ko, *Mechanics of Machines, Mechanisms and Materials*, (CTAM-2019) **49**, 4, 5-19 (2019) (in Russian)
58. V.B. Algin, N.N. Ishin, V.E. Starzhinsky, S.V. Shil'ko, M. Rackov, M. Čavić, *Coll. of Sci. Papers «Actual Problems of Machine Science»*. **8** 172-184 (2019)
59. S.V. Shil'ko, T.V. Ryabchenko, S.L. Gavrilenko, E.V. Shalobaev, *Proc. of the Int. Scientific and Pract. Symp. «Challenges of Additive Technologies Development in Republic Belarus»* (Minsk, Belarus) 194-207 (2017) (in Russian)
60. F.A. Perepelitsa, E.V. Shalobaev, S.V. Shil'ko, *Proc. of the Int. Scientific and Pract. Symp. «Challenges of Additive Technologies Development in Republic Belarus»* (Minsk, Belarus) 128-135 (2017) (in Russian)

61. E.V. Shalobaev, F.A. Perepelitsa, N.S. Krasnorutskaya, *Coll. of Scient. Papers «Instrument-making in XXI century», Proc. of the XII Int. Conf.*, 319-323 (2019) (in Russian)
62. G.A. Demidov, A.H. Karandashev, E.V. Shalobaev, F.A. Perepelitsa, S.V. Shil'ko, V.E. Starzhinsky, V.V. Dubrovskii, *Polym. Mater. and Techn.*, **5**, 3 59-63 (2019) (in Russian)
63. V.E. Starzhinsky, S.V. Shil'ko, E.V. Shalobaev, *Polym. Mater. and Techn.*, **4**, 2 6-31 (2018) (in Russian)
64. S.V. Shil'ko, Yu.M. Pleskachevsky, S.V. Panin, B.A. Lyukshin, *Mechanics of Machines Mechanisms and Materials*, **3-4 (20-21)** 149-157 (2012) (in Russian)
65. S. Detsel, Y.S. Krieger, N.F. Tralger, T.C. Lueth, *Proc. of Int. Conf. on HPPG* 1401-1410 (2019)
66. Y. Sun, T.C. Lueth, *RAAD-2019 Advances in Service and Industrial Robotics*, 357-364 (2019)
67. R. Weidig, H.J. Welner, *Proc. of Int. Conf. on HPPG*, 1421-1430 (2019)
68. J. Fechner, S. Oberle, M. Knöpfle, V. Merz, *Proc. of Int. Conf. on HPPG*, 1431-1442 (2019)
69. A. Pogačnik, U. Kissling, *Proc. of the Int. Conf. on HPPG*, 1461-1472 (2019)
70. R. Weidig, *Proc. of Int. Conf. on HPPG* 147-2294 (2017)

Investigation of the influence of basic technical parameters of ribbon electron flow on the microrelief of the optical glass surface

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Abstract: The article presents the results of a study of the influence of the main technical parameters of a ribbon electron flow on the microrelief of the surface of optical glass. A mathematical apparatus has been developed that allows the processing of probe characteristics obtained by sensing the energy parameters of a paraxial electron flow. The dependence of the influence of the main technical parameters (shape, size and distribution of current density) of a low-energy electronic stream of ribbon form on the microrelief of the surface of an optical glass of the crown variety has been established. This made it possible to evaluate the interaction of the electron flow with the surface of the optical glass. It was also found that the useful current of the electron flow is about 30% of the total emission current of the cathode of the electron gun. It is shown that the following factors can influence the accuracy of determining the technical parameters of a ribbon electron flow by sounding: a decrease in the diameter of the probes under the influence of the electron flow and heating of the probes during measurement. The total error of the probe method for determining the current density of the electron flow does not exceed 8%. Using atomic force microscopy, it was established that after processing the surfaces of optical glass of the crown variety with a low-energy electron-beam of a ribbon-shaped shape, provided that the rational shape, size and distribution of current density both in the working space and on the treated surface are reduced by irregularities from 40-75 nm to 3.5-5 nm. However, it was noted that the surface of the glass after electron flow treatment has a more uniform structure and is free from microdefects, in contrast to surfaces without electron flow processing.

Keywords: RIBBON ELECTRON FLOW, OPTICAL GLASS, SENSING, CURRENT DENSITY, SURFACE MICRORELIEF, ATOMIC FORCE MICROSCOPY

1. Introduction

Electron flow processing (EFP) is one of the most promising types of processing of elements of optoelectronics, microoptics and so on. As it was established in [1-5], the parameters of the ribbon electronic flow have the most significant influence on the quality and efficiency of such processing. However, among the main controllable parameters for EFP, the electron flow parameters (shape, size, and current density distribution across the cross section) are the least stable. That is why various EFP installations, especially in processes requiring high precision machining, are equipped with electronic energy control systems [6, 7].

Among the scientists who investigated the influence of the ribbon electron flow on the surface of the optical glass, the following should be noted: Antonyuk V., Bonda-renko M., Vashchenko V., Guloyan Ya., Kanashevich G., Mazzoldi P., Rud M. and others [8-12].

However, the substantiated data on the influence of the technical parameters of the electron flow on the microrelief of the optical glass surface in the works of these scientists is not considered enough especially in the questions on the operational determination of electronic flow parameters. Previously, a rotary probe method [13] was adapted to measure the parameters of ribbon

electron flows in [14] on the basis of the original method developed by the authors [13], whereby the probing occurs by combing several probes moving on a working trolley.

The purpose of this work is to determine the dependence of the influence of the basic technical parameters of the ribbon electron flow (shape, size and distribution of the electron current density) on the microrelief of the surface of the optical glass.

2. Experimental research method

The Pierce electronic gun (PEG) used for forming a ribbon electron flow has the following disadvantages: the irregularity of the electron flow along the ribbon (associated with the sagging of the tungsten wire cathode when heated to operating temperature and with heat outflow at its clamps), time (associated with the aging of the cathode), failure to observe the shape of the electron flow on the surface of the processed material (associated with the accumulation of electron charge on the dielectric and optical glass surfaces).

The probe module of the primary measuring transducer for determining the characteristics of the ribbon electron flow is a comb of 13 tungsten probes (at a distance of 5 mm between them), which are located in the same plane parallel to each other (Fig. 1).

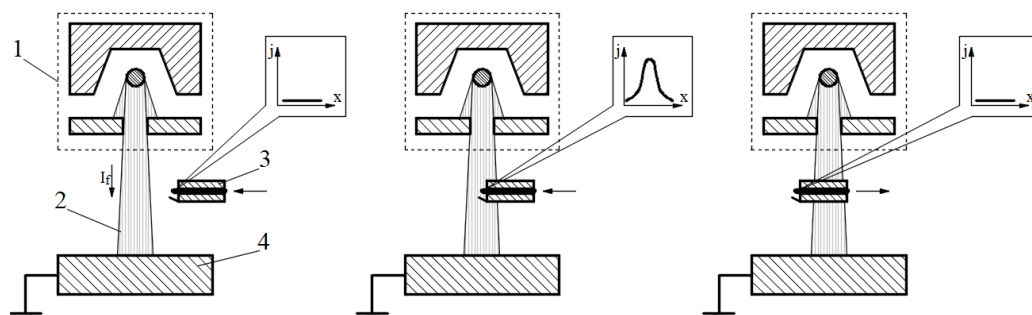


Fig. 1 Scheme of probing the electronic flow of the ribbon form in the working space of the electronic gun:

1 – Pierce electronic gun module, 2 – ribbon electronic flow, 3 – probe measuring transducer module, 4 – electronic flow collector, I_f – electronic flow current.

This design differs from the design proposed in [15] in that in the course of operation on the tungsten probes a voltage of 30-80 V is supplied, which voids the effect of electron repulsion at the edges of the probes due to the action of the Ampere force by diagnosing the current in the probe and allows determine the change in current density distribution in the workspace of PEG along the length of the ribbon electronic flow by a maximum of 60 mm.

To shield the probes from the impact of the secondary electrons from the substrate, they are clamped at the edge of the movable platform so that all flow electrons not selected by the probes do not affect the operation of the transducer.

The current of each of the probes through the copper wire and vacuum electrical input is fed to the recording device [16]. The signal received from each probe, which changes as it passes under the electronic flow, is the result of integrating the current distribution along the cross section of the electronic flow intersected by the tungsten probe.

To obtain a current density distribution across the electron cross section, the recording device conducts a probe current conversion at each position of the probe module. After that, the microprocessor performs numerical differentiation of the probe characteristic and the recalculation of the current density in the position of the probes:

$$j(x) = (i_d(x) - i_d(x - \Delta x)) / d \cdot v \cdot t,$$

where $j(x)$ is the density of the diagnosed current at a point x ; $i_d(x)$ is the current probe diagnosed by the probe module; $i_d(x - \Delta x)$ – the diagnosed current at the previous measurement; d is the probe diameter; v is the speed of movement of the probe module; t is the period between measurements of current values.

High precision quartz timers are used to map each probe current to the probe current x of the probe system and to move it in the transducer (time deviation does not exceed 1 second per day).

The obtained and calculated current density distribution in the PEG workspace is transmitted to the PC for further processing and visualization.

At the same time, to determine the current distribution in the electronic flow, the probe module is positioned at an angle equal to the angle of difference of the electronic flow, Fig. 2.

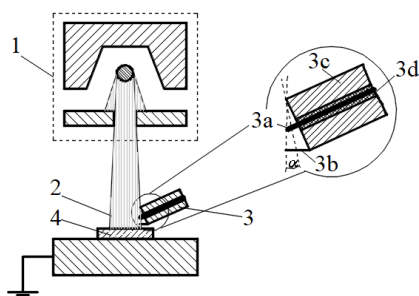


Fig. 2 Scheme of probing the electronic flow of the ribbon form on the surface of the optical glass:

1 – Pierce electronic gun module, 2 – ribbon electronic flow, 3 – probe module of transducer, 3a – tungsten probe, 3b – screen against surface electric charge, 3c – metal casing, 3d – dielectric gasket, 4 – experimental sample optical glass mounted on the electron flow collector, α is the angle of the paraxial difference of the electron flow ($\alpha \leq 10^\circ$).

The main differences of the developed method of sounding are: express-sounding in one cycle with electronic processing, sounding of electronic flow not axial form (in this case ribbon), simple mathematical processing of probe characteristics, sounding is performed in automatic mode, probe characteristics immediately after sounding current and digital densities are transmitted to the automatic electronic processing control system for analysis. Circuits designed to determine the shape of the size and distribution of the current density of the electron flow as a processing tool in the workspace of the PEG and on the surface of the processing material (optical glass) have been developed for probing the ribbon electronic flow.

3. Analysis of probe characteristics of the electronic flow

In Fig. 3 shows the probe characteristics taken by a probe device located in the center of the electronic flow, which is obtained by probing the working space of the PEG (Fig.3.a) and on the surface of the optical glass (Fig.3.b).

Trial testing of the probe device was conducted under the conditions and modes under which electronic processing of optical glass occurs, namely: the distance from the probes to the anode $H = 20$ mm, accelerating voltage $U = 3$ kV, cathode ignition current $I_C = 15$ A, full flow current $I_f = 150$ -200 mA.

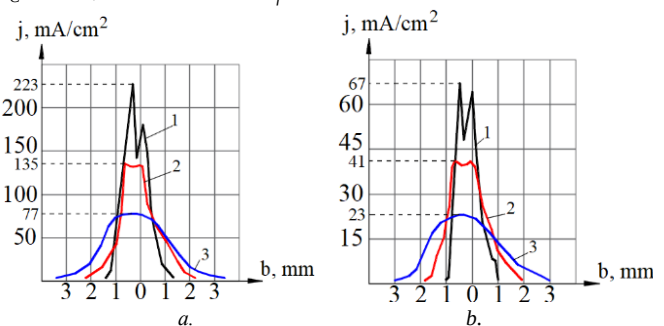


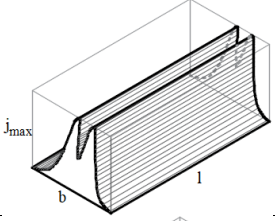
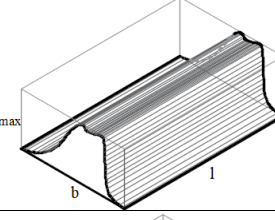
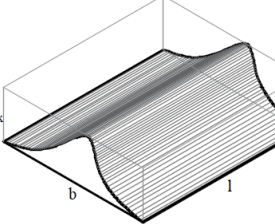
Fig. 3 Probe characteristics obtained in the work space of the PEG (a) and on the surface of the optical glass (b):

a – distribution of the probe current density along the cross section of the electronic flow in the workspace of the PEG; b – density distribution of the probe current over the surface of the optical glass; 1 – $I_f = 150$ mA; 2 – $I_f = 175$ mA; 3 – $I_f = 200$ mA.

As can be seen from Fig. 3, when comparing the results of electronic flow sensing in the workspace of the PEG and on the surface of the optical glass, the distribution forms of the electronic flow in both cases are identical for the same working currents of the electronic flow, the width of the electronic flow varies proportionally to the distances between the probing planes and the angle of difference of the electronic flow (about 8-10%). At the same time, the results of the scan of the electronic current density distribution showed that, regardless of the full working current of the electronic flow, the electronic flow current on the surface of the optical glass (the so-called useful current) is about 30%.

As a result of probing of the ribbon electronic flow during processing of optical glass the basic technical parameters of this flow on the surface of optical glass K8 are established.

Table 1: The main technical parameters of the electron flow on the surface of the optical glass at different currents of the electronic flow

#	Electronic flow processing mode	Form of electronic flow	Length l and width b of electronic flow, mm	The maximum current density of an electronic flow, j_{max} , mA/cm ²
a	$H = 20$ mm, $U = 3$ kV, $I_c = 15$ A, $I_f = 150$ mA		$l = 58$ mm, $b = 2$ mm	$j_{max} = 67$ mA/cm ²
b	$H = 20$ mm, $U = 3$ kV, $I_c = 15$ A, $I_f = 175$ mA		$l = 59$ mm, $b = 3,5$ mm	$j_{max} = 41$ mA/cm ²
c	$H = 20$ mm, $U = 3$ kV, $I_c = 15$ A, $I_f = 200$ mA		$l = 61,5$ mm, $b = 6$ mm	$j_{max} = 23$ mA/cm ²

As a result of the sounding of ribbon electronic flow it is established that in practice under different modes it is possible to obtain different laws of current density distribution, which are different from Gaussian.

4. Results and discussion

To achieve the goal of this work, a number of studies were conducted to determine the dependence of the influence of the basic technical parameters of the ribbon electronic flow on the microrelief of the surface of the processed optical glass.

The microgeometry of the surface of optical glass processed according to the above modes was investigated by the method of

atomic force microscopy on the device "NT-206V" (manufacturer: "Mikrotestmashiny", Belarus) with silicon probes "Ultrasharp CSC12", optimizing the system with a microfibre.

As a result of the conducted researches it is established that the surfaces of the optical glass processed according to the regime: $H = 20$ mm, $U = 3$ kV, $I_c = 15$ A, $I_f = 150$ mA are inhomogeneous, have high porosity and contain microdefects of the surface (cracks, floods, etc.), Fig. 4 (this corresponds to the shape of the electron flow, which has the form of a corresponding dependence, as for the current $I_f = 150$ mA (see Table 1.a). In this case, the microirregularities of such a surface is 40-75 nm.

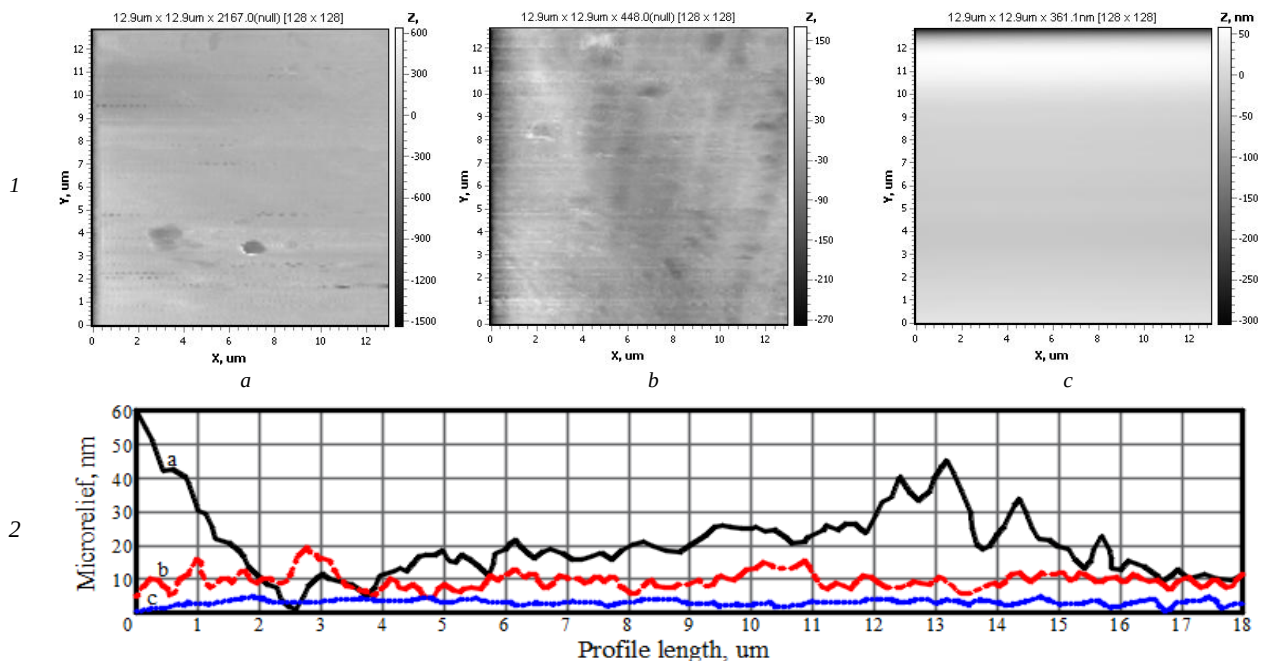


Fig. 4 Topography (1) of the K8 optical glass surface at $13 \times 13 \mu\text{m}$ and the profile (2) of the relief along the main diagonal of the topogram under the following electronic flow processing modes: $H = 20$ mm, $U = 3$ kV, $I_c = 15$ A, $I_f = 150$ mA (a); $I_f = 175$ mA (b); $I_f = 200$ mA (c).

When treating the surface of an optical glass with an electronic flow in the mode: $H = 20$ mm, $U = 3$ kV, $I_c = 15$ A, $I_f = 175$ mA (Fig.4.b, Table 1.b), in fact, as in the previous case surface heterogeneity was observed, and the residual micro-irregularity was reduced to 12-24 nm. Then, by treating the optical surface with a ribbon electronic flow with a maximum current of an electron flow $I_f = 200$ mA (Fig.4c, Table 1c) eliminates microdefects and surface porosity, making it more homogeneous. The residual micro-irregularities are reduced to 3.5-5 nm.

5. Conclusion

Thus, using the method and developed, with the participation of the authors, the means of probing the ribbon electronic flow determined the main technical characteristics (shape, size and distribution of current density) of this flow, which allowed to evaluate the interaction of the electronic flow with the surface of the optical glass. It is also found that the useful current of the electronic flow is about 30% of the total emission current of the electron cathode.

It is established that the accuracy of determining the technical parameters of the ribbon electronic flow by the probing method can be influenced by the following factors: reduction of the diameter of the probes under the influence of the electronic flow and heating of the probes during the measurement process. After about 40-50 measurements there is a significant reduction in the diameter of the probes to 5%, after which there is a need to install new probes with identical characteristics. To reduce the influence of the probe heating during the measurement process, preheating is carried out by several electronic flow passes. The error of the recording device is also taken into account. The total error of the probe method for determining the electronic flow density does not exceed 8%.

The method of atomic force microscopy revealed that after treatment of the surfaces of optical glass varieties of "crown" low-energy electronic flow of the ribbon form, subject to its optimal shape, size and distribution of current density in the working space and on the treated surface is a decrease of micro-irregularities 75 nm to 3.5-5 nm. However, it is noted that the surface of the glass after electronic flow treatment has a more homogeneous structure and is saved from microdefects unlike surfaces without electron beam treatment.

6. References

- 1.M. Bondarenko, I. Bondarenko, V. Antoniuk, et. al., Mater. Sci., Nonequilib. Phase Transform., **2**, 53 (2017), <<https://stumejournals.com/journals/ms/2017/2/53.full.pdf>>
- 2.I. Yatsenko, V. Antoniuk, M. Bondarenko, V. Vashchenko, Int. Sci. J. Innov., **1**, 13 (2015), <<https://stumejournals.com/journals/innovations/2015/1/13.full.pdf>>
- 3.Y.I. Kovalenko, M.A. Bondarenko, E.V. Vertsanova, I.V. Iatsenko, et. al., in: XIV Intern. conf. "Physics and technology of thin films and nanosystems" (Ivano-Frankivsk, May, 20-25, 2013), P. 92.
- 4.I.V. Yatsenko, V.S. Antonyuk, V.I. Gordienko, et. al., Mach. Technol. Mater., **4**, 160 (2018), <<https://stumejournals.com/journals/mtm/2018/4/160.full.pdf>>
- 5.V.A. Vashchenko, I.V. Yatsenko, Yu.G. Lega, O.V. Kirichenko, *Basics of Electron Treatment of Goods from Optical Materials* (Naukova dumka, Kyiv, 2011) (in Ukrainian).
- 6.E. Skoryna, V. Medyanyk, M. Bondarenko, et. al., Int. Sci. J. Innov., **1**, 30 (2018) <<https://stumejournals.com/journals/innovations/2018/1/30.full.pdf>>
- 7.V.A. Vashchenko, O.V. Kirichenko, D.I. Kotelnikov, et. al., Elektronnaya obrabotka materialov, **40** (6), 44 (2004) (in Russian).
- 8.I. Yatsenko, V. Antoniuk, O. Kiritchenko, et. al., Int. Sci. J. Innov., **1**, 9 (2016) <<https://stumejournals.com/journals/innovations/2016/1/9.full.pdf>>
- 9.G.V. Kanashevich, V.A. Vaschenko, M.O. Bondarenko, Bulletin of Cherkasy Engineering and Technological Institute, **2**, 189 (2000) (in Ukrainian).
10. I.V. Yatsenko, V.S. Antonyuk, V.A. Vashchenko, et. al., J. Nano-Electron. Phys., **11**(2), 02014 (2019). doi: 10.21272/jnep.11(2).02014.
11. I.V. Yatsenko, Trudy Odesskogo politehničeskogo universiteta, **1**(48), 65 (2016). doi: 10.15276/opu.1.48.2016.12 (in Ukrainian).
12. T. Fujita, H. Nishihara, J. Koyama, Opt. Lett., **6**, 613 (1981).
13. M.P. Rud, Bulletin of Cherkasy State Technological University, **3**, 49 (2005).
14. I. Yatsenko, V. Antoniuk, M. Bondarenko, V. Vashchenko, in: Intern. scien.-tech. conf. "Innovations in ingeneering" (Burgas, Bulgaria, Septem. 9-12, 2015), **20**/183, 64 (2015).
15. M. Bondarenko, V. Antonyuk, Yu. Kovalenko, et. al., Ukrainian Journal of Mechanical Engineering and Materials Science, **4** (1), 58 (2018) <<http://science.lpnu.ua/ujmeme/all-volumes-and-issues/volume-4-number-1-2018/research-volt-ampere-characteristics-wire>>, doi: 10.23939/ujmeme2018.01.058
16. R. Gaidash, S. Ralchenko, V. Medyanyk, M. Bondarenko, Mach. Technol. Mater., **10**, 398 (2018) <<https://stumejournals.com/journals/mtm/2018/10/398.full.pdf>>

Influence of chemical surface pretreatment on adhesion properties and protective effect of coatings

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Abstract: The quality of the resulting surface treatment is influenced especially by the pre-treatment of the substrate, the design of the surface treatment such as the choice of the coating system, the method and the quality of application. From a variety of chemical surface pre-treatment methods, Bonderite chemical pre-treatment is at the forefront. This chemical pre-treatment is used at ambient temperature, phosphate-free. It forms a nano-ceramic protective layer on steel, zinc and aluminum surfaces. The use of Bonderite gives the coating a high quality, which shows good adhesion and excellent corrosion protection. Contribution is devoted to the evaluation of these properties.

Keywords: SURFACE, CHEMICAL PRETREATMENT, ADHESION, CORROSION PROTECTION

1. Introduction

It is generally known when implementing a quality coating system, we are not able to reach the optimal results (adhesion, durability of coating etc.) as well if such coating is not applied for a suitably pre-modified and cleaned surface. The surface layer is very important from the whole part strain perspective. The properties on the surface are from a physical perspective different as inside the part. They depend on both a chemical composition microgeometry and a material structure. Technological and functional conditions of material elaboration affect physical and chemical properties of part surface. [1, 2]

With the industry development, there is a notable relation with a technology development such as chemical pre-modifications of surface. The aim of chemical pre-modifications is:

- to remove extraneous and own impurities by a chemical disruption of their bonding to the surface by the effect of appropriate tool,
- to remove possible defects of the surface and the surface structural deficiencies,
- to enlarge the surface actual area,
- to activate the surface.

The chemical pre-modification of metal surface involves such means of modifications at which chemical agents react with impurities which are attached or chemically fixed.

The following processes belong to chemical pre-modifications:

1. degreasing
2. staining
3. chemical and electrolyte polishing

Oilinesses on the surface of metals worsen adhesiveness of coatings as well as other properties. Those can cause an appropriate environment for corrosion creation by the effect of decomposition. Moreover, other impurities (old coating, corrosion fumes etc.) affects adhesiveness and visual properties of a respective coating. From the reasons stated above, it is necessary to dedicate a high attention to pre-modification of surfaces prior to the coatings application, as already small impurities on a surface prevent creating of quality coating. [3, 4]

2. Materials and methods

In the experimental part the steel plate S235JRG1 with thickness 2 mm was used. The proportions of testing samples were 100×50×2 mm. The chemical pre-modification was realized by degreasing utilizing two methods:

1. with Bonderite NT at the process parameters: concentration 20%, pressure 0,4 bar, pH 0,09 – 0,12.

2. without Bonderite NT in a degreasing solution Ridoline 1372 at process parameters: concentration 1%, pressure 0,4 bar, bath temperature 45-65 °C, pH 6,5. [5]

The surface pre-modification using Bonderite NT is a modern method for a surface treatment namely a conversion layer which was developed on a nano-technology basis. Such new technology provides advantages such as bath warming is not necessary, application is possible at a room temperature and an ongoing time needed for the dive of parts is approximately only 20 seconds. During applying the nano-structure layer on the materials surface is created, by which the passivation occurs as well and the whole process operation is eliminated what means a cost savings.

Such technology is remarkable also from the ecologic point of view. Along with a low energy consumption the product is characterized by the fact it does not contain any organic components. The conversion layer on a nano-technology basis in comparison with conventional phosphate also increases the area of surface and thus provides a bigger bearing surface for anchoring of subsequently applied coating by which there is its better adhesion, Fig. 1.

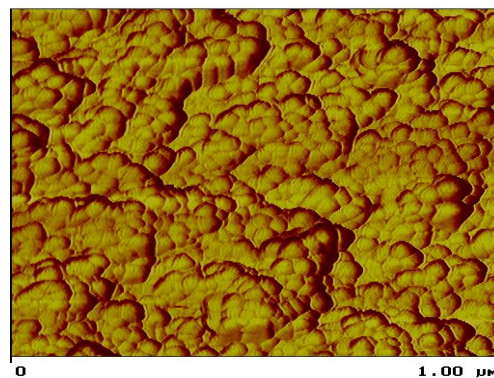


Fig. 1 The appearance of conversion layer based on nano technology

Two of types were used as coating:

- Stiga Pulverit 2020/3691
- Chrome silber Interpon MW031D.

Stiga is a powdery coating substance which basis is created by the combination of epoxide resin and polyester, mensural weight 678 g/cm³, a calcining period 15 minutes at 200 °C.

Chrome silber Interpon MW031D is a powdery coating substance which basis is created by epoxide resins with a chrome parts admixture, mensural weight is 1,7 g/cm³, a calcining period 15 minutes at 200 °C.

The coating substances application was realized by electro-static powder coating system GEMA PG 2, Fig. 2. The

coatings hardening was realized in a calcining furnace at temperatures recommended by the producer – for both coating it was set for 15 minutes at 200 °C.

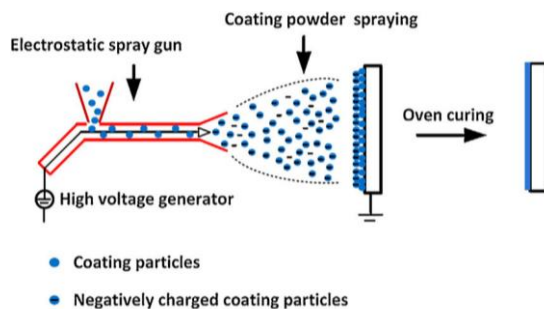


Fig. 2 The schema of electro-static powder coating system

At the experimental samples it was evaluated:

- *Thickness of coatings* in terms of norm STN EN ISO 2808, magnetically, using a device Elcometer 456. Prior to the experiment realization in a condensation chamber, the coatings thicknesses were measured on individual samples.
- *A mirror gloss of coatings* using a reflex geometry in terms of norm STN EN ISO 2813, Fig. 3, using a device Leskomer Pusch messtechnik, type Gloss 3.

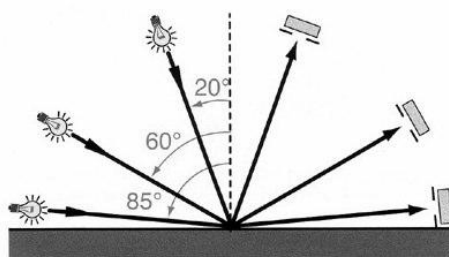


Fig. 3 The schema a mirror gloss of coating

- *The coatings adhesiveness* by a grid method in terms of norm STN EN ISO 2409 by a device Elcometer 1542, Fig. 4. The result was classified by a degree from 0 to 5 in terms of a subject norm. The adhesiveness of individual powdery coating surfaces was evaluated by a grid method before and after the exposition in the condensation chamber.

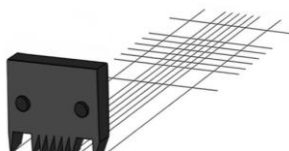


Fig. 4 The coatings adhesiveness by a grid method

- *A corrosion resistance* in a condensation chamber according to a norm STN EN ISO 3231. The samples exposition period in a condensation chamber was 384 hours. Before the exposition in a condensation chamber, the samples were cut on one side by a cross cut up to a basic material to ensure an access of corrosion environment to the basic material and to confirm the coatings resistance against under-corroding process.

3. Results and discussion

On the basis of implemented experiments, the following results were achieved:

The coatings thickness

At samples with Stiga coating with/without using Bonderite NT, the average thickness $68,5 \pm 0,1 \mu\text{m}$ of coating was achieved and at Chrome silber Interpon MW031D coating the thickness of $80,5 \pm 0,1 \mu\text{m}$. The achieved thicknesses respond to the minimal thicknesses which are recommended by the producer.

The mirror gloss of coatings

The average values of mirror sheen of tested coatings are stated in the Table 1. It is possible to conclude that the lowest value was achieved by the Stiga coating with Bonderite NT using and the highest one was achieved by Chrome silber Interpon MW031D coating without Bonderite NT using in both the measured directions.

Table 1 The gloss values coating

The coating type	The gloss value at the angle 60°	
	A transverse direction	A longitudinal direction
Stiga with Bonderite NT using	$89,4 \pm 0,1$	$88,3 \pm 0,1$
Stiga without Bonderite NT using	$90,1 \pm 0,1$	$89,4 \pm 0,1$
Chrome silber Interpon MW031D with Bonderite NT using	$99,0 \pm 0,1$	$98,3 \pm 0,1$
Chrome silber Interpon MW031D without Bonderite NT using	$101,2 \pm 0,1$	$100,1 \pm 0,1$

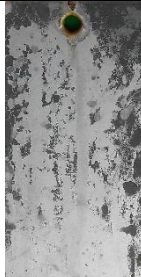
Coatings adhesiveness

At both types of coatings with Bonderite NT using, the degree 0 was evaluated after the exposition in a condensation chamber. That means in cut areas there was no adhesiveness damage detected between the coating and the basis nor at under-corroding of coatings. At the samples without Bonderite NT using the adhesiveness was decreased by the exposition in a condensation chamber, at Stiga coating system, the cohesion damage 2 was achieved and at a coating system Chrome silber Interpon MW031D the cohesion degree of damage 3 was achieved.

Corrosion resistance

The protecting effectiveness of coatings was evaluated by a simulated test with an artificial disruption of a coating integrity (the cross cut). Such disruption enables an access of the atmosphere to the surface of basic substrate. The method was selected by the reason the pores can be found in the coating. In terms of norm STN EN ISO 4628 the corrosion in the surroundings of a test cut was evaluated and moreover the defects intensity and coatings modifications. The evaluated area of sample was 100 mm^2 .

The evaluated results, Fig. 5 confirm the fact the coatings with Bonderite NT using show the lower corrosion degradation. The Stiga coating with Bonderite NT showed a degree 2 after the test while without Bonderite NT using the degree 3. The coating Chrome. The Chrome silber Interpon MW031D coating with Bonderite NT showed a degree 2 after the test, without Bonderite NT using the degree 3.

The exposition time in a condensation chamber					
48 hours		192 hours		384 hours	
Stiga coating without Bonderite NT					
					
area: without manifestations, cut: degree 1		area: without manifestations, cut: degree 2			
				area: without manifestations, cut: degree 3	
Stiga coating with Bonderite NT					
					
area: without manifestations, cut: degree 0		area: without manifestations, cut: degree 1			
				area: without manifestations, cut: degree 2	
Chrome silber Interpon MW031D coating without Bonderite NT					
					
area: without manifestations, cut: degree 1		area: color shade change, cut: degree 2			
				area: color shade change, cut: degree 3	
Chrome silber Interpon MW031D coating with Bonderite NT					
					
area: without manifestations, cut: degree 0		area: color shade change, cut: degree 1			
				area: under-corroding in a form of small brown points cut: degree 2	

4. Conclusion

Based on the achieved results of implemented experiments it is possible to state:

- when evaluating the coatings gloss no proven effect of conversion layer created on a basis of nanotechnology – Bonderite NT was detected,

- the coatings adhesiveness with Bonderite NT using stays without any modifications even after the exposition in a condensation chamber, at coatings without Bonderite NT using the

exposition in a condensation chamber the adhesiveness was decreased,

- the protecting coatings effectiveness, evaluated by a simulated test with an artificial disruption of the integrity by a cross cut, showed a positive effect of Bonderite NT using on a corrosion resistance of tested coatings.

The results of implemented experimental works enable to conclude that Bonderite NT using as a pre-modification method at the subsequent application of powdery coatings do not cause the change of gloss values as one of visual coatings properties, however it positively affects to their adhesiveness, as well as the corrosion resistance.

The experimental results which were obtained thus showed an increased quality of powdery coatings using a modern method of coating chemical pre-modification – a conversion layer Bonderite NT type.

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5. References

1. J. Brezinová J. et al. *Korózia materiálov a špeciálne technológie povrchových úprav*. TU v Košiciach, Košice (2020)
2. Guzanová, et al. J. Adhes. Sci. Technol. 28, 17 (2014)
3. M. K. Bhadu et al. ISRN Corrosion, Article ID 4647140 (2013)
4. Yang, Q. et al. Particuology 31 (2017)
5. J. Malatin *Hodnotenie vytýpovaných vlastností povlakov z práškových hmôt*, TU v Košiciach, Košice (2009)

High pressure die casting mould renovation by cladding

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Abstract: The paper presents the results of the research of the evaluation of the overlay layers quality made by the fusible arc methods. By applying arc welding methods, it is possible to significantly extend the life of injection molds and thus significantly reduce production costs. The newly formed layers must meet a number of requirements so as not to degrade the advantages of high-pressure injection technology over conventional casting technologies. High pressure casting solves most of the problems of conventional casting technologies such as: porosity of the casting, high surface roughness, long casting time, inability to produce thin cross-sections and low dimensional accuracy. During exploitation, the mold surface is damaged, mostly by thermal cracking and combined adhesive-abrasive wear. Material used for high pressure die casting permanent mold is a medium alloyed hot tool steel Uddeholm Dievar. Layers were made using three types of filler materials on the Fronius TransTig 4000. To eliminate the effect of mixing, three layers were made. The quality of the deposits was assessed by non-destructive and destructive tests.

Keywords: CLADDING, RENOVATION, LIFETIME,

1. Introduction

Shape mold parts and mold cores for the casting of aluminum alloys must possess suitable physical and mechanical properties at elevated temperatures. These properties are essentially defined by the thermal and mechanical stresses as well as by the interaction at the interface between the mold and the aluminum alloy melt (Fig. 1). In particular, the high velocities of the turbulent to dispersive filling of the mold cavity by the aluminum alloy melt, the high hydrodynamic pressures generated by the melt on the shape part of the mold and relatively high temperatures on the surface of shape parts of molds can significantly shorten the lifespan of molds and cores. All these phenomena cause the degradation of the surface of mold shape parts by mechanisms of erosion, abrasion, corrosion and heat fatigue of the mold, each of which act at the same time [1-2].

As the main mechanisms of mold damage, they identified wear (abrasive, adhesive, according to the purpose of the mold: mold for casting or die forging), erosion and mechanical and thermal fatigue. Jhavar [3] identified wear-influencing factors as follows: temperature, atmosphere, contact area, load, material properties, finish, velocity, lubrication, shape, vibration, sliding distance and type of motion. The material characteristics of molds and dies are also important, especially hardness, yield strength, elastic modulus, ductility, toughness, work-hardening characteristics, fracture toughness, microstructure, corrosion resistance, and in case of molds and dies in high-pressure die casting also resistance against solution in the melt [3].

Abrasive wear can occur in high-pressure casting molds due to insufficient mold cleaning between injection molding cycles in the area of the fitting surfaces between the mold parts. During this process, solidified particles of cast metal can act as abrasive particles. Depending on the shape and hardness of these particles, one of the following mechanisms of abrasive damage can occur: ploughing, cutting or fragmentation.

Adhesive wear of molds may occur in the event of insufficient lubrication and at high temperatures and friction rates. This results in an increase in the roughness of the mold surface and deterioration of the casting quality and process efficiency. The solubility of the mold material in the melt may also contribute to this. At high friction speeds in the presence of oxygen, oxidation of the mold material may also occur.

Thermal fatigue results from the cyclic change in the temperature of the functional mold surface relative to the material temperature next to the mold surface (Fig. 2). These changes cause thermal stresses and lead to the formation of a network of cracks. Chander [4] and Chen [5] developed a thorough analysis of the thermal fatigue and identified the factors that affect it [6-8]. They have been divided to die temperature cycle-related factors (preheating temperature, surface temperature of the die, holding time at peak temperature, cooling rate), basic die material properties' factors (thermal expansion coefficient, thermal

conductivity, hot yield strength, temper resistance, creep strength, ductility) and to stress raisers' factors (fillets, holes and corners, surface roughness) [9-12].

Ansys software can be used to simulate injection molding processes and calculate the temperature distribution on the surface of the mold part and the heat flow into the mold (Fig. 3).



Fig. 1. Aluminum injection mold



Fig. 2. Cracks on the mold surface

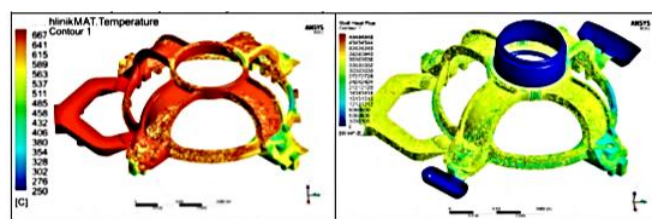


Fig. 3. Temperature field of the mold at $1.5 \times 10^{-3}s$ (left) and heat flux density between Al and the mold at $1.5 \times 10^{-3}s$ (right)

2. Materials and Methods

The material of the test samples by chemical composition and heat treatment regime was the same as the material used for the molded parts of die casting molds Uddeholm Dievar (Tab. 1). Delivered semi-finished product was soft-annealed. Material of the test samples by chemical composition and heat treatment regime was the same as the material used for the molded parts of the die-casting molds. Test samples 2.5 and 3.5 mm thick were taken from rolled Uddeholm Dievar steel bars with a diameter of $\varnothing 50.8$ mm and 25 mm. Delivered semi-finished product was soft-annealed.

Chemical elemental analysis of metal samples and welds was determined with a Belec Compact Port spectrometer. All samples were heat treated mode: heating to 650 °C / 15 min / 850 °C / 15min / heating to 1000 °C / 30min / oil, 2x tempering 580 °C / 2 h / on air to a final hardness of 44 HRC and on both sides 49 ground to a roughness of Ra 0.2. GTAW welds were made on the samples with three types of additional materials - chemical composition of which is in Tab.2 to Tab. 4. The weld was made as a single layer. The diameter of the additional materials was ø 1.6 mm. Additive material was fed manually. The flow rate of the inert atmosphere I 1 - EN ISO 14 175 (100% Ar 4.6) was 18 l / min.

Table 1: Chemical composition and mechanical properties of steels Uddeholm Dievar

Chemical composition in (% wt.) / Fe balance/					
C	Mn	Si	Cr	Mo	V
0.338	0.441	0.125	5.041	2.290	0.532
Mechanical properties					
Tensile strenght R _m [MPa]	Yeld strenght R _{p0.2} [MPa]	Elongation A5 [%]	Reduction of area [%]	Hardness [HRC]	
1490	1210	13	55	44	

Table 2: Chemical composition filler material W/MSG 3-GZ-45-T – DIN 8555

Chemical composition in (% wt.)						
C	Mn	Si	Cr	Mo	Ti	Fe
0.25	0.7	0.5	5.0	4.0	0.6	Bal.

Cladded sample A.

Table 3: Chemical composition filler material W/MSG 3-60 -T – DIN 8555

Chemical composition in (% wt.)							
C	Mn	Si	Cr	Mo	W	V	Fe
0.35	0.4	1.0	5.0	1.5	1.3	0.3	Bal.

Cladded sample B.

Table 4: Chemical composition filler material Cronitec RC 44

Chemical composition in (% wt.)							
C	Mn	Si	Cr	Mo	W	V	Fe
0.35	0.6	0.7	5.3	1.5	0.3	0.8	Bal.

Cladded sample C.

Used cladings parameters for the samples are in Tab. 5. Clads were made on a Fronius MagicWave 4000 Job. W + 2% ThO₂ was used. Diameter of electrode 2.4 mm. Electrode Tip angle 30 °. Arc length 2 mm. Post welding gas flow time 10sec.

Table 5: Used cladding parameters

Cladding parameters				
Method	Sample	Cladding current [A]	Cladding voltage [V]	Current type / polarity
141	A	95	13,4	DC -
141	B	95	13,4	DC -
141	C	95	13,4	DC -

3. Results and discussion

Within experiments, the quality of the clad layers was evaluated by a visual test in accordance with EN ISO 17637, where the surfaces of the clads were evaluated under illumination of 500 lux. Presence of surface defects such as e.g. cracks, surface cavities, spatter, etc. is monitored. Presence of surface defects was not detected on the evaluated weldment surfaces. Light microscope was used on transverse metallographic sections. The microstructure of the welded clads and base material were highlighted by etching in the following etching agents: 120 mL CH₃COOH, 20 mL HCl, 3 g picric acid, 144 mL CH₃OH). Microstructures were observed using OLYMPUS GX71 light optical microscope (OLYMPUS Europa Holding GmbH, Hamburg, Germany). Basic material (Fig. 4) has a

structure formed by fine-grained line sorbitol. The weld metal microstructures are documented in Fig. 5 to Fig. 7.

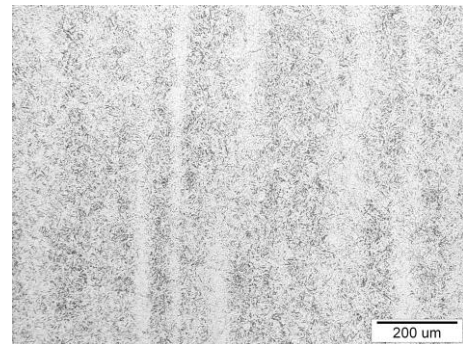


Fig. 4. Structure of base material Dievar



Fig. 5. Structure of clad layers sample A

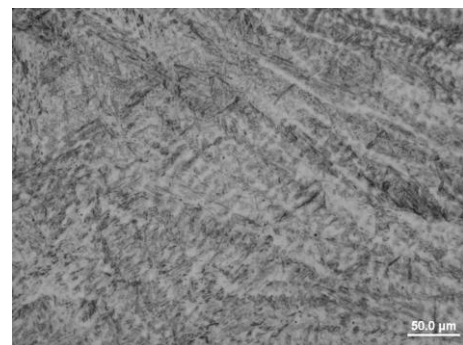


Fig. 6. Structure of clad layers sample B



Fig. 7. Structure of clad layers sample C

Clad metal has a characteristic dendritic structure with oriented grains with a well-readable solidification direction. Mixing of the clad metal with the base material was minimal and the area of mixing of the metal did not exceed 400μm. The HAZ was also narrow, which indicates suitably selected cladding parameters, as well as the good skill of the welder, given that it was not a mechanized feed during cladding, but manual cladding. No internal defects were noted on the transverse sections. The presence of massive carbide inclusions was not observed on the structures. The

structures of the cladding layers are formed by tempered martensite - sorbitol. Which is in accordance with the chemical composition of the realized clads. As part of the evaluation of the clad metal properties, hardness values were determined on transverse metallographic sections, which is documented in the graphs in Fig. 8 to 10.

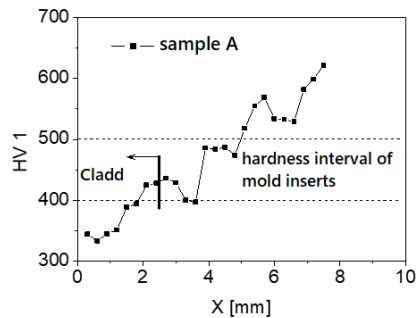


Fig. 8. Hardness of cladd sample A

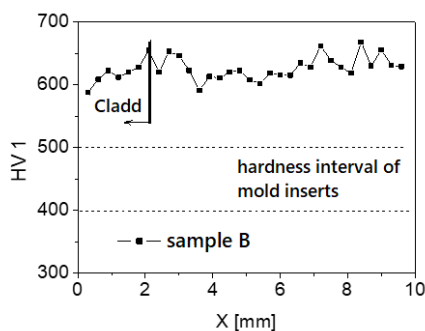


Fig. 9. Hardness of cladd sample B

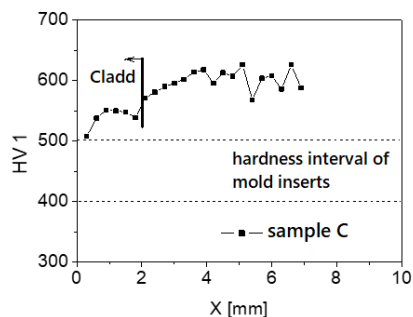


Fig. 10. Hardness of cladd sample C

For sample A, the thickness of cladding was max. 2.3 mm. The hardness values of the cladding layer in the range of 330-430HV1. The maximum hardness value 430HV1 corresponds to the recommended values for injection mold inserts. However, up to a clad thickness of 2 mm for sample A (Fig. 8), the hardness is insufficient and therefore it is not possible to recommend the given type of additional material for the renovation of injection mold inserts. The influence of significant heterogeneity of mechanical properties of the cladding layer compared to the sub-cladding layers will be the goal of further research. In the case of additional materials used in the production of samples B and C, it is possible to observe a significant increase over the measured hardness compared to samples A already in the surface layer of the clad metal, where the measured values exceed the recommended values for injection mold inserts (400-500HV) (Fig. 9, Fig. 10). The finished clads of samples A and B had a height of approx. 2.0mm. The highest hardness values were recorded in the clad layers of samples B. As the injection mold is loaded with a combined load, the service life of which is limited by several factors, it can be high

resp. above-limit hardness (above 430HV) a factor degrading the resulting complex values of resistance to all tribodegradation factors. From the point of view of increased susceptibility to crack initiation resp. formation of surface and subsurface defects. Of the additional materials used, the surface hardness values closest to the required values show clad on sample C. The measured hardness values are in accordance with the chemical composition of the additional materials used. The lowest hardness values were shown by the clad metal made with the additive material W / MSG 3-GZ-45-T - DIN 8555. lower hardness values were probably due to the absence of carbide-forming elements W and V. Chemical composition of the filler materials for the production of samples B and C was similar, corresponding to only a small difference in the measured hardness values of the weld layers.

4. Conclusions

Paper presents a part of the experiments carried out in evaluating the quality of the clad layers of the functional surfaces of the injection molds. These are components exposed in demanding tribodegradation conditions and their service life is significantly limited. Possibilities of surface renewal by cladding resp. cladding and coating (PVD, CVD) are a suitable solution for the restoration of these functional surfaces of molds and cores. To a large extent, they provide significant economic savings for companies. The processes of cladding and local repair of damaged parts of molds are dominated by arc methods, namely GMAW and GTAW welding(cladding). Due to the chemical composition of materials for the production of injection molds, the aim is to minimize the heat introduced into the clads. This can be extinguished by using the pulse welding mode, resp. application of the CMT (Cold Metal Transfer) method. In addition to the presented arc welding methods, energy beam welding methods are being used in an increasing volume, especially laser welding. The laser beam makes it possible to minimize the amount of heat introduced during welding, which significantly minimizes negative metallurgical changes in the sub-weld areas of medium and high-grade steel grades.

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5. References

1. J. Hirsch. Trans. Nonferr. Met. Soc. China. **24**. 1995-2002, (2014)
2. C.G. Pickin, S.W. Williams. M. Lunt. J. Mater. Process. Technol. **211**. 496-502, (2011)
3. S. Jhavar, C.P. Paul, N.K. Jain. A review. Eng. Fail. Anal. **34**. 519-535, (2013)
4. S. Chander, V. Chawla, Mater. Today Proc. **4**. 1147-1157, (2017)
5. C. Chen, Y. Wang, H. Ou, Y. He, X. A. Tang, J. Clean. Prod. **64**. 13-23, (2014)
6. A. Taylan, L. Blaine, Y.C. Yen, Y.C. CIRP Ann. **50**. 404-422, (2001)
7. J. Lin, S. Carrera, A.O. Kunrath, D. Zhong, S. Myers, B. Mishra, P. Ried, J.J. Moore, J.J. Surf. Coat. Technol. **201**. 2930-2941, (2006)
8. J. Brezina, J. Viňáš. *Novus Scientia* 2019, **16**. 172-175, (2019)
9. J. Brezinová, J. Viňáš, M. Džupon, A. Guzanová, D. Draganovská, *PRO-TECH-MA* 2019, **25**. 13-14, (2019)
10. J. Viňáš, M. Džupon, J. Brezinová, J. Brezina. *PZVAR meeting* 2019, **16**. 1-8, (2019)
11. P. Mohyla, Z. Kuboň, R. Čep, A. Janásek, I. Samardzic. *Metallurgija*, **53**. 25-28, (2014)
12. J. Janovec, A. Výrostková, A. Holý. J. Mater. Sci. **27**. 6564-6572, (1992)

Influence of complex ultrasound vibrations and composite lubricants on wear resistance of materials of endoprosthesis

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Abstract: As a rule, parts that are made of titanium alloys are critical parts that can work in corrosive medium, accept alternating loads, have certain parameters of surface quality and surface layer. A finite-element simulation of a burnishing process of titanium alloy Ti-6Al-4V (an alloy that is widely used in medicine, as an example in endoprostheses) with/without ultrasonic loading at various processing speeds was carried out. It is established that when burnishing with ultrasonic vibrations of the tool, it is possible to obtain a qualitatively different picture of the distribution of residual stresses in the surface layer of the part. The features of the contact interaction of the tool with the workpiece surface were established for ultrasonic vibrations of the tool. For finite element simulation two types of ultrasonic vibrations were chosen (according to real ultrasonic tool): longitudinal and longitudinal-torsion vibrations. It is shown that the use of ultrasound can reduce the temperature of the deformation zone, which is extremely important when processing titanium alloys. It was also found that the use of metal-containing lubricant can improve the surface quality parameters after ultrasonic burnishing.

Keywords: TITANIUM ALLOYS, SURFACE PLASTIC DEFORMATION, ULTRASOUND, COMPOUND ULTRASONIC VIBRATIONS, BURNISHING, METAL-CONTAINING LUBRICANT, COMPOSITE LUBRICANTS.

1. Introduction

Titanium alloys are used in various industries: chemical, aerospace, medicine, automotive, shipbuilding, etc. Titanium is an indispensable material for parts of gas turbine engines, mainly for the manufacture of a compressor assembly, i.e. for discs, blades, guide units, intermediate rings, shafts, etc.

In medicine, titanium is used primarily because of the biological inertness in relation to a human organism, high corrosion resistance, high mechanical properties, availability, and relatively low price. The Ti-6Al-4V alloy is widely used in implantology, orthopedics and surgery, which significantly exceeds the "competitors" based on cobalt and stainless steels in operational parameters.

Titanium-based alloys are known for being difficult to machining, especially by surface plastic deformation (SPD) methods. An effective SPD is the burnishing process, as a result residual compressive stresses are formed in the surface layer of the part that prevent the formation of microcracks, and the surface roughness decreases.

In research papers [1-3], the results of diamond burnishing of parts made of titanium alloys VT22 and VT23 with preliminary application of solid polymer lubricant to their surface were presented, as a result of which a high-quality surface was obtained after deformation without its destruction. However, the necessity for this technology is that the manufacturing process is more expensive.

A promising direction in the intensification of SPD processes, including the burnishing process, parts made of titanium alloys is the modification of lubricants with antifriction additives, as well as the modification of lubricants with nano- and ultrafine powders of soft metals (copper, tin, aluminum, etc.). An additional introduction of metal powders allows to reduce the friction coefficient and increase the specific processing force, the value of which provides an increase in residual compression stresses [4, 5]. In most studies, the effect of ultrafine powders on lubricants has been studied in motor oils. In [4, 5] the processes of prolonged contact of engine parts were studied, the volume content of metal powder ranges from 0.5-3.0%. With this powder content, the rheological properties of the lubricant will not change significantly. In SPD processes the specific loads of the contact interaction of the tool with the surface of the part are significant, therefore, it is necessary to increase the volumetric content of metal powder in the lubricant.

An effective way to intensify the burnishing process of difficult-to-treat materials, particularly titanium and its alloys, is to apply ultrasonic vibrations to the tool [6,7,8]. However, in view of the high adhesion of titanium and its alloys titanium seizes with the tool material, resulting in increased tool wear and deterioration of the surface of the workpiece [9].

2. Problem discussion

The wear resistance of friction pair is one of the quality parameters of hip, shoulder and wrist endoprosthesis. Wear resistance defines the life of endoprosthesis and impact of wear products on the human body.

Based on previous research it is proposed to use the ultrasonic burnishing process as surface plastic deformation process at finish stage of machining for increasing the wear resistance of materials of friction pair in endoprosthesis. Minimization of adhesion part of friction during treatment of cobalt-chromium-molybdenum, titanium and zirconium alloys will be obtained by using of compound ultrasonic vibrations of deforming tool and composite lubricants. This treatment will provide a detail with high parameters of surface and surface layer.

The influence of processing speed during ultrasonic burnishing on the surface texture was studied on a workpiece made of titanium alloy VT23. Processing modes: processing speed V : 70 mm/s, 180 mm/s, 300 mm/s and 600 mm/s, static force $P=100$ N, tool material – tungsten carbide, tool radius $R = 3$ mm, lubrication–oil I20. Surface №1 - 70 mm/s, Surface №9 - 600 mm/s (see Fig. 1 and Fig. 2).

At speeds in the range from 70 to 180 mm/s (see Fig. 2, a), a homogeneous texture is observed in the form of alternating dents formed from the indentations of the tool into the surface of the workpiece, light interference is observed on the surface, and no visible damage of material is observed. With an increase in the processing speed to 600 mm/s (see Fig 2, b), a texture with alternating traces of tool indentations is also observed, however, alternating darker regions are also observed, having elongation in the direction of rotation of the workpiece (microdestruction of the material).



Fig. 1. Surfaces of VT22 after ultrasonic burnishing on different conditions.

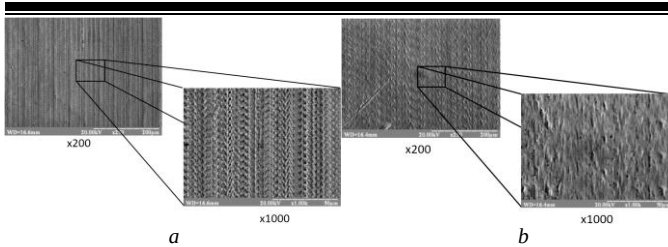


Fig. 2. Surfaces of VT22 after ultrasonic burnishing with tool speed 70 mm/s (a) and 600 mm/s (b).

It is possible to ensure high surface quality parameters at high processing speeds by reducing shear deformations in the surface layer of the workpiece. After treatment of titanium alloys by shot peening or ball rolling, it is possible to obtain a workpiece surface with high quality parameters without destroying it. However, these methods cannot handle thin-walled parts or provide dimensional processing. In this work, we studied the influence of the complex trajectory of the tool using the finite element (FE) method in the QForm program (ultrasonic longitudinal-transverse vibrations in FE simulation, ultrasonic longitudinally-torsion vibrations in full-scale experiment).

3. Objective and research methodologies

FE simulation was carried out according to three schemes: a) - burnishing without ultrasonic vibrations of the tool; b) - burnishing with ultrasonic longitudinal (USL) tool vibrations; c) - burnishing with ultrasonic longitudinal-transverse (USLT) tool vibrations (see Fig. 3).

The FE model considered elastic-plastic deformation with thermal processes. Material - titanium alloy Ti-6Al-4V. The coefficient of friction according to the Coulomb is 0.25. The vibration frequency of 22 kHz was set in tabular form. To obtain a better picture of the distribution of the stress-strain state, the FE mesh of the workpiece was compacted at the area of contact with the tool (see Fig.4).

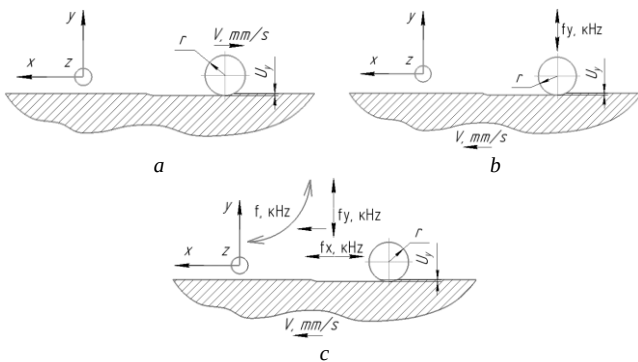


Fig. 3. Burnishing process schemes: a – without US vibrations; b – with USL vibrations of tool; c – with USLT vibrations of tool.

First, a FE simulation of a single loading-unloading of the workpiece was carried out, process is similar to the indentation of the ball during shot peening. Residual compressive stresses are formed in the surface layer after unloading, both in the axial and in the tangential directions (see Fig.5).

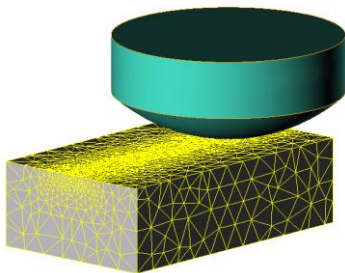


Fig. 4. Finite element model of the workpiece.

It has been established that the temperature of the surface layer of the workpieces during surface plastic deformation without US

vibrations, and with US vibrations at different speeds is almost the same (see Fig.6).

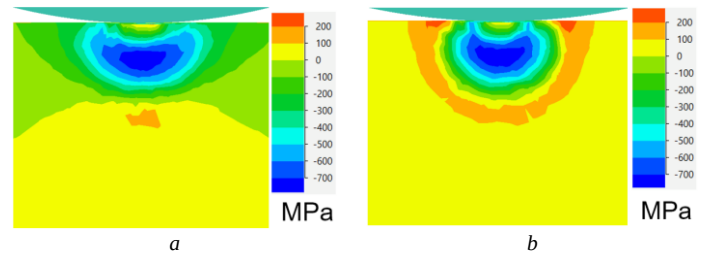


Fig. 5. Distribution of residual axial stresses (a) and residual tangential stresses (b)

At a speed of 300 mm/s, the minimum temperature corresponds to processing with USLT vibrations. To obtain more accurate data on the influence of the processing mode on the temperature the tool must pass a longer distance.

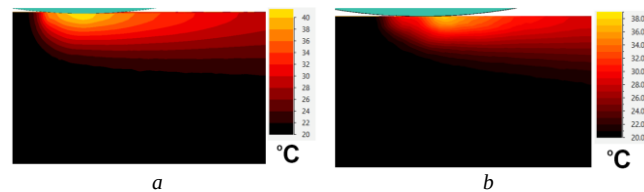


Fig. 6. Temperature distribution in the deformation zone according to process with tool speed 300 mm/s: a – burnishing without US vibrations; b – burnishing with USLT vibrations

The FE simulation showed that the quantitative and qualitative picture of the distribution of residual stresses depends on the type of ultrasonic vibrations and the processing speed. The operational reliability of the product depends on the size and sign of residual stresses. As a result of burnishing process without US vibrations, residual tensile axial stresses and the smallest residual compressive tangential stresses arise on the surface and in a thin surface layer. The largest residual axial and tangential stresses occur when burnishing with USLT tool vibrations (see Fig.7).

With an increase in the processing speed from 300 to 600 mm/s, the distribution of residual stresses over the material depths after burnishing without US practically does not change. After burnishing with USL and USLT vibrations, the picture of stresses changes significantly, the value of compressive residual stresses decreases, at processing speed 600 mm/s the value of residual compressive stresses on the surface is less than in the near-surface layer (in contrast to processing speed 300 mm/s). This can be caused by two factors: a smaller volume of material deformed by the tool due to vibrations and an increased processing speed; increasing shear strain by increasing the processing speed (see Fig.8 and Fig.9).

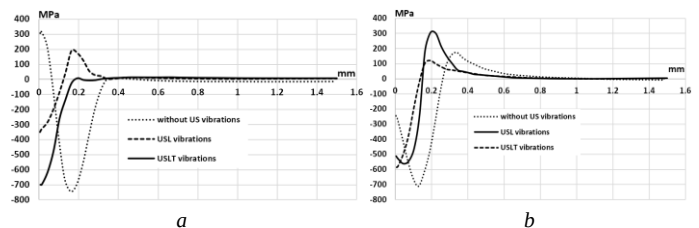


Fig. 8. The distribution of residual stresses in the near-surface layer of material after burnishing process depending on the type of US vibrations of tool ($V = 300$ mm/s): a – axial stresses; b – tangential stresses

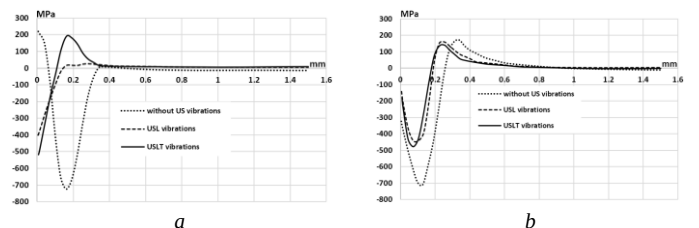


Fig. 9. The distribution of residual stresses in the near-surface layer of material after burnishing process depending on the type of US vibrations of tool ($V = 300$ mm/s): a – axial stresses; b – tangential stresses

The pressure on the workpiece is greater during burnishing without US vibrations than during burnishing with US vibrations. During burnishing with US vibrations, regardless of the type of vibrations, the pressure on the workpiece in the central part will be almost the same, the pressure is greater with USLT vibrations along the periphery of the zone (see Fig. 10). The area of pressure on the workpiece, both during indentation and during lifting the tool, will be greater during USLT vibrations (due to the pendulum movement of the tool).

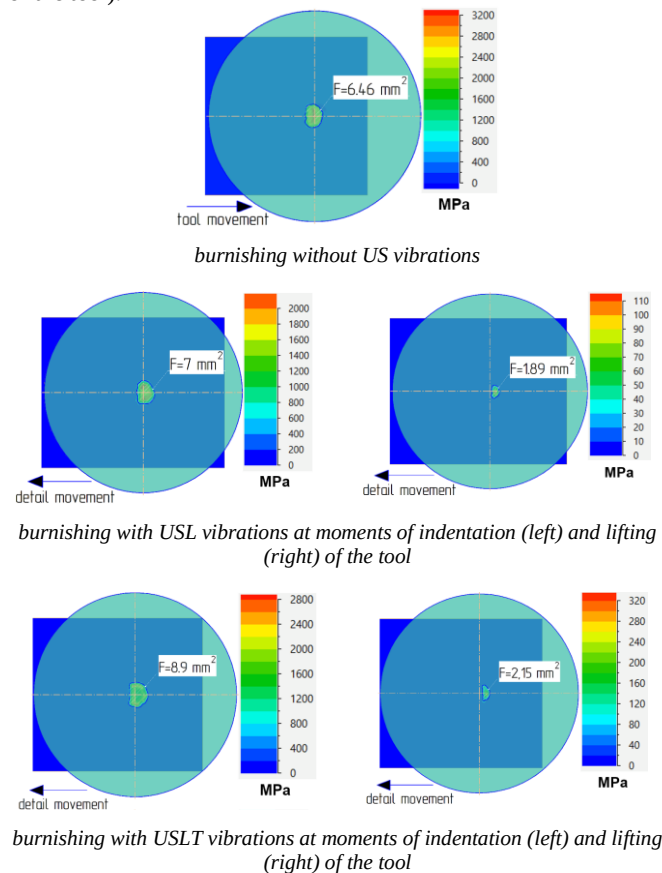


Fig. 10. Pressure spot on the workpiece at the extreme points of the tool movement during deformation ($V=300$ mm/s)

In accordance with the pressure on the workpiece, more tool wear will occur during burnishing without US vibrations. Tool wear is 25-30 times less during burnishing with US vibrations (see Fig.11). True, it is worth noting that the calculation does not consider the dynamic component of the impact of the tool on the surface.

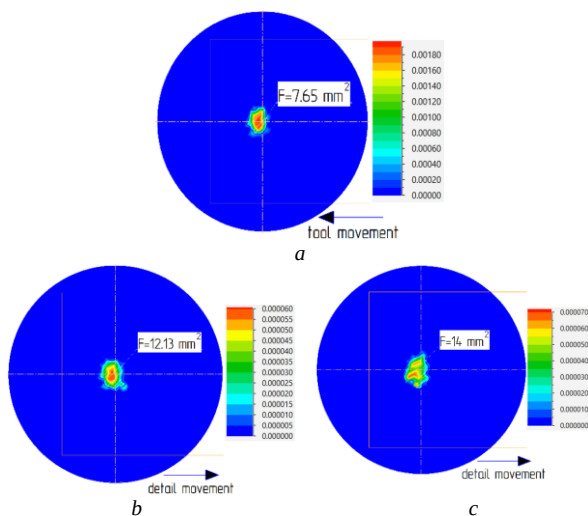


Fig. 11. Tool wear after 3 mm of burnishing pass ($V=600$ mm/s): a – burnishing without US vibrations of the tool; b – burnishing with USLT tool vibrations; c - burnishing with USLT tool vibrations.

The basis of the metal-containing lubricant was industrial oil I20. Powders of copper-Cu and aluminum-Al with an average particle size of $10\text{ }\mu\text{m}$ were selected. The maximum volumetric content of the powder was 32% of the volume of oil.

The surface of the VT22 alloy workpiece, after burnishing at a speed of 300 mm/s with I20, has a rougher texture, traces of the indentation of the tool into the surface of the workpiece are more clearly visible in comparison with the treatment with metal-containing lubricant (see Fig. 12).

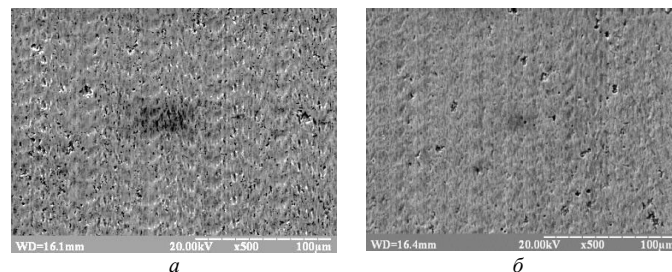


Fig. 12. Microrelief of burnished surfaces at a processing speed of 300 mm/s with copper-containing (a) and aluminum-containing (b) lubricant.

The most uniform surface microrelief, with complete deformation of the machining traces from turning and without visible traces of tool indentation into the surface, corresponds to treatment with I20+Al lubricant

4. Conclusion

It has been established that burnishing with USLT vibrations makes it possible to obtain large values of residual compressive stresses in the surface layer. The use of US vibrations reduces the temperature in the deformation zone and tool wear. The use of USLT vibration during burnishing will allow to process titanium alloys at high speeds without destroying the surface of the detail. The burnishing efficiency with US vibrations depends on the linear speed of the detail material in the contact zone. As a result of simulation and full-scale experiment, it was found that the use of metal-containing lubricants allows to obtain a high-quality surface of parts made of titanium alloys due to the formation of an intermediate layer between the surface of the part and the tool.

The use of metal-containing lubricants extends the technological regimes of the ultrasonic burnishing of titanium alloys, by increasing the processing speed and the specific deformation forces, at which there will be no adhesive seizure of the workpiece with the tool.

5. References:

1. O. Rosenberg, E. Pashchenko, S. Sheikin, I. Rostotsky. *Technological systems*. 2 (2007).
2. A. Titov, T. Labur, A. Puzyrev. *Bulletin of NTUU "KPI". Mechanical Engineering*. 53 (2008).
3. O. Molyar, V. Trofimov. *Collection of scientific articles "Problems of resource and safety of operation of structures and machines"*. pp. 613-617 (2009).
4. A. Kuzharov. *PhD dissertation* (2004).
5. A. Kotnarowski. *Materials science (medziagotyra)*. 12. (2006).
6. E. Lesyuk, V. Alekhine, Kim Chang Sik. *Bulletin of mechanical engineering*. 9, pp. 52-55. (2008).
7. G. Osipenkova, V. Pegashkin, I. Filimonov. *Bulletin of mechanical engineering*. 2, pp. 74-75 (2009).
8. T. Petrovskaya. *Bulletin of Volgograd State Technical University*. 11, pp. 71-73 (2009).
9. V. Titov, V. Nikitenko, A. Titov, A. Plivak, A. Lavrinenkov. *Processing materials by pressure*. 20, pp. 166-172 (2009).

Porosity and corrosion properties of CoCr alloys for dental application

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Abstract: The paper deals with the problem of occurrence of internal defects in materials produced by SLM technology. The influence of the position of materials on the platform during the SLM on selected properties - porosity and corrosion resistance were examined. The reuse of non-compacted powder (three times recycled powder) and its effect on porosity and corrosion resistance of materials was also tested. Porosity was measured on metallographic sections in two perpendicular directions by image analysis, corrosion properties were tested by linear polarization method.

Keywords: CoCr ALLOY, SLM, LASER MELTING, POROSITY, CORROSION RESISTANCE

1. Introduction

One of the most important areas of application of SLM technology is biomedical engineering, where it is possible to use geometric freedom and tailor implants to every patient in a short time. A typical example is the production of hip joints from titanium alloys or dental implants from cobalt-chromium or titanium alloys. The technology makes it possible to produce implants with new functions - hollow structures, gradient porosity, adapted stiffness or surface structure.

One of the most significant advantages of SLM technology is the very efficient use of material, theoretically up to 100%, thanks to the possibility of recycling and reusing unmolten metal powder.

A reliable automatic supply of recycled powder during the entire SLM process is ensured by an additional modular powder supply unit (PSV) connected to the machine. This unit has a 90 liter powder tank, which is sufficient for any production process. It is fully automated, so no manual intervention is required. An integrated ultrasonic screen placed under the tank sieves the metal powder before being fed into the production process. This ensures that large particles or foreign objects do not enter the SLM process. The transport of the powder between the PSV, the SLM machine and the dismantling station is performed using vacuum technology and is fully automated. The transport, screening and storage of the powdered material take place in a closed system under an inert gas atmosphere. Contactless handling ensures maximum safety.

In addition to this system, there is also a semi-automatic screening of the metal powder in an inert gas atmosphere. The metal powder obtained from the overflow containers from the SLM process is manually transferred to the powder supply manual (PSM) station. The sieved powder is collected in separate containers under the system and is ready for further use. Oversized grain returns to the atomization process. To speed up the entire production process, the sieving process is carried out in parallel with the production itself.

Despite this well-operating system, defects, sudden changes in the surface appearance and mechanical properties of the products occur sporadically on the products. In connection with this, the question arises, whether repeated recycling of powder can lead to changes in powder properties that could affect the mechanical properties of the parts produced. It is also logical to ask another question whether the position of the product on the building platform in the SLM process will be reflected in a variation of some material properties of the product. Guzanová [1,2] and Brezinová [3] demonstrated this dependence with DMLS technology and Ti6Al4V powder. The variation of product properties depending on the platform position appears to be related to the different angle of incidence of the laser beam at the centre and at the edge of the platform, resulting in a different projection area of the beam on the powder surface and hence different energy density. Due to the fundamental similarity in operation of the laser beam in DMLS and SLM processes, it is possible to assume this dependence works also in SLM technology.

The aim of the paper is therefore to analyse the porosity, hardness and corrosion resistance of materials produced by SLM technology depending on their location on the building platform when fresh and three times recycled powder is used.

2. Materials and methods

Starbond Easy Powder 30 (Scheffner Dental Alloys, Germany), was used for test samples making. Chemical composition of powder used given in wt. % is as follow: 61% Co, 27.5% Cr, 8.5% W, 1.6% Si, and C, Fe, Mn <1%. Mechanical and physical properties of the material: $R_{p0.2}$ 760 MPa, UTS 1090 MPa, elongation 15%, Young's modulus of elasticity 225 GPa, hardness 425 HV 10, density 8.5 g.cm⁻³. The powder was processed at Mlab Cusing R machine, Germany. Parameters for dental applications, locked and protected by the powder manufacturer, were used in the production of the test specimens. The dimensions of test samples were 20×20×2 mm. Their placement on the build platform and designation of individual sectors, as well as the direction of movement of the recoater blade is shown in Fig. 1. Samples made from fresh, unused powder, and samples made from three-time recycled powder were evaluated. Sectors 1, 3, 5, 7 and 9 were analysed in the experimental part.

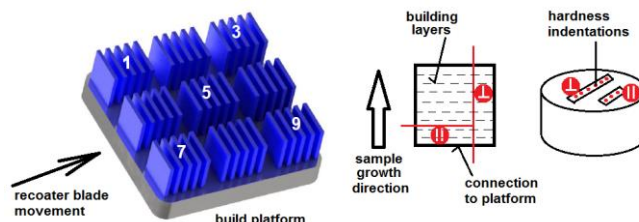


Fig. 1 Positioning of samples, philosophy of metallographic cross-sections collection and measurement of hardness

Metallographic sections taken in two perpendicular directions (perpendicular and parallel to the sintered layers) were used for measurement of porosity by image analysis and also for hardness test. Hardness was measured on a Shimadzu HMV-2 hardness tester under a load of 980.7 mN (HV 0.1) and full load time of 15 seconds. 30 measurements were performed in each sector and direction. Measured values were then subjected to statistical analysis by ANOVA and Tukey's test.

A Potentiostat SP 150 (Bio-Logic Sciences Instruments, France) and a 3-electrode connection were used to evaluate the corrosion properties of the material by the potentiodynamic method: working electrode (measured material), reference electrode (SCE – saturated calomel electrode), auxiliary platinum electrode. The measurement was performed in 9% NaCl solution (saline). First, the material was stabilized in solution for 30 minutes to determine the OCP (open circuit potential). Stabilisation of the corrosion system was followed by polarization ± 250 mV from OCP. The corrosion current density i_{corr} , the corrosion potential E_{corr} , the corrosion rate r_{corr} and the polarization resistance R_p were determined by analysis of the measured curves.

3. Results

Porosity of materials

Metallographic sections were observed on a light microscope, analysed by image analysis, and the porosity was then expressed as a percentage of the total observed area. The results of the material porosity found in the individual sectors and directions for fresh and recycled powder are given in Table 1.

Table 1 Porosity of materials in particular sectors and directions, %

Sector	⊥			
	fresh	recycled	fresh	recycled
1	0.35	0.99	18	19.90
3	0.37	1.25	0.94	0.41
5	3.15	5.4	4.2	7.82
7	0.33	0.25	0.2	0.24
9	0.39	0.2	0.26	0.35

The results show that increased porosity was found in sectors 1 and 5, more pronounced in the || direction. In other sectors, the porosity was up to 1%. The pores in selected sectors are shown in Fig. 2.

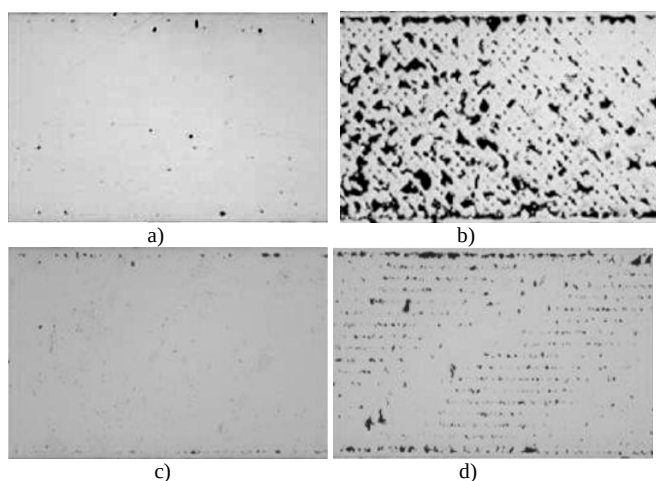


Fig. 2 Porosity of samples made of fresh powder, a) Sector 1, direction ⊥, b) Sector 1, direction ||, c) Sector 5, direction ⊥, d) Sector 5, direction ||

The increased porosity found in particular sectors of the build platform where fresh powder was processed was not coincidental, because in another, independent build platform where the recycled powder was processed, increased porosity was found in the same sectors.

Hardness of materials

Table 2 shows the hardness of materials made from fresh and recycled powder, measured in both directions, as an average of 30 measurements.

Table 2 Hardness HV 0.1 of materials in particular sectors and directions

Sector	⊥			
	fresh	recycled	fresh	recycled
1	465	467	immeasurable	immeasurable
3	472	475	455	451
5	428	435	439	433
7	473	482	452	457
9	488	474	458	463

As can be seen from Table 2, the minimum hardness values occur in sector 5, in both directions, which corresponds with the increased porosity values. The highest hardness values appear in sectors 9 and 7, where the lowest porosity was found. In sector 1, || direction, hardness could not be measured because of the high porosity in the metallographic section plane.

Fig. 3 shows box-plots of hardness including mean value, standard deviation and range.

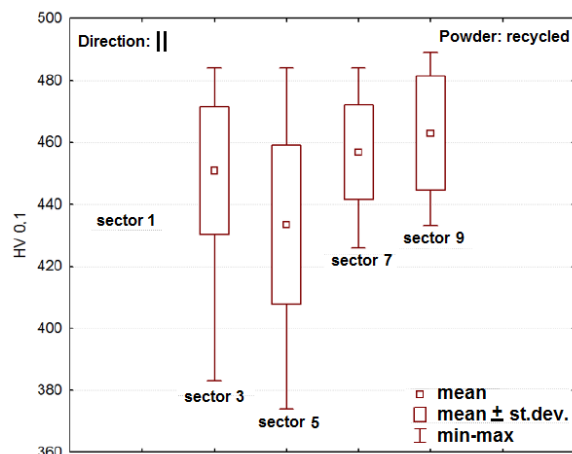
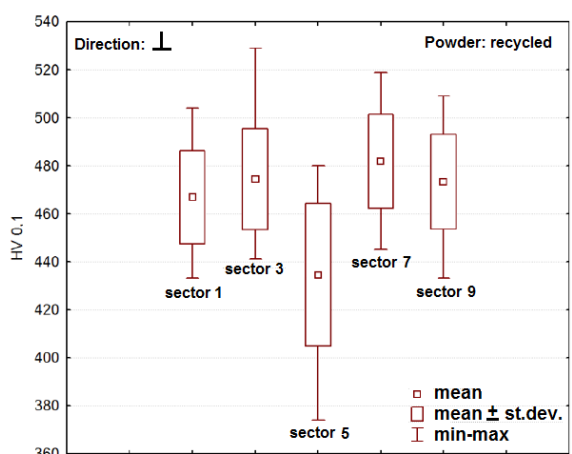
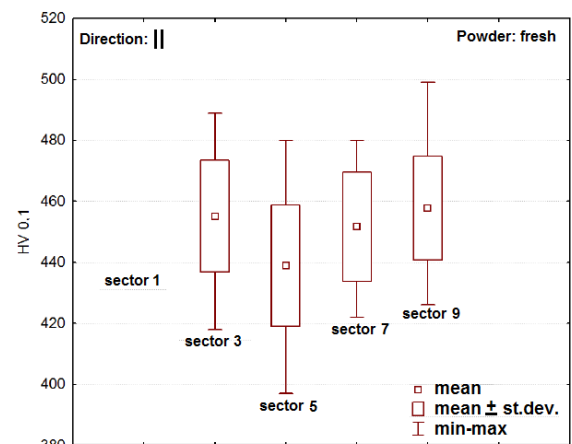
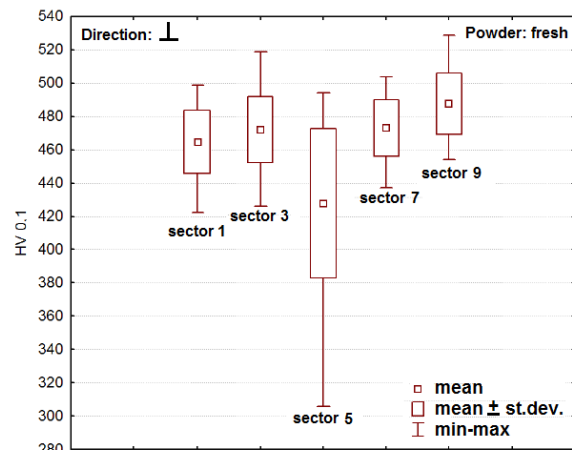


Fig. 3 Box-plots of hardness with standard deviations and range (min-max)

Fig. 3 shows that the hardness measured in sector 5 differs significantly from that in other sectors. This applies both when comparing directions and when comparing fresh and recycled powder. It differs not only by the mean value, which is lower than in other sectors, but also by a wider range of variation. From the observation of the individual box plots it is also clear that the variation range in the $\perp$ direction is lower than in the $\parallel$ direction. Therefore, the measured values had to be subjected to a statistical analysis to confirm or disprove the hypothesis of equality of mean values. On the one hand, comparison of hardness in two directions within each sector was performed by ANOVA (where $H_0: \mu_1 = \mu_2$; $H_1: \mu_1 \neq \mu_2$; $\alpha = 0.05$), and on the other hand Tukey's post hoc test was used for multiple mutual comparison of hardness in individual sectors within one direction ($H_0: \mu_1 = \mu_2 = \dots = \mu_m$; $H_1: \mu_1 \neq \mu_2 \neq \dots \neq \mu_m$; $\alpha = 0.05$). The p-value of was monitored (if $p < \alpha$, hypothesis H_0 is rejected). ANOVA showed $p < \alpha$ between two directions in every sector, i.e. hypothesis H_0 is rejected and statistically significant differences in material hardness in two mutually perpendicular directions within each sector, both for fresh and for recycled powder can be pronounced. The results of the Tukey's test are shown in Table 3.

Table 3 Results of post hoc Tukey's test; dark cells means $p < \alpha$, H_0 rejected, mean values exhibits statistically significant differences

powder		fresh					recycled				
dir	sector	S1	S3	S5	S7	S9	S1	S3	S5	S7	S9
$\perp$	S1	-					-				
	S3		-					-			
	S5			-					-		
	S7				-					-	
	S9					-					-
$\parallel$	S1	-	immeasurable			-	immeasurable			-	
	S3		-					-			
	S5			-					-		
	S7				-					-	
	S9					-					-

The Tukey's test confirmed in sector 5 statistically significant differences in hardness compared to all other sectors. For fresh powder in $\perp$ direction, significant differences in hardness were also confirmed between sectors 1 and 9.

Corrosive properties of materials

Fig. 4 shows an example of Tafel curves and 2nd Stern analysis to determine the polarization resistance R_p .

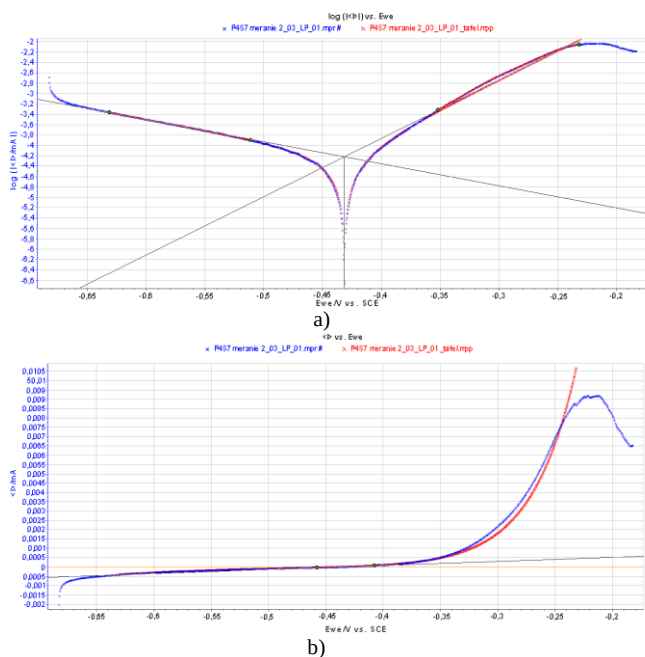


Fig. 4 a) Tafel curves, 1st Stern analysis, b) 2nd Stern analysis

Table 4 shows the calculated corrosion characteristics of the measured materials.

Table 4 Corrosion characteristics of materials

sector		E_{corr} [mV]	I_{corr} [μ A]	bc [mV]	ba [mV]	r_{corr} [mmpy]	R_p [Ohm]
fresh powder	1	-393	0.27	264	76	0.009	83 500
	3	-367	3.84	243	106	0.131	8 260
	5	-416	1.02	208	151	0.035	42 100
	7	-373	0.46	387	61	0.016	81 700
	9	-404	0.32	253	76	0.011	154
recycled powder	1	-410	0.20	238	71	0.007	125
	3	-378	1.92	257	138	0.066	24 000
	5	-403	1.18	242	129	0.040	29 000
	7	-423	0.12	198	75	0.004	250
	9	-409	0.18	270	65	0.006	208

It is apparent from Table 4 that the corrosion rates that characterize the corrosion resistance of the material in a saline solution are at a very low level, although prior to each measurement the material was ground, cleaned and immediately transferred to the measuring cell. The oxidation of the CoCr alloy occurs almost immediately, i.e. during the measurement the electrolyte is actually in contact with the oxide layer of the material, which is manifested by a very low corrosion rate and a high polarization resistance.

4. Discussion

Hardness of materials

Hardness measurements confirmed the logical correlation with the porosity of the materials. Discovery of statistically significant differences in the hardness of materials in two mutually perpendicular directions even in sectors where the porosity was minimal has more importance. The result corresponds to similar measurements in works [1-3]. These differences can be partially eliminated, mitigated by subsequent heat treatment - annealing of materials.

Porosity

If porosity was not the goal, it is a clear defect that reduces the mechanical load-bearing capacity of the products, especially under cyclic loading. Dikova [4] notes that in the bending test of bridges made by SLM technology, the fracture spread from space between separate melted tracks, creating and developing a network of cracks across the volume starting from typical SLM defects. An important finding is that the level of porosity in different positions on the building platform varies dramatically, even if the materials on it were made under the same conditions. Implants placed in these positions will contain an unacceptable number of defects in the structure and will soon experience fatigue failure, shape collapse, etc.

Mertens [5] found that a preheated build platform can serve as an extra energy source and can help densify the processed powder when the laser beam energy seems insufficient to achieve dense components. However, the energy from the preheating does not have such a significant effect as the parameters of the laser beam (power, scanning speed).

The scanning strategy also plays a role. From Fig. 2 can be seen the skin and the core of the product. Qijan [6] notes differences in mechanical properties between core and skin, which, however, still exceed the properties of the same material processed by casting [7].

Corrosion resistance of material

The corrosion rate of the materials does not vary significantly either depending on the position on the plate or depending on the repeated use of the powder. Excellent corrosion resistance is a natural property of cobalt-based alloys. Cobalt alloys show an extremely high of corrosion resistance even in chloride surroundings due to

the spontaneous creation of a chromium oxide (Cr_2O_3) passive layer within the human body [8].

5. Conclusion

The paper presents the results of research carried out on CoCr powder processed by SLM technology for dental applications. The influence of the position of the material on the build platform and the use of fresh and recycled powder on the occurrence of defects in the internal structure of the product was monitored. Sectors 1 and 5 have been shown to be critical positions on the plate where there is a rapidly increased porosity that affects the resulting hardness and consequently the fatigue life of the products. This was confirmed for two independently manufactured platforms (one made of fresh and the second from recycled powder). Significant differences in the hardness of materials in two mutually perpendicular directions can be eliminated by annealing. The question of increased porosity in these sectors should be consulted with the SLM machine manufacturer. Corrosion resistance of materials made from fresh or recycled powder is excellent. Repeated use of powder from previous SLM processes after proper sieving and treatment does not cause degradation of the properties of the products made from them.

6. References

1. A. Guzanová, D. Draganovská, G. Ižáriková, J. Živčák, R. Hudák, J. Brezinová, R. Moro, *Metals* 9, 10 (2019), 1055
2. A. Guzanová, G. Ižáriková, J. Brezinová, J. Živčák, D. Draganovská, R. Hudák, *Metals* 7, 8 (2017), 318
3. J. Brezinová, R. Hudák, A. Guzanová, D. Draganovská, G. Ižáriková, J. Koncz, *Metals* 6, 7 (2016), 171
4. T. Dikova, *Procedia Structural Integrity*, 13 (2018), 461-468
5. R. Mertens, S. Dabdakhsh, J. Van Humbeeck, J.-P. Kruth, *Procedia CIRP* 74 (2018) 5–11
6. B. Qian, K. Saeidi L. Kvetková, F. Lofaj, C. Xiao, Z. Shen, *Dental Materials* Volume 31, Issue 12, December 2015, Pages 1435-1444
7. N.A. Dolgov, T. Dikova, D. Dzhendov, D. Pavlova, M. Simov, *Materials Science. Non-Equilibrium Phase Transformations*, 2, 3 (2016) 3-7
8. Edited by Preetha Balakrishnan, Sreekala M S, Sabu Thomas, *Fundamental Biomaterials: Metals*. Woodhead Publishing, Elsevier, 2018

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Investigation on the efficiency of internal crystallization chemical admixtures for cement concrete - structural characteristics

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Abstract: In recent years, the use of internal crystallization chemical admixtures for concrete and mortar to increase their water-tightness and other physical and mechanical characteristics has been of increasing importance in modern construction. These types of chemical modifiers allow for the effective replacement of conventionally performed waterproofing works (membranes, rolls, brushed or sprayed coatings, etc.) by purposefully improving the physical-mechanical characteristics of structural concretes, rendering them, to one degree or another, impermeable to water or/and aggressive agents from different origins. In the specialized world market for such products there are several leading competing companies - producers of internal-crystallization chemical admixtures, which have different activity in Bulgaria. Based on results of purposeful set of structural investigations (DTA, SEM, BET) conducted the purpose of the report is to assist participants in the construction investment process in understanding the nature, specific characteristics and differences in the performance (effectiveness) of different products in terms of their ability to limit the ingress of water into concrete and reinforced concrete sections, as well as their ability to increase the durability of concrete as the main structural material.

Keywords: PORTLAND CEMENT CONCRETE AND MORTAR, INTERNAL CRYSTALLIZATION CHEMICAL ADMIXTURES, CONCRETE WATERPROOFING, DTA, SEM, BET STRUCTURAL INVESTIGATIONS

1. Introduction

In recent years, the use of internal crystallization chemical admixtures for concrete and mortar to increase their water-tightness and other physical and mechanical characteristics has been of increasing importance in modern construction. These types of chemical modifiers allow for the effective replacement of conventionally performed waterproofing works (membranes, rolls, brushed or sprayed coatings, etc.) by purposefully improving the physical-mechanical characteristics of structural concretes, rendering them, to one degree or another, impermeable to water or/and aggressive agents from different origins [1, 2, 3, 4, 5].

In the specialized world market for such products there are several leading competing companies-producers of internal-crystallization chemical admixtures, which have different activity in Bulgaria.

The admixtures tested and compared are KRYSTALINE Add1, KRYSTALINE Plus 2.5, PENETRON Admix, XYPEX C1000 NF and BETOCRETE-CP-360-WP.

The purpose of the investigation is to assist all participants in the construction investment process in understanding the nature, specific characteristics and differences in the performance (effectiveness) of different products in terms of their ability to limit the ingress of water into concrete and reinforced concrete sections, as well as their ability to increase the durability of concrete as a main structural material.

2. Tests methods and comparative characteristics

The mix design of ordinary reference concrete (Table 1) was used to perform the studies, with the mineral composition of the cement being presented in Table 2.

For the purpose of comparative studies to the mix of reference concrete (Table 1), the appropriate crystallization chemical admixtures are incorporated in the dosage and according to the technology prescribed by their manufacturer.

The homogenization of the fresh concrete is accomplished by adding a metered amount of mixing water to obtain the same workability as assessed by the slump measure. The chosen method of comparison on the basis of "equal workability" of the concrete mixture is directly related to the actual production conditions at the construction site, where the "workability" factor is the key one to the quality of the concrete works performance.

The following physical-mechanical and structural characteristics have been selected to compare the same age of the fresh concrete and the hardened concrete:

- **fresh concrete** - water-cement ratio, consistency by slump test (cm), change of consistency in time after homogenization, air content (%);
- **hardened concrete** - compressive strength (MPa), splitting tensile strength (MPa), the static modulus of elasticity deformation (GPa), the depth of penetration of water under pressure (mm), frost resistance under an accelerated method (loss of mass change and the speed of ultrasound propagation) - cycles, structural studies (low-temperature gas absorption (BET method), differential thermal analysis (DTA), X-ray phase analysis (RFA) and scanning electron microscopy (SEM);
- **cement-sand mortar** - capillary absorption.

Table 1: Concrete mix design.

No	Materials	Quantity, kg/m ³
1.	Portland cement CEM II 42,5 A-LL, Devnya Cement Plant, Bulgaria	330
2.	River sand, fraction 0-4 mm, Quarry "Chepinzi"	810
3.	Crushed stone, fraction 4-11,2 mm, Quarry "Studena"	1060
4.	Mixing water for fresh concrete slump 13 cm (S3)	≈250 (for reference concrete)

Table 2 Mineral composition of the Portland cement used

Cement type	Specific surface, cm ² /g	Mineral composition, % by mass			
		C ₃ A	C ₃ S	C ₂ S	C ₄ AF
CEM II 42,5 / A-LL	3620	9,40	55,50	24,60	10,50

3. Description of crystallization admixtures tested

The description and basic peculiarities of the admixtures tested is given in Table 3. Their dosage rates are in accordance of the respective manufacturers.

KRYSTALINE Add1 and KRYSTALINE Plus 2,5 have the advantage of being dosed in all cases in constant quantities (1,0 kg/m³, or 2,5 kg/m³) regardless of the concrete formulation of the concrete. The only requirement is cement content above 300 kg/m³.

PENETRON Admix, XYPEX C1000 NF and SCHOMBURG BETOCRETE-CP-360-WP are dosed depending on the type and amount of cement used in the concrete mix design, which determines the need for specific calculations and non-constant costs in different projects.

Table 3 Product description and dosage rates

Product	Description	Dosage rates (according producer's recommendations)
KRYSTALINE Add1 Krystaline Technologies SA, Spain	Crystallizing waterproofing admixture with catalytic action to increase the water resistance and durability of concrete. Slightly slows down the concrete setting and hardening times and decreases exothermic. Self-healing cracks up to 0.5 mm wide.	1,00 kg/m ³ (permanent, regardless of the cement content)
KRYSTALINE Plus 2,5 Krystaline Technologies SA, Spain	Crystallizing waterproofing admixture with catalytic action to increase the water resistance and durability of concrete. Slightly slows down the concrete setting and hardening times and decreases exothermic. Self-healing cracks up to 0.5 mm wide.	2,5 kg/m ³ (permanent, regardless of the cement content)
PENETRON Admix PENETRON HELLAS, Greece	Crystallizing waterproofing admixture with catalytic action to increase the water resistance and durability of concrete. Slightly slows down the concrete setting and hardening times and decreases exothermic. Self-healing cracks up to 0.4 mm wide.	3,00 kg/m ³ (1% from mass the cement)
XYPEX C1000 NF XYPEX CHEMICAL CORPORATION, Canada	Crystallizing waterproofing admixture with catalytic action to increase the water resistance and durability of concrete. Slightly slows down the concrete setting and hardening times and decreases exothermic. Self-healing cracks up to 0.4 mm wide.	4,5 kg/m ³ (3-6 kg/m ³ , according producer's TDS)
BETOCRETE-CP-360-WP SCHOMBURG GmbH & Co. KG, Germany	Crystallizing waterproofing admixture with hydrophobic effect.	3,30 kg/m ³ (0,75-1,25% - in function of type and cement content)

4. Results and discussion

The respective physics and mechanical properties of hardened concrete are discussed in other publication of ours [5] (to be published).

The focus of this paper is to emphasize the significant differences in respective micro-structural characteristics obtained by using of advanced direct physics methods - low-temperature gas adsorption (BET method), differential thermal analysis (DTA), X-ray phase analysis (RFA) and scanning electron microscopy (SEM).

4.1. Low temperature gas absorption (BET- method)

Gas adsorption is a modern method of characterizing porous materials. In the case of physical gas adsorption, inert gas (most commonly nitrogen) is adsorbed on the surface of a solid material. Physical absorption is the result of the electromagnetic attraction forces between the particles of the two phases, which have different charges. This occurs on the superficial outer layer of the bodies and on the surface of their pores (in the case of porous bodies). The

reverse process is called desorption. The adsorption process is accompanied by an increase in the sample mass and a decrease in gas pressure. Based on the amount of adsorbed gas and the corresponding gas pressure, so-called an Arizona thermal adsorption curve from which basic parameters of the pore structure of materials can be determined.

The results are presented in Table 4 and Figures 1-5.

Table 4 Micro-pore structure characteristics

CONCRETE TESTED	STRUCTURE CHARACTERISTICS		
	Specific surface of pore structure, S _{BET} , m ² /g	Total pore volume, V _t , cm ³ /g	Pore size distribution by diameter, D _{av} , nm
Reference concrete – without admixture	24	0,09	15
KRYSTALINE Add1 1,0 kg/m ³	19	0,05	10
KRYSTALINE Plus 2,5 2,5 kg/m ³	26	0,09	14
PENETRON Admix 3,0 kg/m ³	30	0,09	13
XYPEX C1000 NF 4,5 kg/m ³	17	0,07	17
SCHÖMBURG BETOCRETE-CP-360-WP 3,3 kg/m ³	44	0,12	11

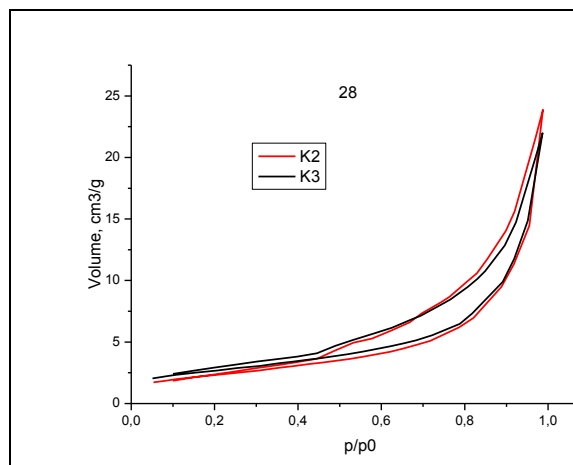


Fig. 1 Total pore volume - KRYSTALINE Add1 (K2) and KRYSTALINE PLUS 2,5 (K3)

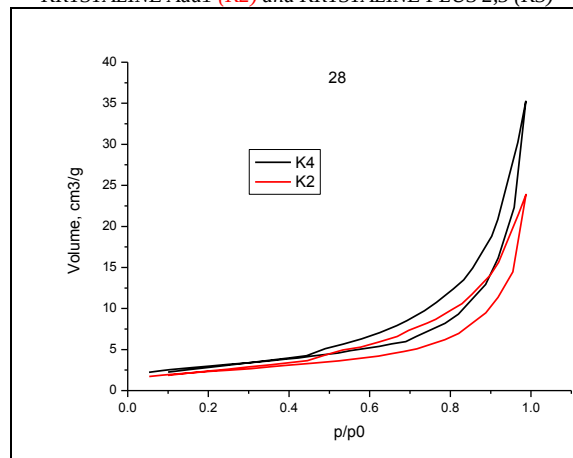


Fig. 2 Total pore volume - KRYSTALINE Add1 (K2) and PENETRON Admix (K4)

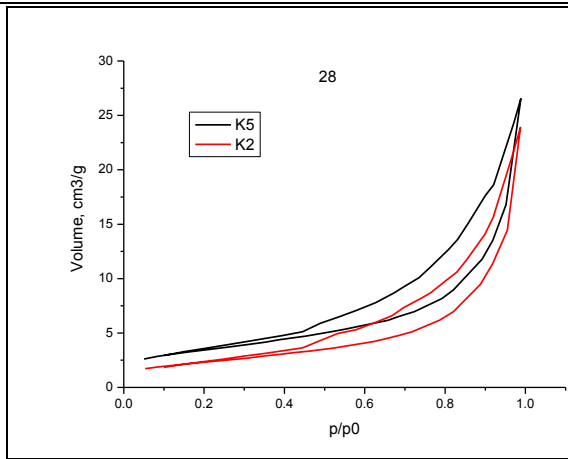


Fig. 3 Total pore volume - KRYSTALINE Add1 (K2) and XYPEX C1000 NF (K5)

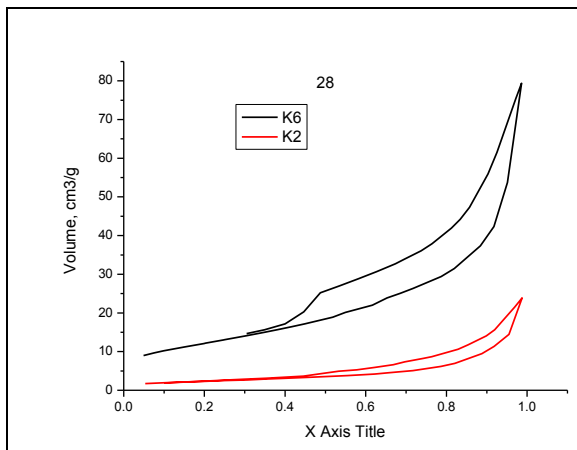


Fig. 4 Total pore volume - KRYSTALINE Add1 (K2) and BETOCRETE -CP-360-WP (K6)

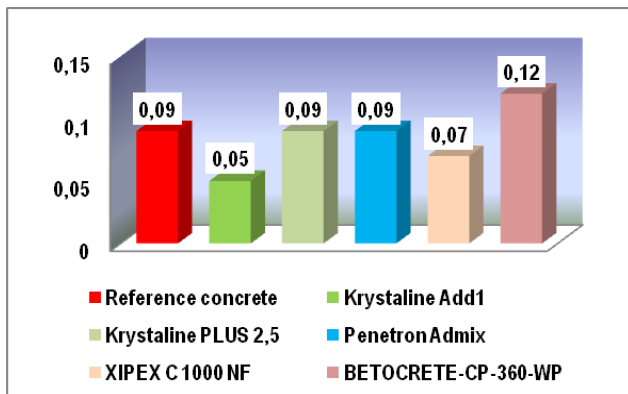


Fig. 5 Total micro-pore volume, cm³/g

With the same workability of the fresh concrete, the crystallization admixture KRYSTALINE PLUS 2.5 and KRYSTALINE Add1 form a fine-dispersed cement stone structure in the concrete with a significantly reduced total micro pore volume, compared to the concrete with the participation of PENETRON Admix, XYPEX C1000 NG and SCHÖMBURG BETOCRETE -CP-360-WP.

4.2. Differential-thermal analysis (DTA)

The results are presented in Table 5 and Figures 6-10.

Differential thermal analysis (DTA) is a method that belongs to the set of direct physical methods for the study of crystalline structure in silicate composites. It is based on the characteristic feature of the hydrated formations in the cement stone to dehydrate in a precisely defined temperature range. The corresponding dehydration is accompanied by a characteristic thermal effect that alters the heat balance of the system. The monitoring of the

respective endo- and exo-effects allows one to judge the phase transformations identified by the release of chemically bound water. Knowing the reference for the individual silicate formations and temperatures of the phase transition, one can directly judge the presence and the indicative amount of the corresponding compound.

Table 5 Structure characteristics

CONCRETE TESTED	BASIC STRUCTURE COMPOSITIONS	
	Portlandite $\text{Ca}(\text{OH})_2$, rel.%	Crystals C-S-H, Calcite CaCO_3 , rel.%
Reference concrete (K "0") without admixture	1,937	8,733
KRYSTALINE Add1 1,0 kg/m ³	1,491	10,685
KRYSTALINE Plus 2,5 2,5 kg/m ³	1,455	11,880
PENETRON Admix 3,0 kg/m ³	1,849	4,878
XYPEX C1000 NF 4,5 kg/m ³	2,999	11,051
SCHÖMBURG BETOCRETE-CP-360-WP 3,3 kg/m ³	1,669	8,232

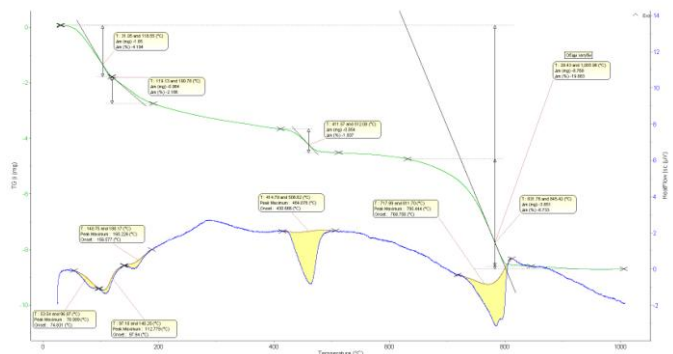


Fig. 5 DTA - Reference concrete

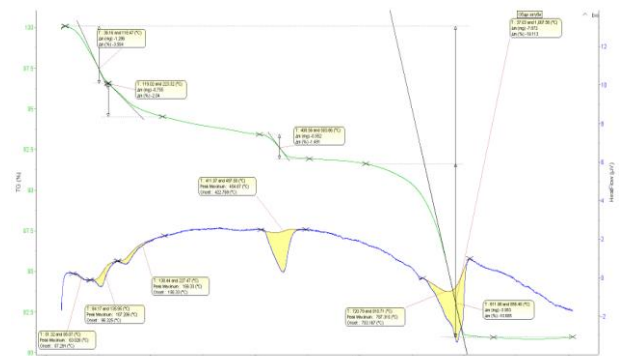


Fig. 6 DTA - KRYSTALINE Add1

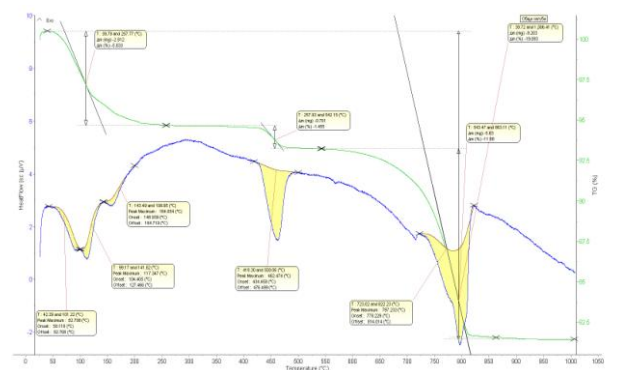


Fig. 7 DTA - KRYSTALINE PLUS 2,5

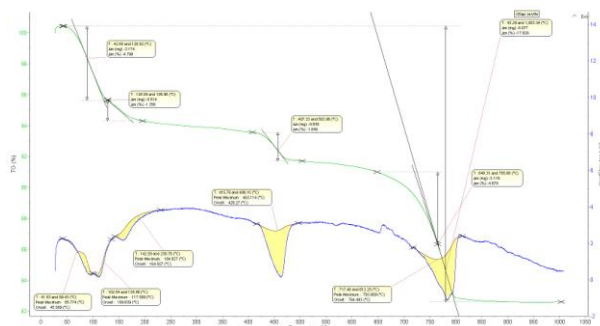


Fig. 8 DTA - PENETRON Admix

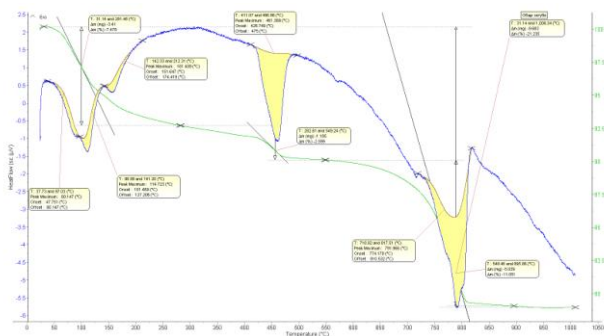


Fig. 9 DTA - XYPEX C1000 NF

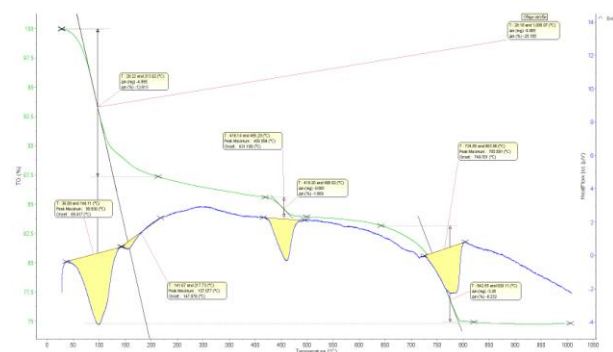


Fig. 10 DTA - SCHÖMBURG BETOCRETE-CP-360-WP

With the same workability of the fresh concrete, the crystallization admixtures KRYSTALINE PLUS 2.5 and KRYSTALINE Add1 form a waterproof crystalline structure with a predominant involvement of CSH-type high-alkalinity hydrate formations (main carriers of high mechanical properties of the composite), compared to concrete with PENETRON Admix, XYPEX C1000 NF and SCHÖMBURG BETOCRETE-CP-360-WP.

4.3. Scanning Electron Microscopy (SEM)

The results are presented in Photos 1-6.

Scanning electron microscopy (SEM) is performed using a high magnification electron microscope (up to 10,000 times), resulting in visual data on the shape and size of individual sub-microscopic crystals, their growth, decomposition and destruction processes, and this base passed is sued for past chemical interactions in solution and solid phase, incl. to seal the structure.

In support of the demonstrated significant advantages with respect to the basic physics-mechanical properties of the crystallization additives KRYSTALINE PLUS 2.5 and KRYSTALINE Add1 over PENETRON Admix, XYPEX C1000 NF and SCHÖMBURG BETOCRETE-CP-360-WP, are the results obtained by using modern direct physics-chemical methods. They show that the concrete with KRYSTALINE PLUS 2.5 and KRYSTALINE Add1 form a denser waterproof crystalline structure

with a dominant participation of high-alkalinity C-S-H hydrate formations, bearing high mechanical performance of the composite.

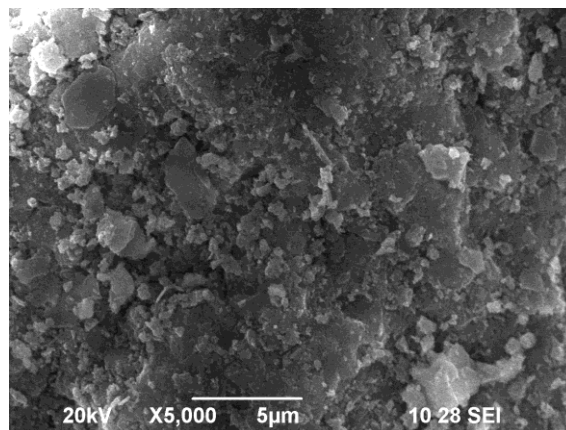


Photo 1 Reference concrete

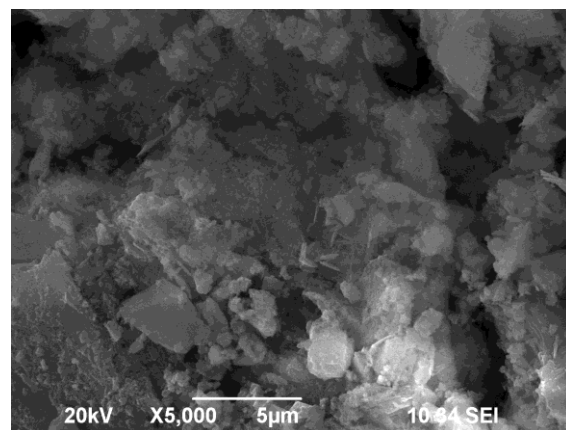


Photo 2 KRYSTALINE Add1

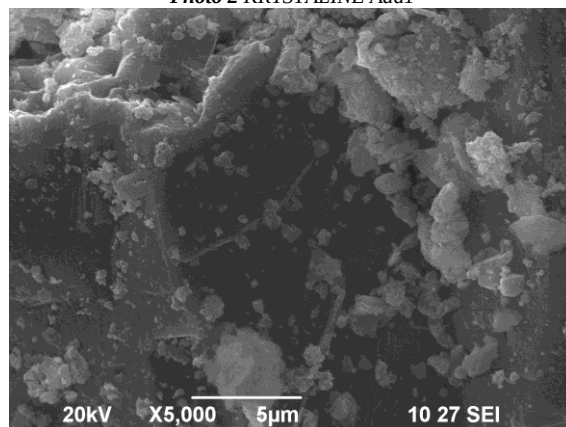


Photo 3 KRYSTALINE PLUS 2,5

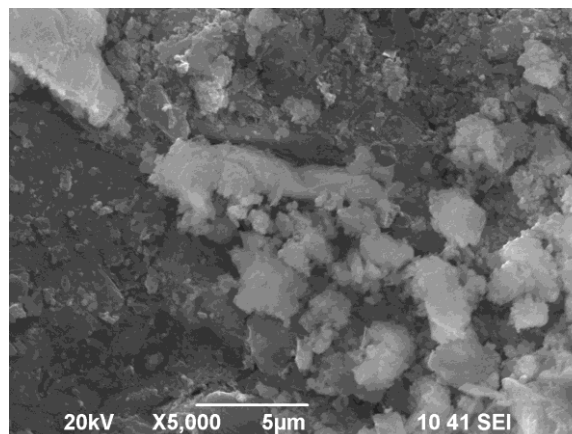


Photo 4 PENETRON Admix

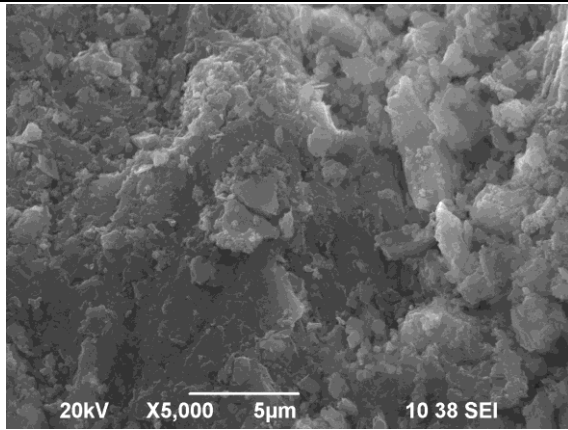


Photo 5 XYPEX C1000 NF

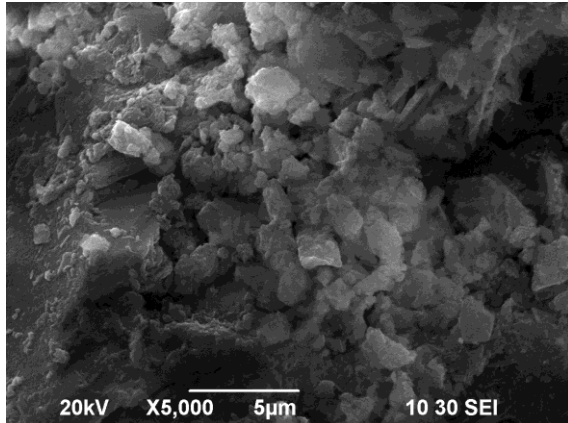


Photo 6 SCHÖMBURG BETOCRETE-CP-360-WP

5. Conclusions

The above comprehensive comparative analysis for the evaluation of the basic physical-mechanical and structural characteristics of the fresh and hardened concrete with 5 types of internal crystallization chemical admixtures entering the Bulgarian construction market, objectively presents the characteristics of the compared products.

In accordance with the stated goal, this **TECHNICAL REPORT** is able to assist the participants in the investment construction process (investors, designers, contractors, project managers and supervisors), in situation of an informed choice, to evaluate the complex advantages of KRYSTALINE PLUS 2,5 and KRYSTALINE Add1 to PENETRON Admix, XYPEX C1000 NF and SCHÖMBURG BETOCRETE-CP-360-WP.

Concretes with the participation of KRYSTALINE PLUS 2.5 and KRYSTALINE Add1 (with a constant dosage rate of 2.5, respectively 1.0 kg/m³), ensure the impermeability and safe watertightness of the concrete cross section, even under water pressure, without the need for additional waterproofing activities of various types - brushed and sprayed coatings, coiled and membrane conventional systems. At the same time, such concrete have increased frost-resistance and durability without the need for accompanying repair and restoration work.

By all tested parameters, concrete with KRYSTALINE PLUS 2.5 and KRYSTALINE Add1 outperformed with PENETRON Admix, XYPEX C1000 NF and SCHÖMBURG BETOCRETE-CP-360-WP one.

6. References

1. F. Klouda, F. Concrete crystallization gives India's greenest airport wings, *Concrete*, vol. 44, no. 3, 2010
2. X. Shaozhu X., Research and development of cement-based permeable crystallization type waterproof materials abroad, *China Building Waterproofing*, vol. 6, 2001.
3. Y. X. Zhang, X. Du, Y. Li, F. Yang, and Z. Li, Research on cementations capillary crystalline waterproofing coating for underground concrete works, *Advanced Materials Research*, vol. 450-451, 2012.
4. S. Bohus S, R. Drochytka, Cement based material with crystal-growth ability under long term aggressive medium impact, *Applied Mechanics and Materials*, vol. 166-169, 2012
5. P. Reiterman, J. Pazderka, Crystalline coating and its influence on the water transport in concrete, *Advances in Civil Engineering*, Vol. 2016, ID 2513514, <https://doi.org/10.1155/2016/2513514>
6. V. Naidenov, M. Mironova, I. Rostovsky, Investigation on the efficiency of internal crystallization chemical admixtures for cement concrete - mechanical characteristics, *International Conference Materials, Methods & Technologies*, 22-26 June 2020 in Burgas, Bulgaria (to be published).

Acknowledgments

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Hydrophilized unsaturated polyester resin-based polymer-silicate compositions

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Abstract: This work is a continuation of the development of hydrophilized unsaturated polyester resin (HUPER). Again, the authors' main aim is a possibility for hydrophilization of unsaturated polyester resin (UPER), but in this case the previously selected hydrophilizer cement 'milk' was replaced by the water glass component without disregarding the contribution of cement to the multicomponent hydrophilizing system. The special thing about this case is that there are a number of hydrophilizers, all of which individually have a hydrophilizing effect on resin, and that they are influenced by each other. This is of utmost importance not only for the hydrophilization technology but also for the research into important accompanying issues, such as kinetics, mechanical strength characteristics, spectrum and derivatographic analysis. This study only addresses some of the issues mentioned for reasons of volume of work. However, due to the possible interest they could arouse in the different fields of chemistry, in medical and technical terms, they are to be developed and resolved in the future.

KEYWORDS: HYDROPHILIZATION, RESIN/MINERAL DISPERSE SYSTEM, CEMENT, WATER GLASS.

1. Introduction

The development of UPER-based polymer/silicate composites is carried out by different types of cement [1,2,4], which are principally known to impart strength to materials and high corrosion resistance. Since literature [1] reports of some negative properties associated with cement impact – deformability, plastic deformation (sagging) – a new approach was sought to develop HUPER. The hydrophilizing system can be a two-component system composed, for example, of sulfate resisting blast furnace cement (SC) and water glass (WG) in different proportions. Thus obtained composite materials can overcome the above-mentioned disadvantages and add a valuable property, such as high relief, to the polymer-silicate surface.

An important motive for research activity is to obtain polymer concrete of high physical and mechanical properties on the basis of aggregate waste. In principle, such recycling of materials is not new [3] but the idea could be developed as the two-component SC/WG system hydrophilizes the resin while influencing the curing time, mechanical indicators (impact strength, tension strength), technological nature of HUPER developed (obtaining at room temperature, capability to be cast into different molds, predictability of casting time, etc.). To achieve the derived factors it is essential to add water, which is a stable, constant and corrective factor for the SC/WG system, as it has a diluting, plasticizing and modifying effect not only on the two-component hydrophilizing system but also on UPER that cures in its presence.

The purpose of this work is to develop HUPER-based polymer-silicate composites using SC and WG, and to establish the dependence of some mechanical properties on the composition of the polymer/silicate system.

2. Materials and methods

2.1. Materials

We used:

Resin of type Vinalkyd 550 PE-R (Orgachim Resins – Ruse) containing 35% styrene and 65% unsaturated polyesters, which is a condensation product of propylene glycol and maleic anhydride. A 50% solution of cyclohexanone peroxide (CHP) in dibutylphthalate was used as a curing initiator, and a 10% solution of cobalt naphthenate (CN) in styrene was the accelerator.

Sulfate-resistant blast furnace cement CEM III A-S 42.5 N SR – Devnya Cement, town of Devnya (SC).

Sodium silicate solution (Water glass - WG) – BEKO Water Glass and Detegrents Factory, town of Troyan.

2.2. Methods

Methods for obtaining compositions based on unsaturated polyester resin hydrophilized with cement were developed at fixed amount of water compared to cement (50%) in the presence of WG, at fixed CN/CHP ratio compared to resin.

Test pieces were examined for impact strength according to Izod by Izod impact testing machine GB1843-2008.

Test pieces were examined for tensile strength and compression strength by means of HZ-1005 Computer-type Tensile Testing Machine. Dumb-bell test pieces for examining the tensile strength are placed in the jaws of the machine. Flexural stress and flexural modulus are calculated according to EN ISO 178:2019.

3. Results and discussion

Polymer compositions with two-component hydrophilizing systems containing WG and SC were developed. The two hydrophilizers were applied according to the following pattern: at constant amount of resin and the relevant CN/CHP redox system, the same amounts of water glass and three different quantities of SC were used. Other two polymer compositions were developed accordingly. Each of them contained a higher amount of WG as compared to the previous composition, and the quantities of SC increased in the same order. Kinetic relations of nine test samples were studied based on that order (Table 1-3):

Table 1. Data on the obtaining of compositions based on UPER hydrophilized by different quantities of SC at constant amount of WG (3% ± 1%) and 50% water of the SC quantity.

Composition No.	SC quantity %	Time [τ, min]	Temperature T max., °C]
1	0	18	99.5
2	12	40	54.5
3	25	29	55.5
4	35	29	43.5

The kinetics of the polymerization process can be presented on the basis of the temperature change at regular intervals. This kinetic relation was examined due to the fact that it generate a certain amount of heat corresponding to the set time intervals in the course of radical copolymerization. Thus, the time tracked from the beginning of polymerization to gelation proves that an exothermic process takes place enabling tracking of the kinetics of formation of any polymer composition. Such kinetic relations are presented in Figures 1-3.

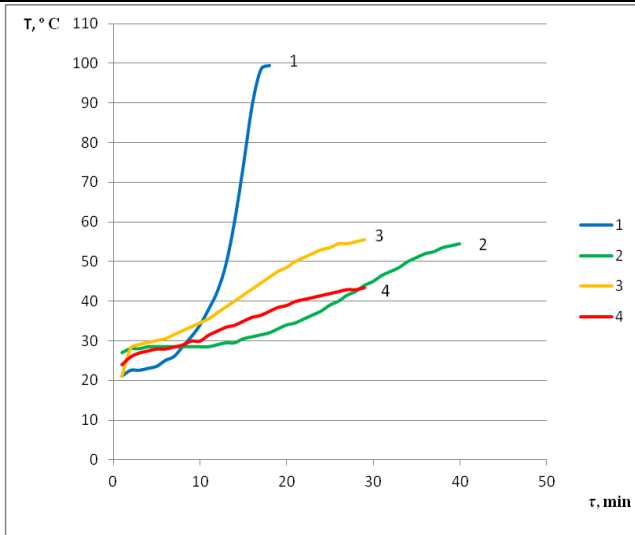


Figure 1. Kinetics of the polymerization process, where curve 1 - 0% SC, curve 2 - 12% ± 2% SC, curve 3 - 25% ± 2% SC, curve 4 - 35% ± 2% SC (according to Table 1)

Table 2. Data on the obtaining of compositions based on UPER hydrophilized by different quantities of SC at constant amount of WG (8% ± 2%) and 50% water of the SC quantity.

Composition No.	SC quantity %	Time [τ, min]	Temperature T max., °C]
1	0	20	73.5
2	12	33	40.5
3	25	27	45.5
4	35	25	39.5

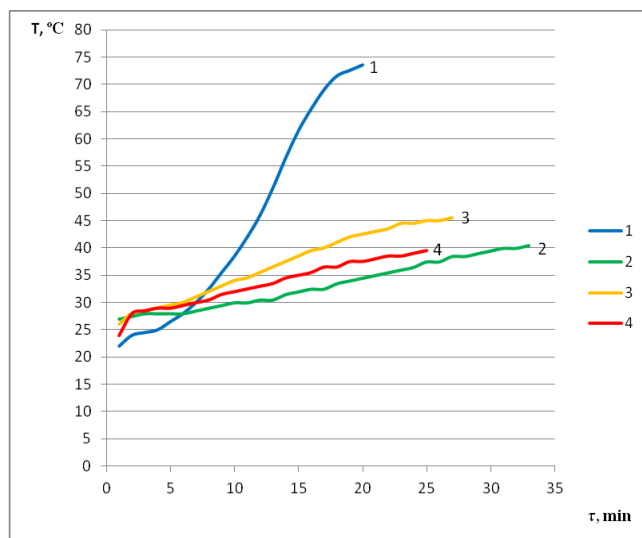


Figure 2. Kinetics of the polymerization process, where curve 1 - 0% SC, curve 2 - 12% ± 2% SC, curve 3 - 25% ± 2% SC, curve 4 - 35% ± 2% SC (according to Table 2)

Table 3. Data on the obtaining of compositions based on UPER hydrophilized by different quantities of SC at constant amount of WG (12% ± 2%) and 50% water of the SC quantity.

Composition No.	SC quantity %	Time [τ, min]	Temperature T max., °C]
1	0	17	48.5
2	12	26	42.5
3	25	26	34
4	35	24	38

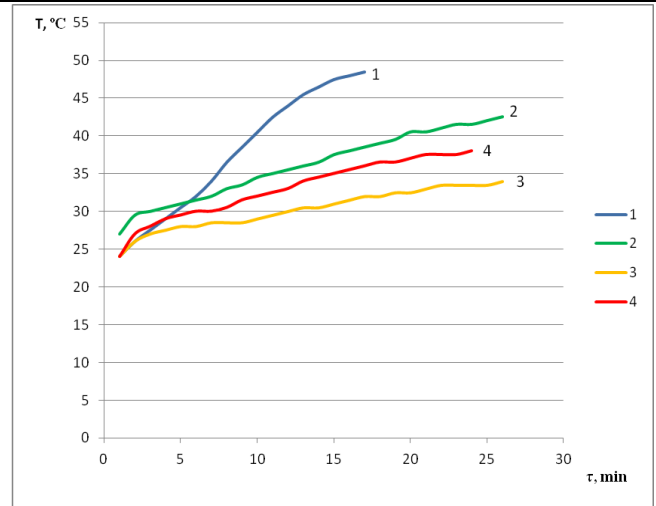


Figure 3. Kinetics of the polymerization process, where curve 1 - 0% SC, curve 2 - 10.85% SC, curve 3 - 24.56% SC, curve 4 - 32.87% SC (according to Table 3)

It is observed that, irrespective of the increase in the amount of WG, gelation time is always the highest at the lowest quantity of cement (12% ± 2%). The increase in SC results in decrease in the gelation time, irrespective of the amount of WG. A large number of studies have been carried out on different polymer compositions, which resulted in deriving temperature/time kinetic relations and seeking the ratio between the two components (SC/WG) where the gelation time changes smoothly or goes to extremes. A determining factor therefore is the gelation time. The change in gelation temperature and underlying conditions, e.g. addition of different fillers, colorants, etc. will be a subject of a subsequent work.

The nine polymer compositions underwent impact strength, tensile strength and flexural strength tests (Figure 4 and Figure 5):

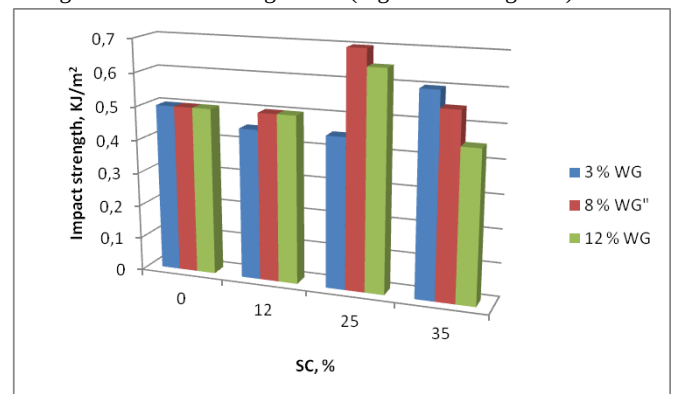


Figure 4. Data on the impact strength in polymer compositions with a constant amount of WG and change in the SC quantity

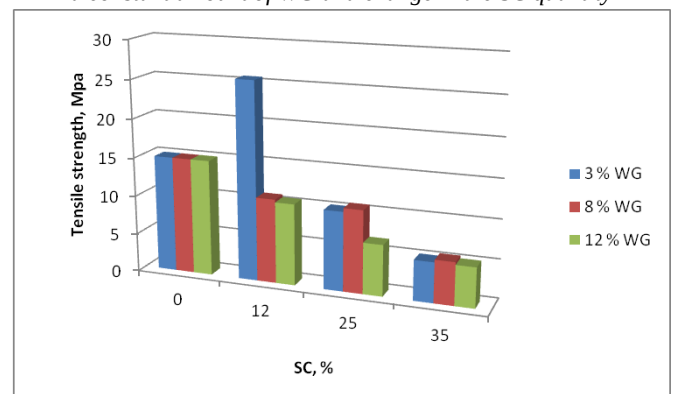


Figure 5. Data on the tensile strength in polymer compositions with a constant amount of WG and change in the SC quantity

Figure 4 and Figure 5 show that there are sharp hikes in mechanical indicators, which prove the strong influence of the two-component hydrophilizing system. This can be both related to the ratio of two hydrophilizers and to a change in the chemistry of curing reaction. These assumptions will be proven or rejected in subsequent works.

4. Conclusion

The results of this work can be summarized by the following important conclusions:

1. Polymer compositions were developed based on UPER hydrophilized with SC and WG, in different proportions, that can be used as composite materials, and the temperature/time kinetic relations were examined based on the exothermic effect of the radical copolymerization;
2. When obtaining different polymer compositions, the effect of the quantitative ratio of the two main hydrophilizers on kinetic relations is significant. For instance, temperatures are highest (between $50^{\circ}\text{C} \pm 5^{\circ}\text{C}$) at WG amounts of up to 20% and SC quantities of up to 80%. At 50/50 quantities for the two hydrophilizers, the temperature decreases to $40^{\circ}\text{C} \pm 5^{\circ}\text{C}$; at the highest amount of WG – 80% and 20% SC quantity, the temperature is $30^{\circ}\text{C} \pm 5^{\circ}\text{C}$. By increasing the WG amount the gelation temperature gradually decreases by 10°C .
3. The gelation time dependence on the same quantitative ratios of the two hydrophilizers was monitored: up to 20% WG the time was 40 ± 2 min, at 50% WG the time was 35 ± 2 min, and at 80% WG the time was 25 ± 2 min. Therefore, the gelation time also depends on the amount of WG, as it gradually decreases by 6 ± 2 min in the order of 20, 50, and 80%;
4. The impact strength goes through an increase and sharp decrease with the best indicators at 8% WG; at 3% WG it increases to the least extent but retains good performance up to the highest content of SC. The split peak of impact strength is most probably due to multivariable interaction in the cross-linked structure of samples;
5. The tensile strength for 8% and 12% WG gradually decreases, as the areas corresponding to the peaks in impact strength show noticeable partial increases in tensile strength. 3% WG manifests strength doubling and sharp drop to the value at 8% and 12% WG, as it develops a second smaller peak similar to that at 8% and 12% WG.

Young's modulus results, relative elongation and flexural strength should be presented and summarised in another work.

5. References

1. Chikhradze, N., F. Marquis, G. Abashidze, D. Tsverava. Production of corrosion-resistant polymer concrete reinforced with various fibers. *World Multidisciplinary Earth Sciences Symposium*. 2019, 362.
2. Conde-Vazquez, C., O. de Miguel-San Martin, G. Garsia-Herbosa. Artificial arenite from wastes of natural sandstone industry. *Materiales de Construcción*. 2019, 69 (333), e178.
3. Hameed, A., M. Hamza. Characteristics of polymer concrete produced from wasted construction materials. In: *Technologies and Materials for Renewable Energy, Environment and Sustainability, TMREES18*, 19-21 September 2018, Athens, Greece. *Energy Procedia* 157, 2019. 43-50.
4. Kristiawan, S., A. Prakoso. Flexural Behaviour of Patch-Repair Material Made from Unsaturated Polyester Resin (UPR)-Mortar. In: *Materials Science Forum Vol. 857. Advanced Materials Engineering and Technology IV*. May 2016. 426-430.

Mineralogical characterization of different clay varieties on behalf of advanced industrial handling

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Abstract: Clay is a group of minerals that which is more industrial demanded material because of the specific strengths of some components of such clays in the fulfilments of some industrial and technological needs. The chemical composition and other important properties of clays are depended on the origin, location and some other environmental factors. The industrial applications might be varied upon the mineralogy of some of clay. In the existing research, three different types of clay were selected as the materials that namely as anthill clay, brick clay and roof tile clay. The selected types of clay samples were collected from three different regions in Sri Lanka. The collected clay samples were characterized using X-ray fluorescence (XRF) spectrophotometer, Fourier transform infrared (FT-IR) spectrophotometer and optical microscope. According to the investigation results, there were observed the presence of Fe as the most abundant element in all of clays at least 75%, large amounts of kaolinite in three clay types, intermediate amount of quartz and trace amounts of rutile in three clay types. In addition that it is possible to present muscovite in brick clays as a trace mineral and some trace amounts of Fe minerals such as glauconite and marcsite in three clay types. When comparing of the mineralogy of such clays mainly those clays are possible to be further developed as the adsorption materials (adsorber) for the recovering of metals from waste water and polluted air and a recovery material to remove some unnecessary components in chemical processes.

Keywords: CLAY, XRF CHARACTERIZATION, FT-IR CHARACTRIZATION, MINERALOGY, CHEMICAL COMPOSITION

1. Introduction

Clay is an industrially demanded soils species among earth resources because of the distinct properties of such clays foremost of the high porosity and less permeability although the properties and chemical compositions of such clays are varied with the origin and formations. The mineralogy of some clay plays a great role in the industrial applications quits as physico-chemical properties of such clays based on the advanced chemical behaviours of those clays most probably the process of adsorption. In the modern industrialized world, it is highly allured in the development or direct uses of natural materials for advanced industrial handling as composite materials and treated raw materials. Clay is a multi purposely applicable raw material due to the series of physico-chemical varieties and diversity in chemical compositions. Based on those features, those clays may have wide range of applications and those applications may be varied according to the physical and chemical characteristics of specified clays [1, 2, 3, 4, 5, 6]. Therefore, the investigation and analysis of common and advanced characteristics of some selected clay are essential necessity prior of the uses. In the existing research there were expected to investigate and analyze the mineralogy of three different clay species which are available in three different areas in Sri Lanka.

2. Materials and Methodology

As the scopes and objectives of the existing research, three different types of clays were selected as the materials for the study namely as follows and the collected (available) areas are shown in Fig. 1.

- Anthill clay- Using in the building of anthill by termite (A 1- Matale Area in Matale District)
- Brick clay- Using in the manufacturing of bricks (A 2- Maduragoda Area in Kurunegala District)
- Roof tile clay- Using in the manufacturing of roof tiles (A 3- Dankotuwa Area in Puttalam District)

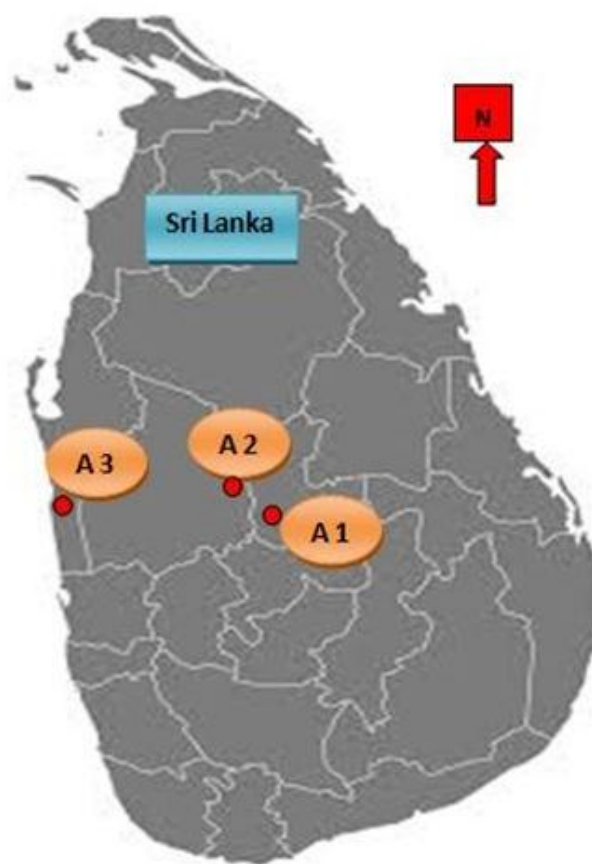


Fig.1. Clay sample collected areas in Sri Lanka

The collected clay samples were stored carefully in non-contaminated polythene bags and some representative clay samples from their original clay bulks were separated for the different experiments and those clay samples were prepared according to the standard defined methods for each experiment.

2.1. Elemental analysis

The representative clay samples were oven dried for 24 hours under the temperature of 110°C until removal of moisture from clays and the dried clay samples were crushed using a ceramic crucible [1-9].

The final representative clay portions were selected using the coning and quartering method which is shown in the Fig. 2.

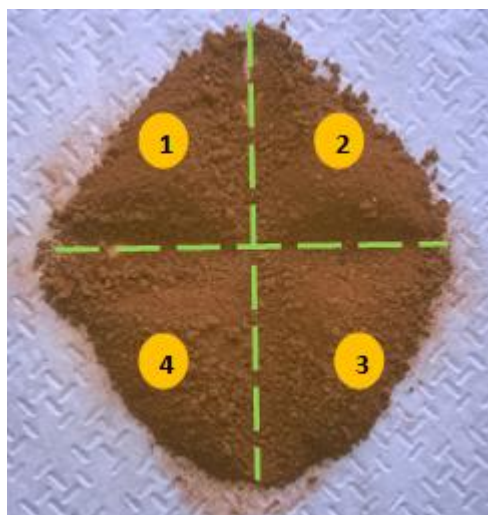


Fig. 2. Coning and quartering method

The selected representative clay samples were analyzed using X-ray fluorescence (XRF) spectrometer.



Fig. 3. X-ray fluorescence (XRF) spectrometer

2.2. Mineralogy and functional group analysis

A selected raw clay portion was separated from each clay bulk. Each of separated clay portion was separately placed in medium size measuring cylinders and the clay portions were dissolved in distilled water while shaking the system. The shaken system was allowed to settle down after a few minutes shaking period. The status of the setting system was observed throughout about two hours and the top most clay portion of each measuring cylinder was collected using medical droppers. The collected clay portion would be the tiniest portion in of each of clay. The collected clay portions were oven-dried for 24 hours under the temperature of 110⁰ C based on the aim of the removal of water and moisture [1-10]. The dried clay samples were crushed using a ceramic crucible to break some clogs and finally a dry clay powder was prepared from each clay type.

The prepared clay samples were analyzed using Fourier transforms infrared (FT-IR) spectrometer.



Fig. 4. Fourier transforms infrared (FT-IR) spectrometer

3. Results and Discussion

3.1. Elemental analysis of clays

According to the analysis of X-ray fluorescence (XRF) analysis, the elemental compositions of clays are given in the following figure and tables.

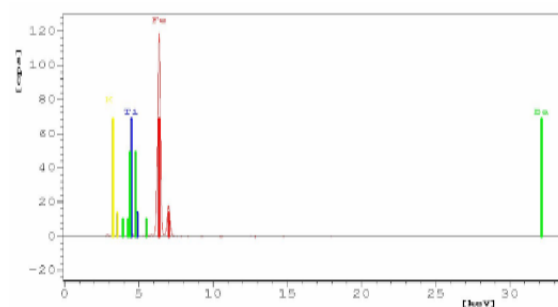


Fig. 5. X-ray fluoresce (XRF) spectroscopy of anthill clay

Table 1: Elemental composition of anthill clay

Color of the Peak	Element	Atomic Number (amu)	Content (%)
Red	Iron (Fe)	26	82.08
Blue	Titanium (Ti)	22	4.84
Green	Barium (Ba)	56	0.79
Yellow	Potassium (K)	19	12.28

Based on above results, the higher Fe content was observed with the trace elements of Ti, Ba and K from anthill clay. Usually such elements would be presented in clays as their oxides because of the reaction with water or moisture [1, 2, 4, 5, 6, 10].

In the analysis of observed results, relatively higher Fe content indicates the suitability of some advanced chemical applications such as the adsorption of other metals or catalyst since it is non-toxic [2,4,6,7]. The industrial applications of such clay can be further described with the mineralogy of anthill clay. In addition, the content of K indicates some relatively higher acidity for anthill clay and Ba is non-toxic element whereas Ba²⁺ is highly toxic in aqueous solutions. But that factor may not be considered in the existing study and further researches because the Ba content is trace in anthill clay (<1%) [1-4].

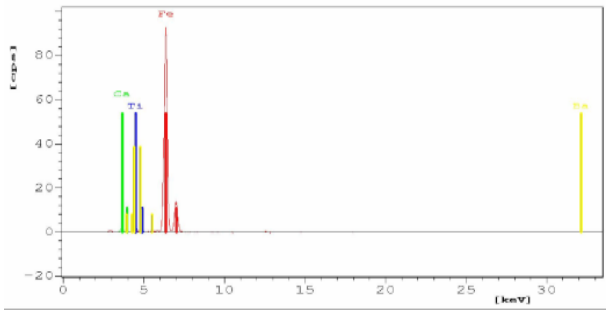


Fig. 6. X-ray fluoresce (XRF) spectroscopy of brick clay

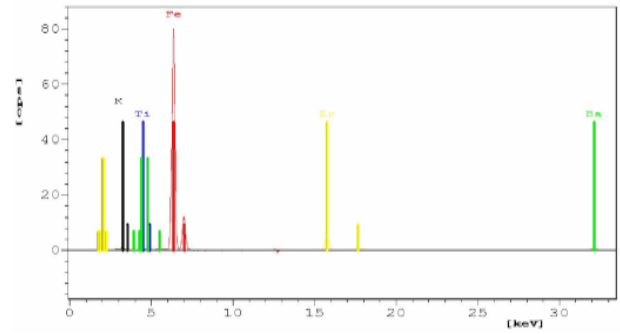


Fig. 7. X-ray fluoresce (XRF) spectroscopy of roof tile clay

Table 2: Elemental composition of brick clay

Color of the Peak	Element	Atomic Number (amu)	Content (%)
Red	Iron (Fe)	26	84.38
Blue	Titanium (Ti)	22	5.92
Green	Calcium (Ca)	20	7.56
Yellow	Barium (Ba)	56	2.14

The X-ray fluorescence (XRF) results of brick clay showed the majority of Fe with other trace elements Ti, Ca and Ba. It was not found any K content in brick clay and that observation denotes that the acidity of brick clay should be relatively lower when comparing with other clays which are composed of potassium. The trace content of Ca indicates the plasticity of the clay because the CaO causes the higher plasticity for clays. The plasticity is an indicator for the resistance of such material against the heat [1-6]. Therefore, it is possible to expect some heat resistant applications from brick clays. Apart from that the brick clay may be applied in advanced chemical process which is called as ion exchange because the Ca^{2+} is identified as a foremost exchangeable ion that present in clays or clayey soils.

Ion exchanging is a mechanism which is mostly used in the waste water treatments as a unit operation to remove some unnecessary/undesirable or toxic ions from waste water and the replacing of the removed ions with other necessary/ desirable or non-toxic ions. The possible exchangeable cations which are present in clays are as follows [1, 4, 6, 9, 10, 11, 12].

- Mg^{2+}
- Na^{+}
- K^{+}
- NH_4^{+}
- Ca^{2+}
- H^{+}
- Ba^{2+}

The ion exchange process is usually applicable in the waste water treatments based on following tasks [1-12].

- Reducing or removal of hardness (softening)
- Removal of nitrogen
- Removal of heavy metals
- Desalination of sea water

Table 3: Elemental composition of roof tile clay

Color of the Peak	Element	Atomic Number (amu)	Content (%)
Red	Iron (Fe)	26	75.72
Blue	Titanium (Ti)	22	2.95
Green	Barium (Ba)	56	5.30
Yellow	Zirconium (Zr)	40	3.36
Black	Potassium (K)	19	12.67

When considering the elemental composition of roof tile clay, it was composed majority of Fe as usual with Ti, Ba, Zr and K. Therefore, it is possible to expect some applications of roof tile clay in followings [1-8].

- Adsorber for some other metals (Fe content)
- Applications in catalytic purposes (porous structure and Fe content)
- Ion exchanging material (Ba^{2+} , Fe^{2+} and K^{+})

In the overall analysis of the elemental compositions of three different clays, some of advanced properties and related applications can be emphasized. However, the applicability of such clays on those tasks would be descriptively confirmed with the mineralogical analysis results forever.

3.2. Mineralogy and functional groups analysis

According to the Fourier transforms infrared (FT-IR) analysis, the FT-IR spectroscopes are shown in following graphs.



Fig. 8. FT-IR spectroscopy (transmittance) of anthill clay

The FT-IR spectroscopy (transmittance) of anthill clay showed major peaks at some specific wave number. The descriptions of the relevant functional groups are given in the Table 4.

Table 4: Functional groups and assignments of anthill clay

Wave Number (cm ⁻¹)	Assignment
3695	OH stretching of inner surface hydroxyl groups
3628	OH stretching of structural hydroxyl groups
999	Si-O stretching
910	OH deformations of inner hydroxyl groups
527	Al-O-Si deformation
460	Si-O-Si deformation
411	-

According to the general investigation of the major peaks of the FT-IR spectroscopy of anthill clay, it is possible to conclude that the presence of kaolinite accordingly with the peaks of wave numbers at 3695cm⁻¹, 3628 cm⁻¹, 910 cm⁻¹, 527 cm⁻¹and 460 cm⁻¹. Apart from the major clay mineral, it is feasible to identify the mineral muscovite according to the peak of the wave number at 999 cm⁻¹. The muscovite is a mineral which is belonged to the group of mica. It can be distinctively identified because of the white color of that mineral when comparing with the other available colors of minerals in mica group. The chemical formulas of kaolinite and muscovite are given in the below [1, 2, 4, 11, 12].

- Kaolinite - Al₂(Si₂O₅)(OH)₄
- Muscovite – KAl₂(AlSi₃O₁₀)(OH)₂

In the further analysis of the FT-IR spectrum of anthill clay, there would be a probability to present the ferrous mineral which is named as pyrite accordingly with the peak of the wave number at 411 cm⁻¹ although it is an insufficient observation to make some fixed conclusion or decision.

Therefore, the anthill clay should be a good adsorber for some other metals because of the presence of kaolinite due to the chemically activation of the functional groups such as the hydroxyl groups. The anthill clay is possible to be recommended for the waste water treatment applications such as the removal of heavy metals and pathogens as well.

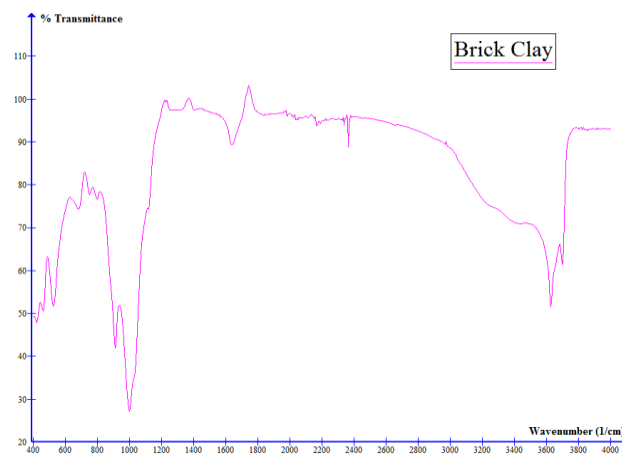


Fig. 9. FT-IR spectroscopy (transmittance) of brick clay

Table 5: Functional groups and assignments of brick clay

Wave Number (cm ⁻¹)	Assignment
3702	OH stretching of inner surface hydroxyl groups
3629	OH stretching of structural hydroxyl groups
1001	Si-O stretching
909	OH deformations of inner hydroxyl groups
530	Al-O-Si deformation
469	Si-O-Si deformation
420	-

The FT-IR spectroscopy of brick clay showed the presence of kaolinite because the peaks were identified with respect to the wave numbers at 3702 cm⁻¹, 3629 cm⁻¹, 909 cm⁻¹, 530 cm⁻¹and 469 cm⁻¹. The peak of the wave number at 1001 cm⁻¹ indicates the present of muscovite in brick clay. Therefore, the industrial applications of brick clay would be same as the anthill clay such as the removal of heavy metals from the waste water [2, 3, 4, 10, 11, 12].

Those clays would be applicable in the removal of following metals from the waste water including heavy metals.

- Cobalt
- Copper
- Nickel
- Manganese
- Arsenic

- Cadmium
- Chromium
- Mercury
- Lead
- Zinc
- Uranium

The metallic contamination of water is a serious incident in the less quality of drinking water which causes some diseases for the human beings and animals. Therefore, the development of clay based treatment systems may be seen in the future.

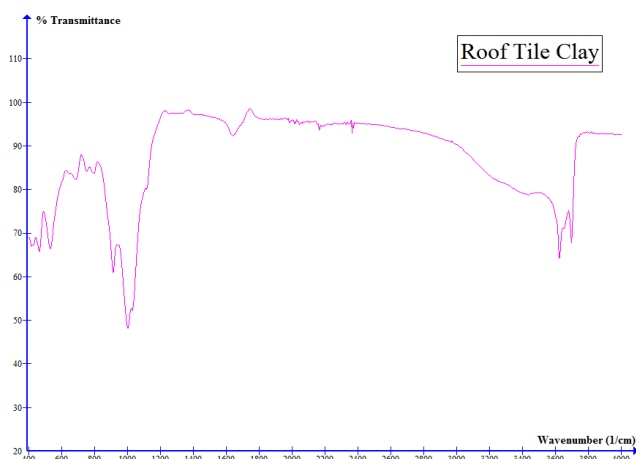


Fig. 10. FT-IR spectroscopy (transmittance) of roof tile clay

Table 6: Functional groups and assignments of roof tile clay

Wave Number (cm ⁻¹)	Assignment
3696	OH stretching of inner surface hydroxyl groups
3623	OH stretching of structural hydroxyl groups
1001	Si-O stretching
915	OH deformations of inner hydroxyl groups
530	Al-O-Si deformation
463	Si-O-Si deformation

The presence of kaolinite was confirmed in roof tile clay because of the distributions of peaks of wave numbers at 3696 cm⁻¹, 3623 cm⁻¹, 915 cm⁻¹, 530 cm⁻¹ and 463 cm⁻¹ as usual. Also the present of muscovite was confirmed referring the peak of wave number at 1001 cm⁻¹. The roof tile clay would also be useful in the

industrial purposes such as the treatment of waste water [1, 2, 4, 11].

As the special industrial application for the roof tile clay, it can be expected the applications in the removal of inorganic contaminations from the waste water such as the fluorides because of the presence of zirconium also with clay minerals such as kaolinite [4, 11].

In addition that the major peaks of wave numbers at ~ 450 cm⁻¹ and ~1000 cm⁻¹ were observed in three spectrums and that evident indicates the presence of quartz in three clay types even as a trace mineral [1, 2, 3, 4, 11].

4. Conclusion

As the results of the existing research, there were obtained at least 75% of Fe in each of clay with some of trace metals such as K, Ba, Ti, Ca and Zr in trace amounts < 13% while observing kaolinite, muscovite and quartz as the major minerals with some ferrous minerals. By considering the results and analysis of the outcomes, it seems that those clays would be some robust raw materials in the industrial applications namely as the ion exchanging material, adsorber, catalyst and heat resistant material.

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6. References

1. Andrianainarive lo Mahandrimanana, Ranaivoson Joseph, Int. J. of Mat. and Chem. **3**, 99 (2013)
2. Ahmad Saat, Zaini Hamzah, Zaharidah Abu Bakar, J. of Nuc. and Rel. Tech. **6**, 230 (2009)
3. R. Baranowski, A. Rybak, I. Baranowska, Pol. J. of Env. Stu. **5**, 473 (2002)
4. Yanyan Chen, Caineng Zou, Maria Mastalerz, Suyun Hu, Carley Gasaway and Xiaowan Tao, Int. J. of Mol. Sci. **16**, 30223 (2015)
5. T. W. Parker, J. of Cl. Min. **8**, 135 (1969)
6. Jana Madejove', Peter Komadel, J. of Cl. and Cl. Min. **49**, 410 (2001)
7. C. I. R. de Oliveira¹, M. C. G. Rocha, A. L. N. da Silva, L. C. Bertolino, J. of Ceram. **62**, 272 (2016)
8. E.W. Maina, H.J. Wanyika, A.N. Gacanja, Chem. and Mat. Res. **7**, 43 (2015)
9. M. B. Adamu, Nig. J. of Bas. and App. Sci. **18**, 6 (2010)
10. B. Davarcioglu, Épitóanyag. **62**, 55 (2010)
11. Rajani Srinivasan, Adv. in Mat. Sci. and Eng. **2011**, (2011)
12. Chunguang Yu, Xuena Han, 2nd International Workshop on Materials Engineering and Computer Sciences, 290 (2015)