

Coatings and surface engineering. Industry oriented research

Renno Veinthal, Priit Kulu, Arkadi Žikin, Heikki Sarjas,
Maksim Antonov, Vitali Podgurski and Eron Adoberg

Department of Materials Engineering, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia; renno.veinthal@ttu.ee

Received 31 July 2012, in revised form 9 August 2012

Abstract. R&D activities in the field of surface engineering are conducted in three areas: thermal sprayed (TS), plasma transferred arc (PTA) welded and physical vapour deposited (PVD) wear resistant coatings. In the field of TS coatings, the study is aimed at the production of composite coatings based on recycled hardmetal powders and commercial Fe-based self-fluxing alloy powders, in PTA welding – at the production of thick metal-matrix composite hardfacings, based on Fe- and Ni-based commercial spray powders and hardmetal/cermet reinforcements. Potential areas of application of coatings are the following cost-sensitive areas like mining, energy production, road building, agriculture, etc. Thin hard PVD coatings (mono-, multilayer and composite coatings of TiN, TiAlN, AlTiN; nanocoating nACo, etc.) and different coating systems (hardmetal + coatings, high speed steel + coatings, nitrided steel + coatings) were studied. To extend the application areas of thin hard coatings, the duplex coatings and duplex treatments (self-lubricated films on PVD coatings, laser hardening of PVD coated surfaces) were investigated. As a result of the studies, the principles for coatings selection under different operation conditions are formulated.

Key words: coating, surface engineering, PTA, PVD.

1. INTRODUCTION

Basic documents of the European Technology Platform for Advanced Engineering Materials and Technologies (EuMat) have emphasized a critical role of competition between companies of advanced engineering materials including multifunctional materials, materials for extreme conditions, hybrid and multi-materials. Among them are coatings able to support the development of new goods and products by radical improvement in the characteristics of widely used

conventional materials, by substitution of traditional materials with most eco-efficient ones and by replacement of rare and/or scarce materials with less critical or expensive alternatives [1]. Areas of research interest of the Department of Materials Engineering (DME) of TUT are closely related to the trends of EuMaT, including coatings and surface engineering, recycling and reuse.

In many industrial processes such as in crushing, conveying, mixing and separating in the field of mining, steel and iron industry, cement industry, coal power plants, overground and underground working, recycling and environmental protection, the wear of instruments and other work equipment plays a significant role and also contributes to the costs. The choice of materials, which can increase wear resistance of work instruments, is highly important. One successful method for increasing instrument lifespan is surface treatment. The process of surface treatment helps to control friction and wear, improve corrosion resistance and reduce costs [2,3].

One of the most economical methods for surface treatment (to improve the service life and efficiency of metal parts subjected to wear) is hardfacing. However, hardfacing by welding is best defined as the process of deposition by one of the various welding techniques; a layer or layers of metal of specific properties is deposited on certain areas of metal parts that are exposed to wear. The possibility to apply such weld overlay coatings selectively and in different thicknesses to suit exact requirements makes hardfacing by welding also a very economical method of combating wear.

The basic research in the field of coating and surface engineering at DME of TUT has three main targets:

- production of cermet powders, as components of spray powders;
- technology of thermal sprayed, PTA welded and PVD coatings;
- testing and characterization of tribosystems.

2. MAIN RESEARCH AREAS

2.1. Cermet powders for composite coatings

Research in the field of thick hard coatings is oriented to the production of composite powder coatings based on recycled cermet powders and commercial Ni- and Fe-based alloy powders and aimed to applications in such cost-sensitive areas as mining, energy production etc.

To produce the hardmetal/cermet powders from used hardmetal/cermets parts, the high-energy mechanical milling with a semi-industrial disintegrator system DS-350 (for preliminary milling) and a laboratory disintegrator system DSL-175 (for final milling to produce the powder with particle size of 20–100 µm) was used. Grindability, chemical composition, particles granularity and angularity were studied by sieving analysis, laser granulometry, SEM analysis and mathematical methods [4]. Potential application areas of novel powder compositions and mixtures for thermal spray have been determined [5,6].

2.2. Thermal spray

Composite coatings, produced by HVOF spraying on the basis of iron self-fluxing alloy powders with WC-Co reinforcement (ranging from 25 up to 50 vol%) were studied [5]. Post treatment (laser cladding) was applied to improve the properties of sprayed coating [6].

The microstructural analysis, mechanical characterization and tribo-testing (in abrasion, erosion and impact wear conditions) of the spray fused coatings were performed. For comparison, the nickel self-fluxing alloy based coatings were studied and advantages of Fe-based coatings, reinforced by WC-Co hardmetal, were demonstrated considering the formation of structure with optimal properties (Fig. 1).

Experiments with other reinforcements ($\text{Cr}_3\text{C}_2\text{-Ni}$ and TiC-NiMo) are in progress, being more prospective for applications at elevated temperatures.

Plasma transferred arc (PTA) hardfacing process is one of the most promising and cost-efficient technologies for the production of thick wear-resistant coatings [7,8]. This technology emerged from the basic principles used in traditional welding surfacing techniques. Compared to these processes, PTA hardfacing provides a higher deposition rate and a relatively low dilution. Also the PTA hardfacing technique allows the deposition of a wider compositional

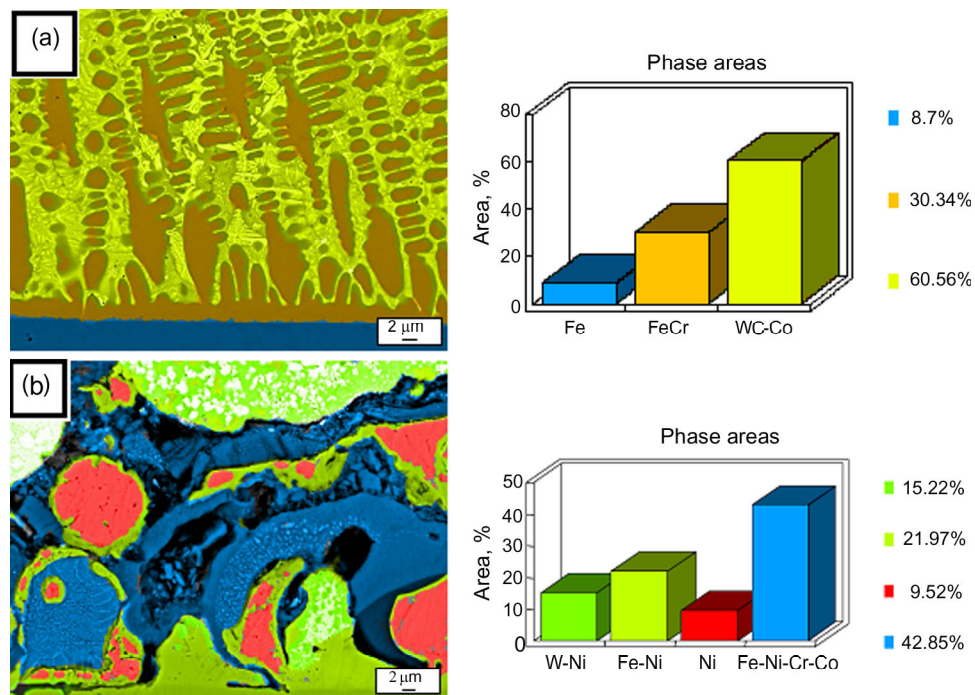


Fig. 1. Microstructure of thermal sprayed coatings: (a) FeCrSiB-20 vol% WC-Co; (b) plasma sprayed laser remelted self-fluxing alloy NiCrSiB - 20 vol% (WC-Co) coating.

spectrum of metallic and composite coatings since the coating consumables used are in powder form and not in wire or as-cast rod form [7].

Hardfacing by PTA welding is a well-established process, widely used in industry, offering high range of wear-protective coatings. Most commonly fabricated coatings are metal matrix composites (MMCs), consisting of a Ni-, Co- or Fe-based matrix, reinforced with hard ceramic particles like tungsten carbides. However, high market requirements lead to permanently increasing prices for WC. Consequently, high requirements also lead to an increase in the waste of cemented tungsten carbide. Therefore, research and development of alternative solutions, such as reusing or recycling hardmetal scraps containing tungsten carbide, has become important in recent years [8,9]. It has been shown that hardmetal scrap can also be successfully applied using PTA hardfacing process, providing good wear resistance [10]. Figure 2 shows a SEM micrograph of recycled WC-Co reinforced hardfacing.

Another common problem, which can occur during PTA hardfacing, is dissolution of primary carbides. Due to the extremely high temperature during processing, the carbides are often dissolved in the binder phase and subsequently recrystallized and re-precipitated [11]. This is especially true when processing chromium carbides as reinforcements [12,13]. Such structures can decrease corrosion and wear resistance of the material, skewing its industrial requirements [11]. Application of cermet particles can help to overcome the problem of carbide dissolution, and as a result increase wear and corrosion resistance of hardfacings [13].

Figure 3 shows the microstructures of Cr_3C_2 and cermet particles ($\text{Cr}_3\text{C}_2\text{-Ni}$) reinforced hardfacings. The developed coating is characterized by homogeneous distribution of cermet particles throughout the matrix, where the Cr_3C_2 reinforced coating consists mostly of re-precipitated spine-like phases.

Based on latest research, it can be outlined that PTA hardfacings is a very promising approach for the production of new industrially orientated materials for combating wear. As a result of these studies, the principles for coatings selection under different abrasive wear conditions are formulated [14,15].

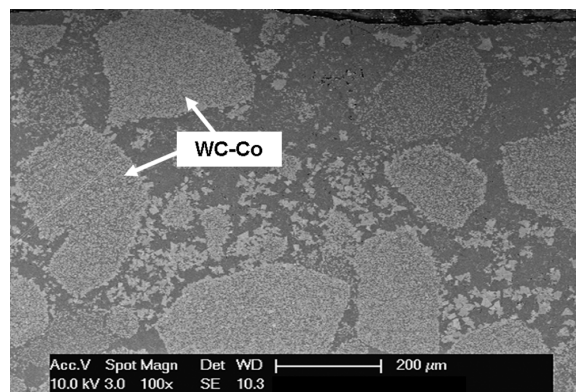


Fig. 2. SEM micrograph of NiCBSi hardfacing, reinforced with WC-Co particles.

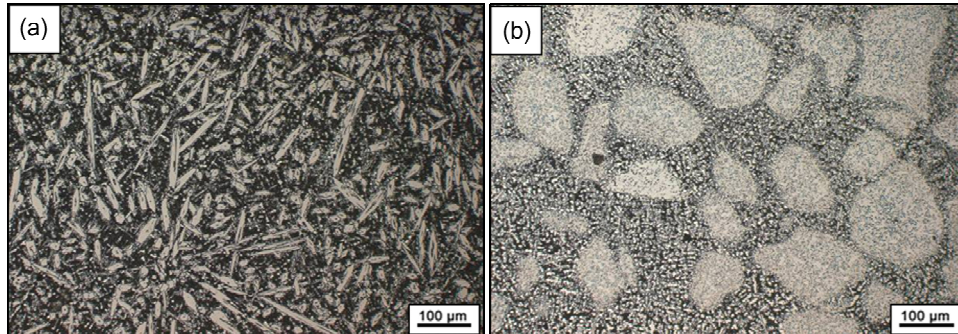


Fig. 3. Optical microscopy images of NiCrBSi hardfacings: (a) reinforced with Cr_3C_2 particles; (b) reinforced with Cr_3C_2 -Ni cermet particles.

2.3. Physical vapour deposition

In the field of thin hard coatings, physical vapour deposited coatings (mono-, multilayer and composite coatings of TiN, TiAlN, AlTiN; nanocoating nACo) and different coating systems (hardmetal-coating, high speed steel (HSS) coating, nitrided steel coating) were studied.

Different commercial coatings (TiN, TiCN, Ti/AlN and nACo) on WC-Co substrate with different surface roughness were investigated (Fig. 4). The relationship between surface roughness, coefficient of friction (CoF) and wear resistance

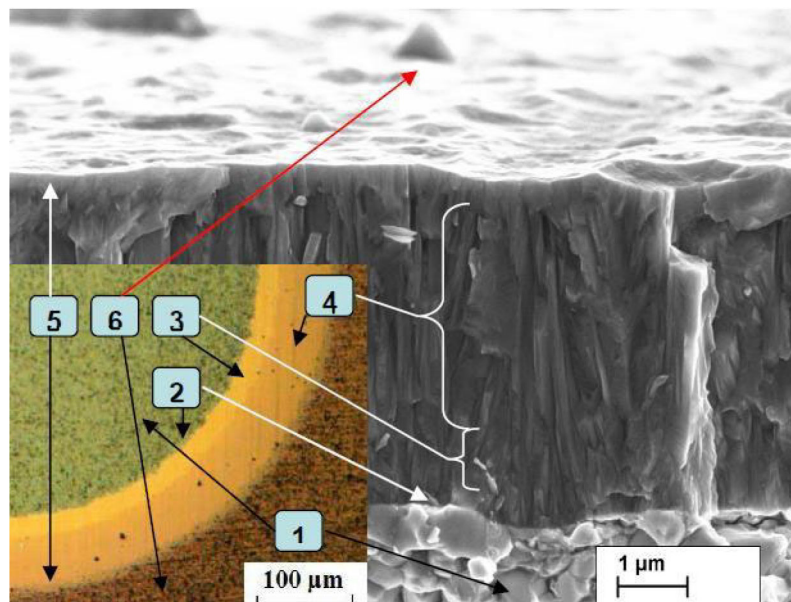


Fig. 4. Optical microscope and SEM images of fractured surface of hard PVD TiCN-coating on WC-Co hardmetal: 1 – WC-Co substrate; 2 – Ti adhesion layer; 3 – TiN coating; 4 – TiN gradient coating; 5 – C-rich TiN top layer and 6 – coating surface with microdroplets.

was clarified. To decrease the droplet phase on the surface and increase the bonding strength of coatings, a research for optimization of deposition parameters was performed. Besides the classical WC-Co hardmetal substrates the PVD coatings on TiC-NiMo cermets were studied. The properties of coatings (adhesion, nano-hardness, cracking resistance and surface fatigue) using indentation methods (Rockwell hardness test, cyclic indentation and impact wear) were studied and recommendations for the use of coatings for tooling were proposed [16].

To extend the application areas of thin hard coatings, the duplex coatings and duplex treatments (PVD coatings on plasma nitrided steel, laser hardening of PVD coated surfaces) were considered.

As a result of the research related to thin coatings, the architecture of different coating systems for different loading conditions is optimized, the technological parameters of deposition and other technological means for improving coatings quality and performance are elaborated and the principles for coatings design and selection for users (toolmakers) are formulated.

A new area of research is coatings based on carbon-diamond coatings (DC), as well as diamond-like coatings (DLC) along with carbon nanofibres (CNF) and/or carbon nanotubes (CNT) reinforced coatings.

2.4. Testing and characterization of tribomaterials

Wear and friction are essential processes for bodies in contact, experiencing relative motion and these phenomena have to be studied at different levels ranging from the field test, where the final product is tested in real life conditions (automobile running on highway, for example), followed by bench test, sub-system test, component test, simplified component test and model test, where a piece of material, from which the component is made, is tested [17].

There is a trend of growing interest toward wear testing at high temperature, testing of coatings and surface layers at micro- and nanoscale and development of laboratory test methods enabling testing of materials or components in conditions close to working ones with a high level of the test conditions control.

High efficiency of thermal processes in energy applications is realized at high temperatures and therefore materials are to be evaluated for these conditions. Devices for studying erosion at temperatures up to 700 °C are efficiently used. A new device with the possibility to introduce protective gases, minimizing oxidation, is being developed. It allows studying the effect of oxidation on high temperature erosion rates. Another device has been developed to study the three-body abrasion at temperatures up to 1000 °C with the possibility to run an experiment for several days and test 36 samples simultaneously in two abrasives. A device enabling sliding and abrasive testing at temperatures up to 450 °C is equipped by sensors for measuring coefficient of friction to reveal effect of additives providing self-lubrication properties.

Innovative coatings increase profitability of tribo-systems exploiting unique properties of structurally arranged coatings (gradient and composite structures at nano-level). However, testing of coatings (especially the thin ones) requires

additional precise measurements. In situations of mild wear, the mass loss is often very small in relation to the total mass of the worn component. For many machine elements it can be assumed that the wear appears on an atomic scale. A precision balance typically has a resolution of 10^{-6} of the maximum load (e.g., 0.1 mg resolution at 100 g load), which naturally sets a limit to the minimum load possible to quantify in relation to the total weight of the component. In order to monitor the wear rate, an analytical balance with repeatability of 0.02 mg, tactile and optical surface measuring station should be used. A new 3-dimensional optical system with improved precision has been ordered. A new device for surface fatigue testing is applied for the assessment of coating resistance to repeatable impacts (usually 10^3 – 10^7 impacts). A ball cratering device combined with the micro-abrasion tester is used for measuring the coating thickness, structure analysis and estimation of wear resistance. A new device for sliding test in various configurations with controlled environment (temperature, humidity) has been ordered. The technique allows single and repeated indentations; single and multi-pass scratching of the material subjected to as low load as 500 μ N is used for measuring surface layer properties.

A device, enabling adjustment of inertia and rigidity of the loading system while keeping the load at the same level, is designed and successfully applied for testing rough coatings for protection of stamping tools. It also allows measuring vibration parameters (velocity, acceleration, amplitude) in required directions. The full-scale device is designed and used for bench tests of chains to study the effect of chain material, design and test conditions (abrasive, humidity, type of oil, etc). High-energy disintegrator type impact wear tester is modified and intensively used to test real components (rock drilling bit inserts, for example). Centrifugal accelerator is updated to study low angle (lower than 15°) erosion that is characteristic of straight ducts. A drum-type device was built for high-speed sliding wear conditions with extended length of the wear track, providing time for restoration of the surface layer between the subsequent sliding events.

Research in the field of residual stresses in materials and coatings was aimed at the development of the material layer removal method for the determination of residual stresses and of the method of residual stresses determination in the multilayered coatings on cylindrical specimens from an isotropic material (the so-called force method).

To achieve high impact wear resistance, residual stresses in powder coatings must be compressive [14]. The residual stresses in PVD coatings on nickel and steel specimens were determined experimentally (the residual stresses in monolayers of Ti, TiN, TiCN, TiAlN, AlTiN and nACo-(AlTi)N/a-Si₃N₄ coatings).

3. Applied research

It has been indicated that despite clear key drivers, large barriers exist in the application of new technologies. One of the identified barriers is the lack of understanding between the industrial and scientific communities, which is also identified as a challenge for Estonia in general [18].

The improvement of wear resistance of tools by applying high-technological thin hard coatings is in the scope of interest of many Estonian metal-working companies and tool-makers. The goal of applied research is to implement PVD and CVD coatings architecture for increasing working reliability of cutting tools by studying processes of advanced coatings pre- and post-treatment and wear mechanisms. Thin hard coatings are used in many industries, where most important applications are manufacturing of cutting, punching and forming tools for metal and wood engineering industries. Perspectives and economic importance of this research was recently recognized in the study [18] conducted by Spinverse OY (inducted by the Ministry of Economic Affairs and Communication) in order to identify the key materials technologies for Estonian industry. As a result, the Estonian Materials Technology Program has been launched and a major project “Advanced Thin Hard coatings in Tooling”, concerning the study of wear resistant materials, coatings and tribological processes, including cutting and punching tool materials with the development of thin hard coating architecture, was initiated. As project partners, leading metal-working companies such as Norma AS, Metaprint OÜ, Kitman AS, Terätoimituse Eesti OÜ and MP & Partners Engineering OÜ (Trinon) and others are involved in applied research, performing industrial tests with advanced thin hard coatings.

Combination of hardmetals and PTA welded coatings, applied to the parts of soil removal and transfer machines, exposed to abrasive wear is a competitive solution for several companies producing heavy duty machinery. An applied research project “WearHard” (also supported by the Estonian Materials Technology Program) was recently initiated for the creation of new cost-efficient products with higher wear resistance, increased service life and new enhanced engineering designs, by focusing on the research and development of strengthening technologies, based on recycled hardmetal-based plasma fused coatings and polymer-ceramic composite materials. Meiren Engineering OÜ and Paide Machinery Factory (Paide Masinatehas AS) are involved as project partners.

REFERENCES

1. European Technology Platforms on Advanced Engineering Materials and Technologies (EuMaT): <http://eumat.eu/> (03.05.2011).
2. Mellor, B. G. *Surface Coatings for Protection Against Wear*. Woodhead Publishing, Cambridge, UK, 2006.
3. Bach, F. W. Laarmann, A. and Wenz, T. *Modern Surface Technology*. Wiley, Weinheim, 2004.
4. Kulu, P., Käerdi, H. and Mikli, V. Retreatment of used hardmetals. In *Proc. TMS 2002 Recycling and Waste Treatment in Mineral and Metal Processing: Technical and Economic Aspects*. Lulea, 2002, vol. 1, 139–146.
5. Kulu, P. and Zimakov, S. Wear resistance of thermal sprayed coatings on the base of recycled hardmetal. *Surface Coat. Technol.* 2000, **130**, 46–51.
6. Surzhenkov, A. *Duplex treatment of Steel Surface*. PhD Thesis, Tallinn University of Technology, TUT Press, 2011.
7. Deuis, R. L., Yellup, M. and Subramanian, C. Metal-matrix composite coatings by PTA surfacing. *Composites Sci. Technol.* 1998, **58**, 299–309.

8. Branagan, D. J., Marshall, M. C. and Meacham, B. E. High toughness high hardness iron based PTAW weld materials. *Mater. Sci. Eng.* 2006, A **428**, 116–123.
9. *Recycling and Reuse of Scrap Metals*. Nuclear Energy Agency. OECD, Paris, 1996.
10. Zikin, A., Ilo, S., Kulu, P., Hussainova, I., Katsich, C. and Badisch, E. Plasma transferred arc hardfacing of recycled hardmetal reinforced nickel-matrix surface composites. *Mater. Sci. (Medžiagotyra)*, 2012, **18**, 12–17.
11. Katsich, C. and Badisch, E. Effect of carbide degradation in a Ni-based hardfacing under abrasive and combined impact/abrasive conditions. *Surface Coat. Technol.*, 2011, **206**, 1062–1068.
12. Nurminen, J., Nötkki, J. and Vuoristo, P. Microstructure and properties of hard and wear resistant MMC coatings deposited by laser cladding. *Int. J. Refract. Met. Hard Mater.*, 2009, **27**, 472–478.
13. Zikin, A., Hussainova, I., Katsich, C., Badisch, E. and Tomastik, C. Advanced chromium carbide-based hardfacings. Forthcoming. <http://dx.doi.org/10.1016/j.surfcoat.2012.04.039>.
14. Kulu, P. Selection of powder coatings for extreme erosion wear conditions. *Adv. Eng. Mater.*, 2002, **4**, 392–397.
15. Kleis, I. and Kulu, P. *Solid Particle Erosion: Occurrence, Prediction and Control*. Springer, London, 2008.
16. Gregor, A. *Hard PVD Coatings for Tooling*. PhD Thesis, Tallinn University of Technology, TUT Press, 2010.
17. Zum Gahr, K.-H. *Microstructure and Wear of Materials*. Tribology Series 10, Elsevier, Amsterdam, 1987.
18. Feasibility Study for an Estonian Materials Technology Programme. <http://www.mkm.ee/innovatsiooniuuringud/> (31.05.2012).

Pinnete- ja pinnatehnoloogiaalastest uuringutest

Renno Veinthal, Priit Kulu, Arkadi Žikin, Heikki Sarjas,
Maksim Antonov, Vitali Podgurski ja Eron Adoberg

On antud ülevaate pinnetealastest uuringutest Tallinna Tehnikaülikoolis. On vaadeldud termopihustus-, plasmakeevitus- ja aurustus-sadestuspinnetealaseid uuringuid ning nende rakendusi tööstuses. Pihustuspinnete osas on käsitletud kõvasulampulbrite saamist teisest toormest desintegraatoritehnoloogiat kasutades ja nendest komposiitpulbrite saamist. Uurimisobjektiks on kiirleek- ja plasmapiindamise teel saadud paksud kulumiskindlad pinded: struktuuri formeerumine, koostise optimeerimine ning pinnete abrasiivkulumiskindlus. Aurustus-sadestuspinnete osas on põhitähelepanu õhukestel kõvapinnetel (mono-, multikiht-, komposiit- ja nanostruktuursed pinded). Uurimisobjektiks on ka sadestuspinnete disain, tehnoloogia, alusmaterjali eel- ja pinnete järeltöötlus, aga ka süsinikupõhised õhukesed kihid (teemandilaadsed, süsinikanokiud- ning torudega armeeritud pinded). Tööstusele orienteeritud töödest on tutvustatud eelkõige tööriistade ja instrumentide tugevdamiseks mõeldud õhukeste kõvapinnete ning ka paksude plasmakeevituspinnete alaseid uuringuid. On toodud ülevaade olulisematest rakenduslikest teadusprojektidest (2012–2014) Eesti materjalitehnoloogia programmi raames.