

Functional Material Solutions

2007 **2008** 2009 2010



Editor: Jari Koskinen
Graphic design: Tuija Soininen

Copyright: © VTT Technical Research Centre of Finland 2008

FUNCTIONAL MATERIAL SOLUTIONS ENABLING BREAKTHROUGH PRODUCTS



INTRODUCTION

VTT Technical Research Centre of Finland is a multi-technology contract research organization under the auspices of the Finnish Ministry of Employment and the Economy. VTT's mission is to produce research and innovation services that enhance the international competitiveness of companies, society and other customers through new technology and science-based innovations. Thereby VTT creates the prerequisites for growth, employment and well-being.

The targeted impact of all research at VTT is sustainable development of the society and the generation of new products and business. The research at VTT is gradually changing from the pure technology oriented R&D to research on business processes and services.

Materials technology plays a critical role in product solutions aimed at material and energy efficiency in accordance with the principles of sustainable development. Structural change in industry has rapidly accelerated the growth in VTT's materials research, raising it to be one of VTT's core fields of activity. Solutions based on material science have been developed

consistently at VTT for several years. The development has been carried out in close collaboration with industry and other players in the Finnish innovation chain. The volume of material research at VTT is about 400 man years per annum and its relative volume has increased gradually. Material development has an important role as an enabling technology for solving global technological problems. For example, nanotechnology is transitioning from a promising to an enabling technology that can be found in large volume products. The major trends in materials technology are the minimization of environmental impact, conservation of energy, integration of ICT to all fields of technology, differentiation of products and the demand for more user friendly products.

Figure 1 illustrates the focus on VTT's current research activities on materials technology. We provide solutions to all industrial sectors. The cross-sectoral competence areas are the following:

- nanomaterials and nanotechnology
- biobased materials and polymers
- Functional materials
- materials for emerging energy technologies and machinery
- materials for the built environment

FOCUS AREAS OF FUNCTIONAL MATERIAL RESEARCH

The aims of the functional material research at VTT is to provide its customers enabling technology to produce products with higher functionality, develop competitive production methods, add value to products in order to differentiate from competitors. The type of projects varies from high-risk, basic-research-type projects to R&D projects which are commissioned directly by industry.

The research of functional materials is a broad and generic activity based on the cross-technological approach.

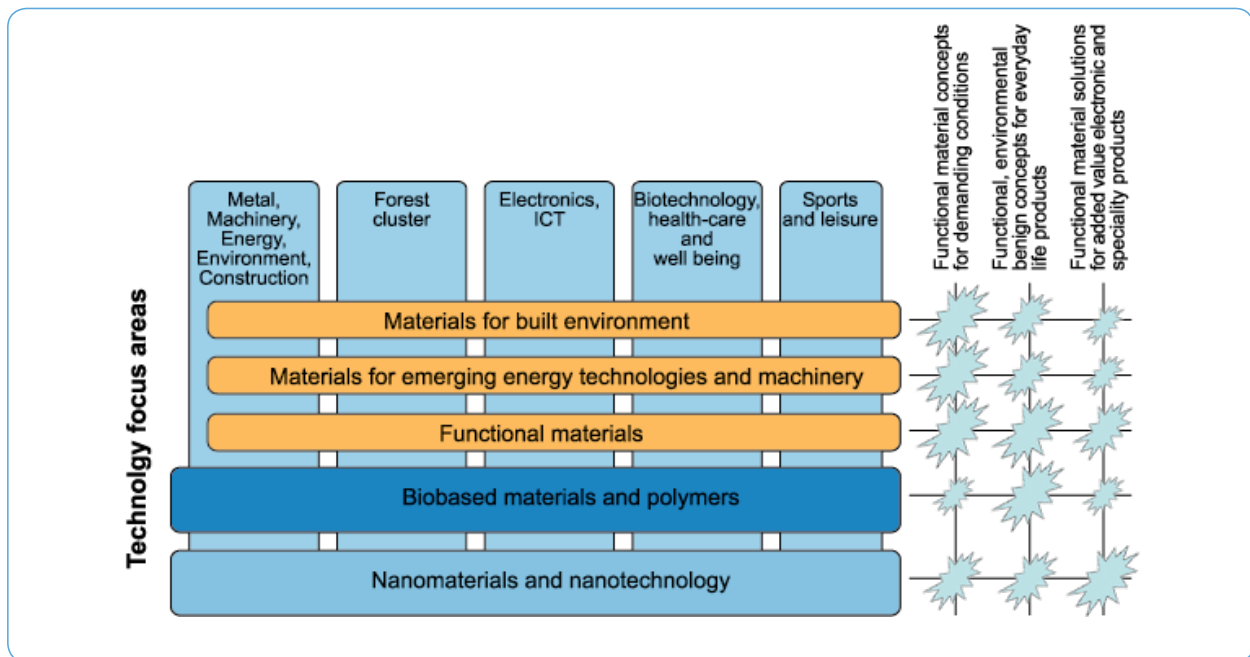


Figure 1: Focus and impact aim of VTT's current materials research activities.

The development of novel materials science is exploiting physics, chemistry, biology and engineering sciences. The three main focus areas in functional material development are utilizing biological phenomena, hybrid integrated materials and materials for advanced energy technology.

Bio-materials provide an example of nature to develop functionality in several different approaches. One approach is to learn from the processes of nature – biomimetics. For example, stimulus-responsive materials react to the changes in the environment. Self-assembly, self-cleaning and self-repair are common properties found in nature. These functionalities of nature have been simulated by applying nanoparticles, sol-gel coatings and dendrite polymers. The shape change of materials and components has been demonstrated by using electroactive polymers, piezo electrics and shape change materials. Another approach is to apply bio-materials directly. This has been done in a broad range of applications to develop materials which are bio-degradable, lightweight with high strength, antimicrobial, etc. The diagnostics technology is strongly dependent on the development of surfaces with bio-active molecules.

The hybrid materials, where active materials are combined with structural materials is an important focus area. When sensors are embedded into material structures, machines with embedded intelligence have been

demonstrated. This allows the material to monitor, for example, the structural health or the change of the ambient environment. A very important approach to develop functional hybrid materials is to apply surface coating technologies. In most circumstances the component interacts with its environment through the surface and the properties of the component is determined by the surface. Functional surfaces which bear sensing and adapting properties have been developed. The control of vibration and noise is a grand challenge in motors and structures of moving machines and vehicles. The adapting materials to control vibration have been demonstrated by applying hybrid materials which respond to the change of magnetic and electric fields and temperature. Composites with embedded smart materials have been demonstrated as materials to construct shape change structures and components.

The grand challenge of the problems of environmental change is closely related to the production and use of energy by humans. The development of alternative strategies to the existing technologies contributes to the demand to develop new functional materials. Some examples of the broad activities at VTT in the field of materials for energy technology are the following: oxygen combustion, facilitated oxygen transport, adapting wind turbine blades, energy harvesting, fuel cells, novel batteries and super capacitors, hydrogen storage and novel insulators.

IMPACT AND MARKET POTENTIAL

Functional materials are an essential part of our everyday life. New materials with improved functionality will be on the market and materials exhibiting more than one functionality will appear in applications. Worldwide there is an expectation of strong growth in the future for functional materials. In most cases, applications within automotive and consumer electronics are presenting the best opportunities, but there is a growing expectation that medical applications will become an increasingly promising area, particularly for piezoelectric and sensor-suited materials.

The economic impact of the development of functional materials is expected to be substantial. At present, the commercial exploitation of a novel material takes several years or even several decades. The short incubation time from innovation to market seen in ICT technology is expected to occur in other fields of material technology as well. This is driven by the increased speed of change in the engineering and production technology in general. The potential size of the market for material development is related to the production of all industrial goods, which makes up one-third of the GDP globally[1].

THIS PUBLICATION

In this publication a set of the most recent activities of functional material development have been selected. The development of bionanomaterials is reviewed and novel results related to hydrophobin proteins have been demonstrated. The development bio sensing material for molecular recognition has resulted into more sensitive and molecule-specific sensors. The volume of medical diagnostics is estimated to be about €17 billion. The fuel cell material development base on bio-materials and carbon nanotubes is reported. The market volume of fuel cells is expected to grow to about €3 billion by 2011. The use of novel phase change materials to store and release heat by demand is also reported. Enhancement of aluminium and cast iron and cast steel by advanced material technology

[1] www.cia.gov/library/publications/the-world-factbook/fields/2195.html

is discussed in two reports. These are examples of how to enhance the properties of traditional engineering materials. The aims of this report are to motivate industry to apply functional materials solutions in the development of new innovative products, and to tell about the process of making business from technology.

The primary contact people listed on the next page are currently in charge of setting the direction of materials research and take care that the whole organization delivers what we have promised. We would like to thank all who have contributed to this publication.

Espoo, December 2008



Jari Koskinen

Research professor, Functional materials



Anne-Christine Ritschkoff

Vice President, Strategic Research, Applied materials

Management of Material Research



Anne-Christine Ritschkoff

Vice President Strategic Research,
Applied Materials
anne-christine.ritschkoff@vtt.fi
tel. +358 20 722 5546



Eva Häkkä-Rönnholm

Vice President
Research and Development
eva.hakka-ronnholm@vtt.fi
tel. +358 20 722 4930

Research Coordinators and Technology Managers



Mika Paajanen

Research Coordinator, Nanomaterials
mika.paajanen@vtt.fi
tel. +358 20 722 3316



Ali Harlin

Research Coordinator, Research
Professor, Bio-based materials and
polymers
ali.harlin@vtt.fi, tel. +358 20 722 6386



Jari Koskinen

Technology Manager, Research
Professor, Functional materials
jari.koskinen@vtt.fi
tel. +358 20 722 5413



Pekka Pohjanne

Research Coordinator, Materials in
energy and machinery
pekka.pohjanne@vtt.fi
tel. + 358 20 722 6863



Markku Leivo

Research Coordinator, Materials in
the built environment
markku.leivo@vtt.fi
tel. +358 20 722 6933



Liisa Heikinheimo

Technology Manager, Materials
performance
liisa.heikinheimo@vtt.fi
tel. + 358 20 722 5354



Erja Turunen

Research Manager, Advanced
materials
erja.turunen@vtt.fi
tel. +358 20 722 5425

Contents

INTRODUCTION

Functional Material Solutions Enabling Breakthrough Products	3
--	---

TABLE OF CONTENTS	7
--------------------------------	----------

Biomimetics in Controlling the Structure of Materials	8
Production of Carbon Nano Nonwoven by Electrospinning a Polymer Precursor	11
Development of Enzyme Catalyzed Electrodes for Printable Fuel Cell Applications	14
Highly Specific Layers for Molecular Recognition	17
Temperature Stabilization of Sensitive Products by Phase Change Materials During Transportation	20
Dielectric Properties of Polymer Nanocomposites Produced with POSS Chemicals	22
Computer Modelling and Simulation Approach to Developing Wear Resistant Materials	25
Nanostructured Thermal Sprayed Coatings	30
Tailored Properties for Cast Surface by Using Exothermic Reaction	33
Added Value for Aluminium Surfaces using Hybrid Sol-Gel Coatings	36

BIOMIMETICS IN CONTROLLING THE STRUCTURE OF MATERIALS

Markus Linder, PhD.

One central goal in materials science today is to be able to control structures down to the molecular level. Biomolecules are naturally part of such systems, and it is therefore an interesting option to look at biology for inspiration for new materials. We have used proteins to construct hybrid materials with inorganic nanoscale components such as carbon nanotubes and metallic nanoparticles, and have shown that this is one possible way to control the nanoscale structure of such materials.

INTRODUCTION

One central goal in materials research today is to control the arrangement of molecules within the material. Examples from nature and materials research have led to the understanding that this is the route towards functional and better performing materials. Natural materials such as mussel shells and bone have a composite structure where structurally hard domains are embedded in a matrix which gives a combination of tensile strength, stiffness and toughness. Miniaturization in electronics and new manufacturing techniques such as printing also set

new demands for materials. As miniaturization progresses to smaller and smaller structures, we are turning to self assembly as a means of manufacture. Nanoscale electronic components such as carbon nanotubes could find their positions within complex structures by self-assembly, thus making structures that are smaller than current ones, using techniques that are faster and require less investment in processing equipment.

In the self-assembly of functional components and the manufacture of complex high-performance materials, nature is still unbeatable. The study of these for technological use is called biomimetics. We find numerous examples in nature, and we know that life is dependent on these concepts. It is therefore logical to look at nature for ideas and concepts. Self-assembling components, nanoscale motors and complex materials are found everywhere. The molecules of nature have unbeatable properties that would make the molecules themselves attractive as components in man-made devices. Precision of size and structure is one example. Proteins can have a size of several nanometres, with molecular weights of tens of thousands

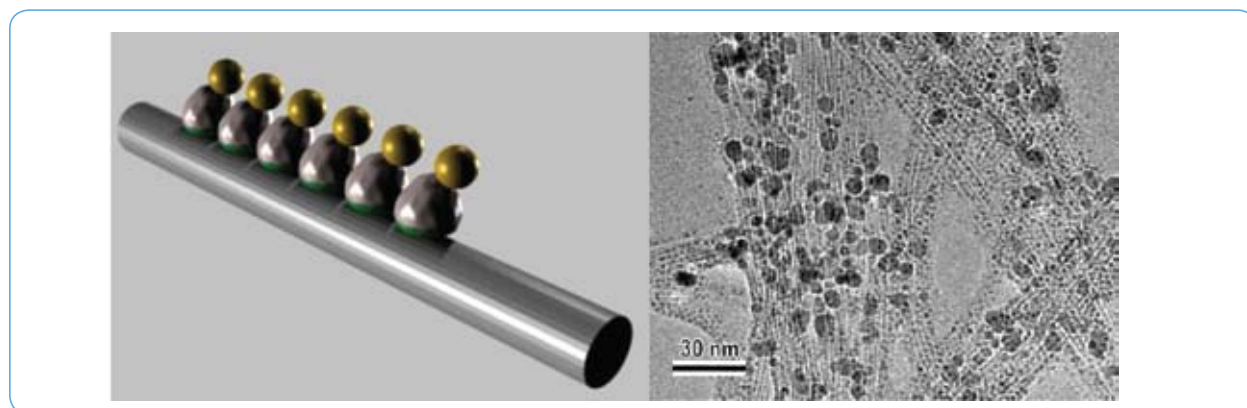


Figure 1. Organizing gold nanoparticles along single-walled carbon nanotubes (SWCNTs). On the left is an illustration showing one SWCNT with a row of proteins (hydrophobins) bound to it. On the protein there are single gold nanoparticles. On the right is an electron microscope image showing the real material. Along the carbon nanotubes we see ordered lines of gold nanoparticles (1.4 nm). The protein is not seen and the large particles are residual catalyst particles from the SWCNT synthesis.

of grams per mole. They are still defined on the atomic scale with the exact positions of every atom. In addition, the techniques of molecular biology have opened the possibility to engineer these structures and change the molecules with atomic precision.

Biological molecules have evolved to function in environments of certain humidity and conditions such as temperature and pH. Nonetheless, there are no fundamental limitations such that these molecules could not function in entirely different and much harsher environments. The chemical structure of proteins is very stable and needs, for example, strong acids and high temperatures to be hydrolyzed.

RESULTS AND DISCUSSION

However, it is not simple to turn these into useful knowledge or adapt them to man-made synthetic materials and components. For research to progress we need good models that are as simple as possible, and yet address the key questions. In our fundamental research in this field we have turned to some systems that are manageable. We have looked at a group of proteins called hydrophobins. These proteins are used by some microbes for surface attachment and have two properties that we are primarily interested in; they attach strongly to some surfaces and they self-assemble into very ordered structures at interfaces [1]. In addition we are able to use recombinant DNA technology to modify their molecular structures. In one example we showed that we can use these properties to structurally modify single-walled carbon nanotubes (SWCNT) [2]. We used the self-assembly and surface adhesion of hydrophobins to solubilise SWCNTs. By engineering the protein we could bind metallic nanoparticles to the protein. Altogether, this resulted in a material in which gold nanoparticles were positioned with exact spacing along SWNTs in an ordered way (see Figure 1). The work shows that it is possible to combine different nanomaterials in a very defined structural way using proteins. The specific functionalization also opens a

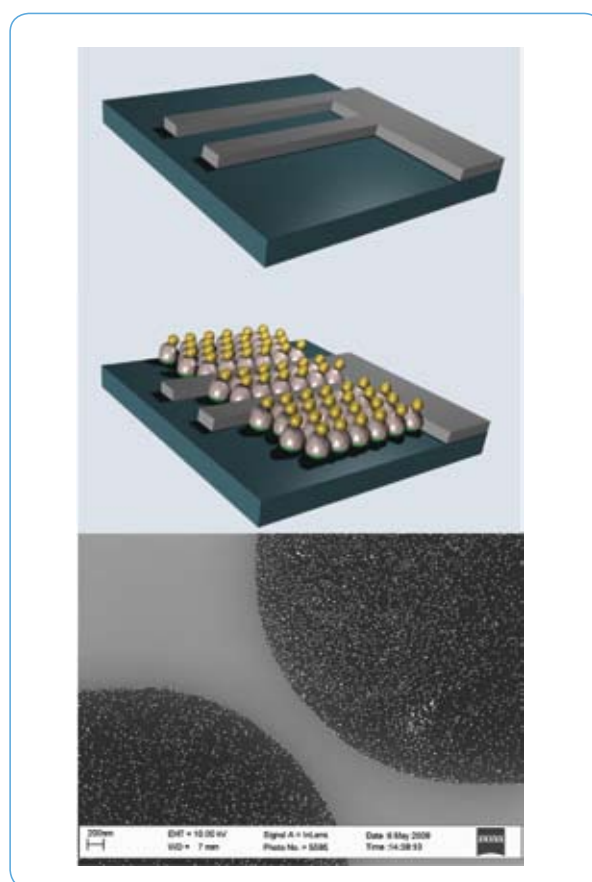


Figure 2. By binding proteins (hydrophobin) selectively to certain surfaces, patterns of nanoparticles can be produced. In this case a pattern of silicon oxide on top of a silicon wafer was used. Selective binding of the protein to the silicon, and the positioning of gold nanoparticles on top of the protein in a selective way produces a pattern of nanoparticles on the patterned surface (bottom).

route towards methods for other types of self-assembly, as for building larger structures. An example of this is shown in Figure 2, where the selective binding of hydrophobins to certain surfaces was utilised to produce patterns of gold nanoparticles by self-assembly. In this

case, lithography was used to first make a pattern of silicon and silicon oxide. By tuning the solution conditions, the hydrophobin could be made to bind only to the silicon, and due to an engineered additional functionality in the hydrophobin, we could make it in turn bind cold nanoparticles, and thus a sandwiched composite structure was formed. This is an example of combining top-down lithography techniques with bottom-up self-assembly to produce a material that has a defined structure from the nanometre scale to macroscopic dimensions.

CONCLUSION

In conclusion, we have shown that biomolecules can be used to produce complex nanostructured materials, where non-biological components are combined in a highly controlled and ordered way. We speculate that in the future this could be a way to build devices and functional materials that depend on the nanoscale combination of different functionalities. Applications are probably still years ahead, but technological development has reached a point where it is possible to see biomimetics as a realistic alternative in the future. Applications are likely to be found ranging from electronics to bio-based consumer materials.

ACKNOWLEDGEMENTS

This work has been carried out by the Nanobiomaterials group together with collaborators. The persons involved are Katri Kurppa, Arja Paananen, Geza Szilvay, Päivi Laaksonen, Riitta Suihkonen, Hua Jiang, Albert Nasibulin, Markku Kainlauri, Jani Kivioja, Esko Kauppinen, and Jouni Ahopelto. Financial support has come from the Frontier programme at VTT and the Academy of Finland.

REFERENCES

1. Linder MB, Szilvay GR, Nakari-Setälä T, Penttilä ME: Hydrophobins: the protein-amphiphiles of filamentous fungi. *Fems Microbiology Reviews* 2005, 29:877-896.

2. Kurppa K, Jiang H, Szilvay GR, Nasibulin AG, Kauppinen EL, Linder MB: Controlled hybrid nanostructures through protein-mediated noncovalent functionalization of carbon nanotube. *Angewandte Chemie-International Edition* 2007, 46:6446-6449.



CONTACTS

Markus Linder
Chief Research Scientist
markus.linder@vtt.fi
Tel. +358 20 722 5136

PRODUCTION OF CARBON NANO NONWOVEN BY ELECTROSPINNING A POLYMER PRECURSOR

Ali Harlin, Pirjo Heikkilä (TTY)

Modified carbon fibres provide major advantages, such as high catalytic efficiency of the fuel cell and flow management in the cell, improving power generation and speed of correspondence. Breakthrough material performance is achieved by implementing precursor modification in electrospinning in combination with a carbonation process.

INTRODUCTION

The electrospinning method is a promising and intriguing method that enables the preparation of nanofibres as a commercial process. In electrospinning, a polymer solution is drawn into fibres utilizing electrostatic forces. Simple electrospinning equipment consists of a nozzle, a collector and a voltage source. Voltage applied between the nozzle and the collector has a magnitude of some tens of kilovolts. When electrical forces exceed the critical limit, the solution is ejected from the tip of the cone and the jet is accelerated towards the collector.

Electrospinning produces small fibre diameters, ranging from less than 10 nm to some mm, typically below 0.5 mm. A high specific surface area is dependent on the fibre diameter. The length of electrospun fibres can easily be many kilometres. A wide variety of polymers can be used, including commodity plastics, engineering plastics, specialty plastics, and natural polymeric materials.

Electrospun fibre net products have high porosity, good interconnectivity of pores, small pore size, low basis weight, and high permeability. Some properties of the fibres and web depend on the process variables; for ex-

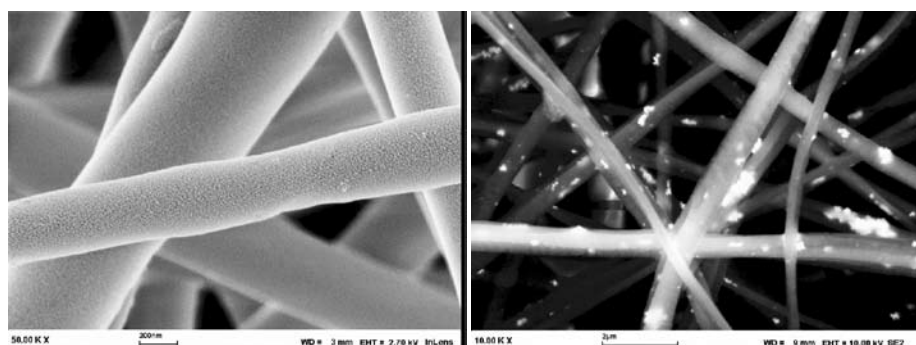
ample, short distances may lead to inadequate drying of fibres which are fused to each other. Electrospun fibre net products can be used in many fields of application:

- Filters and membranes
- reinforcement in composite materials
- chemical and biological protection and protective clothing
- sensor applications
- tissue engineering
- wound dressings
- drug delivery materials
- solar and fuel cells
- batteries
- catalyst applications
- nanoelectronics and optoelectronics
- sound and thermal insulation
- fibre templates in preparation of nanotubes with TUFT process
- preparation of carbon nanofibres.

METHOD

Smaller CNFs with a very high specific surface area can be obtained. The smaller the size of the precursor fibre, the higher the crystallinity of carbonized fibre that can be achieved, leading to a higher electrical conductivity and mechanical strength of carbonized fibre web. The properties of electrospun precursor

Nano fibre containing carbon nanotubes (left) and platinum particles (right)

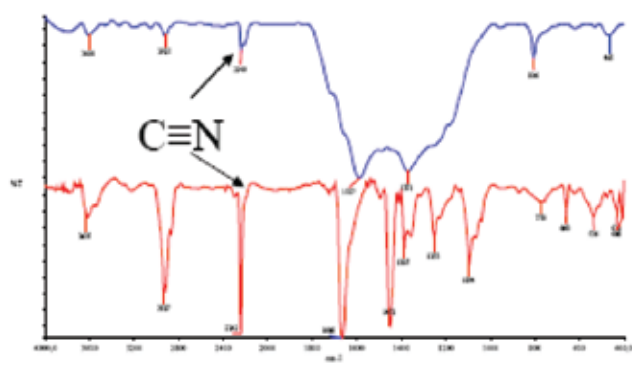




Nano fibre network



Appearance of oxidized PAN web, right, and the same sample after carbonization at 800 °C, left.



FTIR spectra of electrospun sample (blue) and the same sample before oxidization (red).

sor fibres can be adjusted in many ways. Higher graphitization degrees and ordered structures are achieved in carbonization at higher temperatures. The electrical properties of carbonized electrospun web can be affected by varying the porosity of the web and controlling the activation temperature.

EXPERIMENTAL

Electrospun PAN precursor fibres are typically prepared from a solution of *N,N* dimethylformamide (DMF). The specific surface area of graphitized normal-sized PAN fibres is typically below ten m²/g, but the use of an electrospun precursor can increase the specific surface area to hundreds of m²/g. Stabilization of PAN is carried out prior to pyrolysis. At temperatures of between 260 °C and 400 °C, PAN forms stable ladder structures which will bond together into a graphite sheet during pyrolysis.

The carbonization process of polymeric fibres can be influenced with a catalyst. The presence of an iron(III) acetylacetonate catalyst enables a graphite structure. A graphitizing catalyst can also be a nano-sized transition metal (e.g. Pt, Cu, Fe, Ni, Co).

End-use related additives can also be added to the precursor solution. For example, in fuel cells metal salts such as PtCl₂ and PdCl₂ within the electrospun fibres have been reduced by the subsequent process into metallic catalyst nanoparticles having sizes as small as 5 nm. Activated carbon nanofibres can be prepared using the catalytic effect of a transition metal or other compounds to form mesopores on the surface of electrospun fibres.

An electrospun PAN web was prepared using a continuous multi-nozzle electrospinning system at TUT. The PAN/DMF solution was used with a polymer concentration of 14.5 wt.% and a viscosity of 2050 cP. The electrospun web was prepared on a metal grid so that it could

be easily removed. Properties: Fibre diameter 359 nm \pm 97 nm, Thickness 104 μ m and Areal weight 5.2 g/m².

Carbonation was conducted at VTT in a special safety gas oven, which requires special expertise and advanced control technology. The samples were measured by FTIR spectra of the electrospun sample oxidised at 260 °C at TUT (in blue), and the same sample before oxidation (in red).

CONCLUSION

The production of carbon nano nonwoven by electrospinning a polymer precursor is an attractive choice for medium size fuel-cells in power tools and fuel cells in vehicles with a power of 1-100kW. Alternative applications are possible using supercondensators and battery or EMI shielding

ACKNOWLEDGEMENTS

MARAPOKE Advanced Material Solutions for PEM Fuel Cells 1.10.2007 - 31.12.2009.

- Project funded by Tekes (Finnish Funding Agency for Technology and Innovation) and project consortium.
- Research partners: VTT, Tampere University of Technology, Helsinki University of Technology and Åbo Akademi. Industrial partners: Ahlstrom Glassfibre Oy, Beneq Oy, Finetex Technology Oy, Outokumpu Oyj and Premix Oy.
- Team working with electrospinning and carbonization of precursor fibres: Pirjo Heikkilä and Ali Harlin (TUT), Lisa Wikström, Pertti Kauranen and co-workers (VTT).



CONTACTS

Ali Harlin
Research Professor
ali.harlin@vtt.fi
Tel. +358 20 722 6386

DEVELOPMENT OF ENZYME CATALYZED ELECTRODES FOR PRINTABLE FUEL CELL APPLICATIONS

Maria Smolander, Matti Valkiainen



Figure 1. Demonstration of the printed biofuel cell as a power source for a digital thermometer.

the biocathode the electrons are then transferred to the electron acceptor, typically dioxygen or peroxide, through an enzymatic reaction. The electron transfer can take place either directly between the enzyme and the electrode, or more commonly through a mediated electron transfer where the redox mediators shuttle the electrons between the enzyme and the electrode.

Biofuel cells offer an inexpensive alternative to classical fuel cells, which rely on transition metals as

catalysts. Due to the usage of biocatalysts, the cell can also be operated under mild conditions, i.e. at or near room temperature and in neutral pH. In addition, the wide variety of reactions catalysed by enzymes allows a wide range of possible fuel substances to be used. An ideal biofuel cell should generate both a high current and a high potential, and it should be stable enough for the application.

Printing enables cost-efficient mass production of electronics and other functionalities on large and flexible substrates like plastic, paper and fabrics. The development of new printable functional materials can be harnessed in several application areas, such as displays, sensors, power sources and printed RFID tags. In many applications, the printed power sources should be biodegradable or possible to incinerate with normal household waste. The production costs should also be reasonable.

Printed electronics with an integrated power source has remarkable market potential in several mass-market consumer products, e.g. as package-integrated functionalities (sensors, displays or entertaining features, etc.). One of the main requirements is that the power source should be biodegradable or possible to incinerate with normal household waste. The main goal of our research has been to meet these demands in a printable fully enzymatic biofuel cell suitable as a power source, e.g. for an active RFID tag.

INTRODUCTION

Biofuel cells are devices capable of directly transforming chemical energy to electric energy via electrochemical reactions involving enzymatic catalysis [1,2]. At the bioanode the fuel, such as sugar or alcohol, is oxidised with the help of a suitable oxidoreductase enzyme, and the electrons are transferred to the anodic electrode. At

The miniaturized biological fuel cell has the potential to meet these demands. The low peak current capacity of an enzymatic fuel cell can be improved by integrating the cell with a printed capacitor. The main goal of our research is to develop a printable fully enzymatic biofuel cell based on the use of enzymes as catalysts on both the cathode and anode electrodes. The power supply development aims to meet the demands of, for instance, active RFID tags.

MATERIALS AND METHODS

A wide variety of different oxidoreductases can potentially be applied as biocatalysts in biofuel cells, converting chemical energy from renewable chemicals to electricity with high overall efficiency. The work carried out at VTT focused especially on the construction of printable enzyme electrodes. The cathode electrode is based on fungal laccases as biocatalysts. Since one of the prerequisites of a biofuel cell-based power source is as high a cell potential as possible, and in order to avoid complex serial connections or stack-structures, we have focused on the fungal *Trametes hirsuta* laccase, which has a relatively high redox potential. Bacterial dehydrogenases and oxidases have been studied as biocatalysts for the anode half cell.

As described in Smolander et al. [3], conductive inks based on these biocatalysts were formulated, and the maintenance of enzymatic activity in printed layers based on these inks was determined. Finally, stand-alone power source prototypes were constructed based on the use of these bioactive layers.

RESULTS AND DISCUSSION

The first challenge in the development of a completely printable biofuel cell was the formulation of a printable enzyme-containing conductive ink, in which the enzyme maintains its electrochemical activity both before and after printing. Most conductive inks are based on various solvents to disperse the conductive material and

other components (e.g. binders and stabilisers), whereas enzymes, need aqueous solutions for optimal stability and catalytic activity. Different water soluble inks were therefore considered, and two commercially available inks reported to have a relatively high conductivity were selected for the printing tests with the fungal laccase. The composition of these inks was further optimised. As a result of this optimisation work we were able to incorporate laccase enzyme in its active form in different types of conducting inks, and dry printed layers could be produced.

These dry printed layers maintained their enzymatic activity for up to several months, and could also be heat-treated to some extent without considerable loss of activity, allowing for heating and drying phases, if needed, in the industrial manufacturing of these printed layers.

Furthermore, fuel cell prototypes could be constructed utilising an optimized printed laccase-ABTS layer as the cathode and a printed Zn layer as the anode. If the humidity within the printed cell was well controlled, a voltage of between 0.8V and 0.6V could be maintained for several days under a 2.2 k Ω load. On the basis of the performance data of the cell, together with the finding that the printed layer could be stored dry for several months, it is likely that the power source could potentially be manufactured with reel-to-reel adjustable methods, stored dry and activated by the addition of moisture to the cell. Compared to fuel cell constructions reported earlier for implantable systems and/or working in electrolyte solutions [4,5], this type of printed standalone fuel cell described is a completely novel system, which would be able to operate in a dry environment with the aid of an internal moisture reservoir.

CONCLUSIONS

Printed electronics with integrated power sources has remarkable market potential in several mass-market consumer products, e.g. as package-integrated func-

tionalities (sensors, displays or entertaining features, etc.) or as part of diagnostic devices. One of the main requirements is that the power source should be biodegradable or possible to incinerate with normal household waste.

Printable electrodes based on biocatalysts would offer an inexpensive way to mass-produce disposable devices such as biosensors and power sources based on biofuel cells. By using suitable conductive inks the enzymatic activity can be maintained in the printed layer. It was also demonstrated that biofuel cells can be manufactured at an industrial scale by utilizing silk screen printing. The low peak current capacity of an enzymatic fuel cell can be improved by integrating the cell with a printed capacitor. The development of printed capacitors, requiring changes to material selections and redesigning of the configuration, is currently taking place.

ACKNOWLEDGEMENTS

Collaborators at VTT, especially Anu Koivula, Harry Boer, Robert Roozeman, Rolf Rosenberg, Kirsi Immonen, Otto-Ville Kaukonen, Pia Qvintus-Leino, Hannu Helle, Salme Jussila, Pauliina Saurus, Anu Vaari, Ville-Mikko Ojala, Johanna Pelkonen and Jari Keskinen and project partners Helsinki University of Technology (TKK), Åbo Akademi (ÅA), University of Galway, University of Southampton, University of Rome, Hebrew University and BVT are thanked for their collaboration.

The research has been supported by TEKES (the Finnish Funding Agency for Technology and Innovation) and European Commission FP6.

Industrial participants Joutsenpaino, Ciba Speciality Chemicals, Evox Rifa, Tervakoski, Stora Enso, Asperation, Avantone, GE Healthcare, Hansaprint, Metso, M-Real, Perlos, UPM-Kymmene, Akzo Nobel Inks, Enfucell and Panipol are thanked for their contributions.

REFERENCES

- [1] Minter SD, Liaw BY, Cooney MJ. Enzyme-based biofuel cells. *Curr Opin Biotech* 2007;18:228-234.
- [2] Davis F, Higson SPJ. Biofuel cells—Recent advances and applications. *Biosens Bioelectron* 2007;22:1224-1235.
- [3] Smolander M, Boer H, Valkiainen M, Roozeman R, Bergelin M, Eriksson J-E, Zhang X-C, Koivula A, Viikari L. Development of a printable laccase based biocathode for fuel cell applications. *Enzyme and Microbial Technology* 43 (2008) 93 -102.
- [4] Mano N, Mao F, Heller A. Characteristics of a miniature compartment-less glucose-O₂ biofuel cell and its operation in a living plant. *J Am Chem Soc* 2003;125:6588-6594.
- [5] Palmore GTR, Kim HH. Electro-enzymatic reduction of dioxygen to water in the cathode compartment of a biofuel cell. *J Electroanal Chem* 1999;464:110-117.



CONTACTS

Maria Smolander
Senior Research Scientist
maria.smolander@vtt.fi
Tel. +358 20 722 2836

HIGHLY SPECIFIC LAYERS FOR MOLECULAR RECOGNITION

Inger Vikholm-Lundin

We have developed a method for producing a layer that recognise only the target molecules we want to identify and ignore all other molecules present in a solution. This highly specific layer is composed of antibodies or any receptor molecule with a molecular recognition capability.

We have also according to a novel concept developed a synthetic receptor that has the same response as that of a highly sensitive antibody layer.

INTRODUCTION

Immunoassays are commonly used to measure the concentration of a variety of hormones, allergens, viruses and bacteria in clinical laboratory tests. Such tests are of great importance in the diagnosis of cancer, HIV and others. Presently, there is an increasing need for more easy-to-use immunoassays for use in emergency units, doctor's offices or even at home to aid more rapid clinical diagnosis. Immunoassays are based on the very specific and tight binding of an antibody to an antigen. This binding between antibodies and antigens has traditionally been measured by radioimmunoassay, solid phase enzyme immunoassay and fluoroimmunoassay. All these approaches rely on a marker molecule, such as a radioisotope, an enzyme or a fluorescent probe, that allows quantification of the antibody-antigen complex. In most cases, the result is not obtained until several incubations, washing and separation steps have been carried out. We are developing molecular sensors that allow monitoring of the antigen-antibody binding directly and which do not require the use of labelled species.



The molecule that recognise the target molecule to be detected for example the antibody is mostly adsorbed on the sensor surface or covalently coupled via functional groups. Most of the molecules on the surface therefore take up the wrong orientation or have lost their activity. We have previously oriented antibodies by covalent coupling of antibody fragments to linker lipids embedded in a host monolayer matrix of phospholipids to achieve a high antigen binding efficiency.¹⁻³ Other molecules than the target molecule was however also adsorbed on the layer. In order to reduce this non-specific binding to the layer our new approach was to embed all other parts of the antibodies than the recognising part in a repellent polymer (Figure 1). Considerable effort has been taken to replace the antibodies with robust and inexpensive synthetic receptor molecules.⁴ We have also made input in this research field.

We have used surface plasmon resonance (SPR) to investigate the binding capacity of molecular layers composed of antibody Fab'-fragments and the repellent polymer, but also that of synthetic receptors.¹² The immobilisation methods has been demonstrated for anti-human IgG,⁵⁻⁹ anti-C reactive protein,⁸ anti-*helicobacter pylori* and anti-morphine¹⁰ antibody fragments.

MATERIALS AND METHOD

Human IgG and polyclonal goat anti-human IgG F(ab')₂ (Jackson ImmunoResearch), CRP and monoclonal anti-CRP F(ab')₂ (Medix Biochemica) and anti-morphine Fab'-fragments have been used. The lipoate derivative Lipa-DEA used to prepare the syntetic receptor and the repellent polymer was prepared as described elsewhere.^{8,12}

Glass slides coated with a thin film of gold were assembled into the SPR device (either the SPRDevi from VTT, Tampere, Finland, or the Biacore 3000 from Biacore, Uppsala, Sweden) and the monolayer of antibody Fab'-fragments and disulphide bearing polymer, pTHMMAA were prepared as previously described.⁸ The surface was blocked with 0.5 g/l bovine serum albumin (BSA), rinsed with buffer and the interaction with antigen or patient samples was determined in phosphate buffer or serum/PBS (1/100). Layer formation of the synthetic receptor has also been described elsewhere.¹²

RESULTS AND DISCUSSION

When Fab'-fragments of human IgG were directly coupled to gold there was a threefold higher response on binding of antigen compared to that of a layer composed of F(ab)₂-fragments.^{5,6} The antibody F(ab)₂-fragments were adsorbed on the surface in a randomly oriented fashion. The antibody Fab'-fragments are covalently attached on the gold through the cysteine groups opposite the antigen binding site are thus oriented and can because of that bind a higher amount of antigen.

When the antibody Fab'-fragments were applied to the gold surface and the remaining free space in between the antibodies were filled up with the repellent pTHMMAA polymer, a considerably lower amount of molecules were non-specifically adsorbed to the layer and the specific binding was even higher than without the polymer. A large part of the antibody fragments seemed to be attached in a site-directed fashion through the free thiol bonds (Figure 1). Coupling of the antibody Fab'-fragments and the polymer, and thus both the amount of NSB and antigen binding, but also the ability to regenerate the layer is dependent on the immobilisation or-

der. When Fab'-fragments and pTHMMAA were immobilised on the surface from the same solution up to 80% of the antigen could be removed, indicating a high degree of site-directed immobilisation of the antibody fragments. About 60% of the antigen could be removed, when the fragments were coupled directly onto a clean Au surface before the polymer or if low concentrations of polymer were attached onto gold before the Fab'-fragments. The highest response to hIgG was obtained when the antibody fragments were attached onto the surface before the polymer. The total antigen binding is almost ten-fold to that reported by others.¹¹

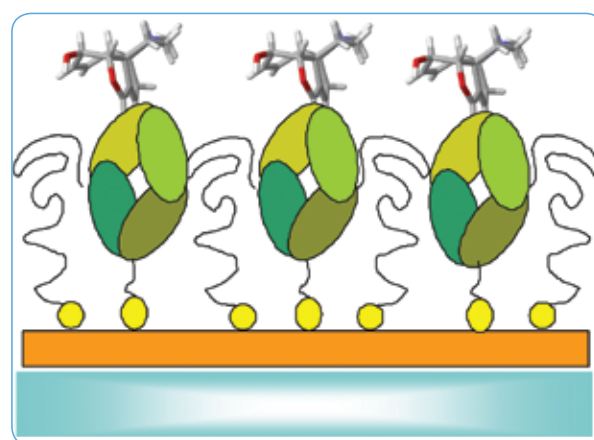


Figure 1. Schematic view of site-directed antibody Fab'-fragments and polymer covalently attached onto gold and interaction of the layer with antigen.

The occurrence of low concentrations of CRP can give an indication of a hearth attack. CRP could be detected in a concentration range of 1 ng/ml – 50 µg/ml from a spiked buffer solution. The response was 5-fold to that of a F(ab)₂-fragment/polymer layer. The non-specific binding of BSA was only 1% of the CRP binding and a detection limit of 1.5 ng/ml could be obtained. CRP was successfully detected in patient samples with good reproducibility. The layer would be sensitive enough to analyse the CRP concentration in human serum for predicting cardiovascular disease. By modifications of the polymer such as length and repellent properties, the immunological response of the layer could most probably be further improved.

We have also according to a new concept developed a synthetic receptor that has the same response as that of the oriented antibody layer.^{10,12} The approach to produce synthetic receptors has been to use versatile, bifunctional self-assembling ligands, which in the presence of a tem-

plate are capable of forming imprinted Self-Assembled Monolayers, i-SAMs.¹² The compounds carry a disulphide moiety on one side for anchoring to the gold surface and a variable functional group on the carboxylic acid side for complexation with the template. After self-assembly, the template is washed out of the self-assembled film, and “footprints” may be formed in the layer, which allow re-binding of the template. In a preliminary study morphine was chosen as the model template and various lipoate derivatives were used for i-SAM formation. A large collection of lipoate derivatives was screened by molecular dynamics simulations in various solvents and a set of ligands showing favourable interactions with morphine in aqueous environment was selected for synthesis. Imprinted SAMs made from one of these ligands and morphine showed a binding comparable to that of the site-directed antibody Fab'-fragment monolayer.¹⁰

CONCLUSION

Antibody Fab'-fragments can be directly coupled onto gold and the space in between the fragments can be filled up with a non-ionic hydrophilic polymer. The antibody fragments should be embedded in the protein repellent host matrix in such a way that only the antigen binding part of the antibody sticks out from the monolayer surface. NSB to the host matrix and to the antibody fragments could be substantially reduced and a high antigen binding capacity could be obtained.

The immobilisation method is generic and can be used for coupling any antibody in an oriented manner to the sensor surface. There are several advantages with the method:

1. It is simple and easy to perform in only a few steps.
2. The site-directed orientation of the antibodies ensures a high specific binding of antigen with a minimum amount of antibody needed for immobilisation.
3. The non-specific binding is low due to the repellent polymer.
4. A membrane-like environment is provided by the polymeric host matrix that protects the antibodies from unfolding.
5. The layer is reasonable stable, and can be regenerated for repeated use.

Synthetic receptors shows great promise with a similar response as that of the oriented antibody monolayers.

REFERENCES

1. Vikholm, I., Albers, W.M. “Oriented Immobilisation of Antibodies for Immunosensing”, *Langmuir* 14 (1998) 3865-3872.
2. Vikholm, I., Albers, W.M., Välimäki, H. Helle, H. “In situ Quartz Crystal Microbalance Monitoring of Fab'-fragment Binding to Linker Lipids in a Phosphatidylcholine Monolayer Matrix. Application to Immunosensors”, *Thin solid Films* 327-329 (1998) 643-646.
3. Vikholm, I., Viitala, T., Albers, W.M., Peltonen, J. “Highly Efficient Immobilisation of Antibody Fragments to Functionalised Lipid Monolayers”, *Biochim. et Biophys. Acta* 1421 (1999) 39-52.
4. Sellergren, B. (Ed.), 2001. *Molecularly Imprinted Polymers: Man-made Mimics of Antibodies and their Application in Analytical Chemistry*. Elsevier, Amsterdam.
5. Vikholm, I. “Self-assembly of Antibody Fragments and Polymers onto Gold for Immunosensing”, *Sensors & Actuators B* 106 (2005) 311-316.
6. Vikholm-Lundin, I. “Immunosensing Based on Site-Directed Immobilization of Antibody Fragments and Polymers that Reduce Nonspecific Binding”, *Langmuir* 21 (14) (2005), 6473 -6477.
7. Vikholm I. and Sadowski, J. “Method and Biosensor for Analysis”, FI20011877A; 2003-03-25; US20070254382; 2007-11-01.
8. Vikholm-Lundin, I., Albers, W. M. “Site-Directed Immobilisation of Antibody Fragments for Detection of C-Reactive Protein”, *Biosensors & Bioelectronics* 21 (7) (2006) 1141-1148.
9. Albers, W.M., Auer, S. Helle, H., Munter, T. and Vikholm-Lundin, I. “Functional Characterisation of Fab'-fragments Self-Assembled onto Hydrophilic Gold Surfaces” *Colloids and Surfaces B*, in press.
10. Vikholm-Lundin, I., Pulli, T., Albers W.M., Tappura, T., “A Comparative Evaluation of Molecular Recognition by Monolayers Composed of Synthetic Receptors or Oriented Antibodies.” *Biosensors & Bioelectronics* 24 (2008) 1042-44.
11. Bonroy, K. Frederix, F., Reekmans, G., E. Dewolf, E., R. De Palma, R., Borghs, G., Declerck, P., Goddeeris, B., *J. Immunol. Meth.* 312 (2006) 167.
12. Tappura, K., Vikholm-Lundin, I. and Albers, W. M. “Lipoate-based Building Blocks for Construction of Imprinted, Self-Assembled Molecular Thin Films” *Biosensors and Bioelectronics* 22 (2007) 912 - 919.



CONTACTS

Inger Vikholm-Lundin
 Chief Research Scientist
 Inger.Vikholm-Lundin@vtt.fi
 Tel. +358 20 722 3363

TEMPERATURE STABILIZATION OF SENSITIVE PRODUCTS BY PHASE CHANGE MATERIALS DURING TRANSPORTATION

Pertti Kauranen, Lisa Wikström

EXECUTIVE SUMMARY

Phase change materials can be used for storing heat or cold in buildings, vehicles, textiles and electronics, or for temperature stabilization of sensitive products. In this study they have been tailored for temperature stabilization of blood preparates during transportation.

INTRODUCTION

Large amounts of thermal energy can be stored in a narrow temperature interval as the latent heat of fusion in melting and crystallization processes. The use of the latent heat of a phase change material (PCM) is an effective way of storing heat or cold. PCMs are used to protect sensitive materials such as medicine, blood products and foodstuffs from cold and heat during transportation. Additional applications of PCMs are the protection of electronic devices from overheating, functional textiles, the heating and cooling of buildings and heat accumulators for car engine preheating.

This paper presents a case study concerning the utilization of PCM in temperature stabilization during transportation of sensitive products. PCM-stabilized cold boxes offer a small-scale alternative to mobile refrigerators. At a larger scale, temperature-sensitive products are typically transported using mobile diesel engine-driven refrigeration units in vans, lorries and trucks, or electric refrigerators in containers.

Blood preparates are transported in PCM-stabilized cold boxes by the Red Cross Finland Blood Service. Whole blood and trombocytes are transported at $+22 \pm 2^\circ\text{C}$ (room temperature), red cells at $+4 \pm 2^\circ\text{C}$ (cool) and plasma at below -20°C (frozen). A commercial PCM is used for room temperature, an ice gel for cool, and dry ice for frozen transportation.

For room-temperature transportation the regulations are changing and the PCM used at the moment doesn't meet these new temperature regulations. Because of its low

sublimation temperature, dry ice causes problems in the handling of plastic red cell packaging.

METHOD

The performance of alternative commercial PCMs was studied, and suitable ones were tested at VTT and verified by independent testing by Red Cross Finland. The tests at VTT were carried out with a differential scanning calorimeter (DSC) and with tests in a cold box at limiting temperatures of -26°C and $+35^\circ\text{C}$. Because the performance of commercial room-temperature PCMs was not satisfactory, a new PCM was tailored by VTT for this specific need.

RESULTS AND DISCUSSION

A commercial PCM paraffin recommended by VTT has been shown to outperform the state-of-the-art ice gel in red cell transportation in independent testing by Red Cross Finland. The replacement of dry ice with a eutectic salt solution could mitigate the problems associated

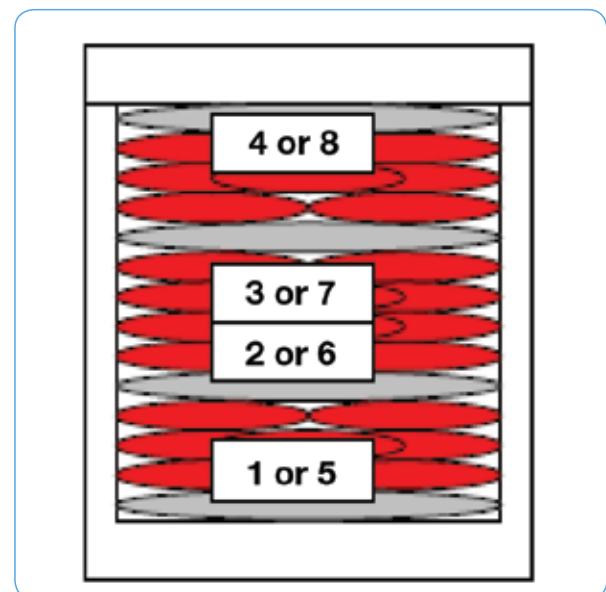


Fig. Test box at Red Cross Finland, red pieces are blood products, and gray pieces are PCM.

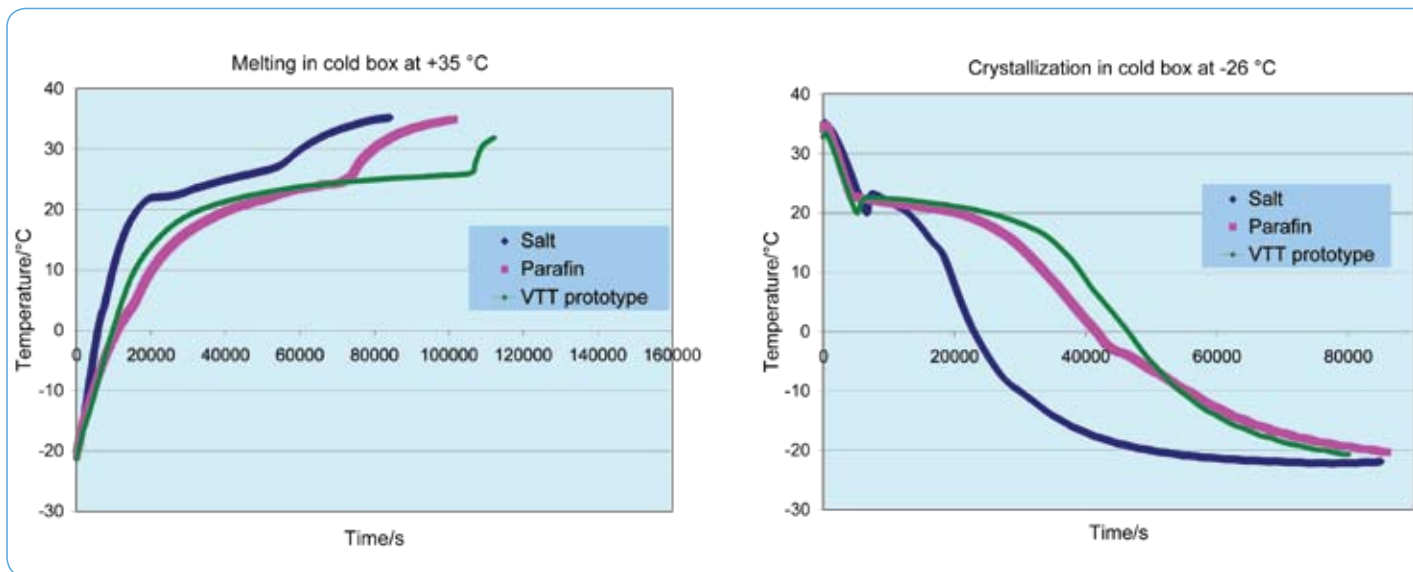


Fig. 1. Comparison of VTT Prototype cold packs to commercial counterparts for room temperature stabilization (+22 +/-2 °C).

with the damage dry ice does to plastics used for red cell packaging.

For the transportation of whole blood and trombocytes, a new PCM prototype was tailored. At summer temperatures (+35 °C) the VTT prototype could keep the PCM temperature within the required limits for about 8.5 hours, compared to 6.8 hours or 5.1 hours with the commercial PCMs. The VTT prototype also performed well at cold temperatures. The tests were done in an empty cold box without blood preparates.

CONCLUSION

Thermal energy storage using PCMs is a fascinating possibility. There are a number of commercial PCMs available, but they cover only a discrete number of temperatures and do not meet all application needs. The weaknesses of commercial PCMs can be partly eliminated by modifying the PCMs and careful design of heat exchangers or packaging, but in some cases completely new PCM materials are needed.

The high prices of energy and the trend towards sustainable energy production will increase the need for PCMs and other advanced energy storage solutions.

ACKNOWLEDGEMENTS

Funding by Tekes, Lumikko Ltd, Danisco Sweeteners Ltd, Eurocon Ltd, VAK Ltd, Red Cross Finland Blood Service, Itella Ltd, Easy Km Ltd, EHS-Group Ltd and, Tuoretie Ltd is gratefully acknowledged.

REFERENCES

Alanen, Raili; Heikkinen, Jorma; Keskinen, Jari; Laitinen, A.; Rämä, Miikka; Sipilä, Kari; Wikström, Lisa, Intelligent Products and Systems. Technology theme - Final report. Ventä, Olli (ed.). VTT Publications 635. VTT. Espoo (2007), 151 - 176

<http://www.motiva.fi/pcmakku>



CONTACTS

Pertti Kauranen
Senior Research Scientist
pertti.kauranen@vtt.fi
Tel. +358 20 722 3575

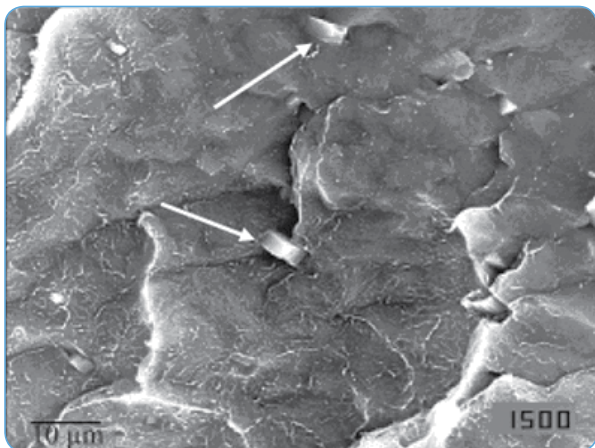


Fig. 2. Fracture surface of 3 wt.% octamethyl POSS PP. POSS crystals indicated with arrows. The nano-dispersed material was composed of two intermixed regions with different POSS contents.

epoxy. The reactive side groups are designed to take part in the curing reactions of the epoxy. The POSS chemicals were mixed with epoxy resin. An anhydride hardener and a tertiary hardener catalyst were added during mechanical mixing for 30 min. The POSS content varied from 0-4.8 wt.%. The molecular structure of the different POSS molecules is shown in Fig 1. The materials processing is described in more detail elsewhere [vⁱ]

Materials characterization

The materials composition and structure were analysed with various methods, including SEM, AFM, RAMAN, and TEM. AFM was used in a non-contact tapping mode by analysing the energy dissipation of the oscillating cantilever tip-sample interaction.

The physical properties were evaluated with the following methods: The lightning impulse (LI) and AC breakdown strength measurements were done immersed in mineral oil at room temperature by using a setup described in reference [vⁱⁱⁱ]. The LI tests were done by using 50kV, 6A high-voltage power supply. In the AC breakdown tests the voltage applied was 50 Hz AC, with a 2 kV/s rate increase until breakdown occurred.

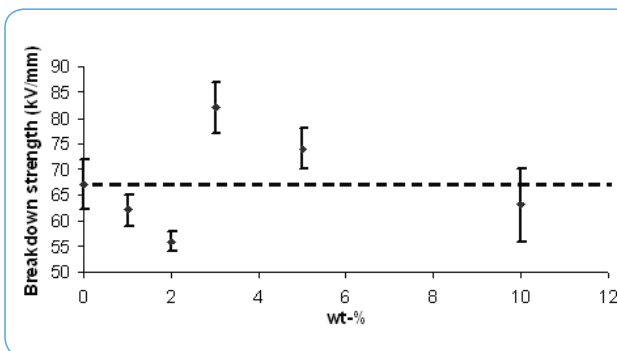


Fig. 3. Influence of octamethyl POSS amount on AC breakdown strength of PP (reference line dotted).

RESULTS AND DISCUSSION

Morphology

The AFM and SEM measurements indicate a dispersed PP POSS nanocomposite structure. In some compositions (particularly 3 wt.%), some POSS crystals with a size of 3-5 μm were embedded in the polymer. They were observed with SEM from the fracture surface produced at liquid nitrogen temperature (Fig 2.). Also the nano-dispersed material was composed of two intermixed regions with different POSS contents.

In the fractured surface of the POSS epoxy nanocomposite, some 150 nm particles are visible. The AFM and TEM investigation of the POSS epoxy indicated that the material is composed of two intermixed polymers with different POSS contents. The feature sizes were roughly 20 nm in diameter. The TEM images indicate aggregates containing tens of POSS molecules.

AC and LI breakdown strength

AC and LI breakdown voltages for POSS PP as a function of POSS composition are shown in Figures 3 and 4. The greatest AC breakdown strength was achieved with the 3 wt.% POSS concentration. The increase in breakdown voltage was 22%. The greatest LI breakdown strength was achieved with a 10 wt.% POSS content. The increase in breakdown voltage was 11%.

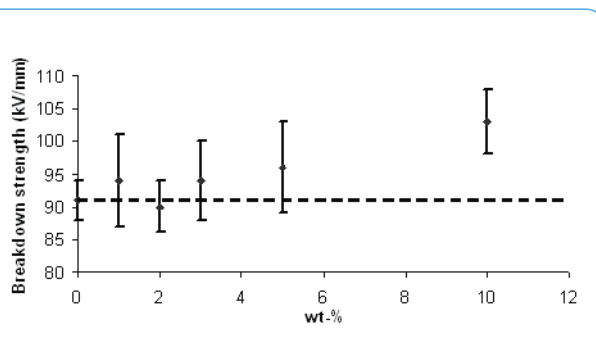


Fig. 4. Influence of octamethyl POSS amount on LI breakdown strength of PP (reference line dotted).

In LI breakdown measurements of 1 wt.% octaglycidyl-dimethylsilyl POSS epoxy composite, seven samples out of ten did not break. When the voltage was raised high enough, a flashover occurred in the transformer oil. With the reference epoxy, only one sample did not break.

POSS particles significantly enhance the insulation properties of the POSS PP and POSS epoxy. It is assumed that the POSS nano particles act as electron scavengers in the polymer matrix. Electrons are impeded by the POSS molecule surfaces. If the dispersion is increased and more nanoparticle surfaces are active, it is expected that the insulation properties will be further enhanced.

CONCLUSION

The addition of nanoparticles has been demonstrated to be a powerful means of enhancing the properties of polymers. The breakdown high-voltage properties of PP and epoxy can be increased by 10-20% by applying POSS nanoparticles with proper functionalization. Further dispersion is assumed to enhance the properties even more. These materials will have great potential as insulators in novel high-power networks and devices, as well as in microelectronics, with its demands for ever-reducing dimensions.

ACKNOWLEDGEMENTS

The assistance of the large number of co-workers mentioned in references 6 and 7 is greatly acknowledged. The work was financed by TEKES (Finnish Funding Agency for Technology and Innovation) and by the industrial participants of the HYDSO project .



CONTACTS

Mikko Karttunen
Senior Research Scientist
mikko.karttunen@vtt.fi
Tel. +358 20 722 3544

COMPUTER MODELLING AND SIMULATION APPROACH TO DEVELOPING WEAR RESISTANT MATERIALS

Kenneth Holmberg, Erja Turunen, Anssi Laukkanen, Helena Ronkainen, Tommi Varis, VTT and Kim Wallin, Academy of Finland

VTT researchers have been pioneers in international science with their computer modelling and simulation techniques for the development of coated surfaces with superior wear resistance and low friction properties. They have introduced a novel PPSP (Performance-Properties-Structure-Processing) multi-scale concept that is based on linking wear and friction performance by micro-FEM computer models to mechanical surface properties, surface microstructure and coating processing parameters. The modelling methods have been applied on 1–5 µm thick hard coatings, such as TiN, DLC and MoS₂, on steel as well as on about 200 µm thick thermally sprayed WC-CoCr coatings developed through a Process Mapping concept. The novel approach offers completely new possibilities of systematic and focused material development of wear resistant and low friction coated surfaces with the aim to control and prolong the lifetime of machine components and industrial tools.

INTRODUCTION

Wear is a major issue in our modern society since about 30–50% of the industrial production in industrialised countries is used to replace worn out products. Wear of products and components results in high maintenance costs, interruption in production, unpredicted breakdown that may cause human safety risks, high energy consumption and environmental pollution. Very commonly people are used to wear – it has always been there – and if a product is worn out it is just replaced without thinking that there are possibilities to influence wear. The rapid recent technological and scientific development has brought many new tools and techniques that make it possible to develop new materials and new constructions that can radically reduce and sometimes even eliminate wear.

Wear is defined as the process of continuous material removal from a surface due to the loading from a contact-

ing moving substance or substances. Wear is a part of the field of science and technology named *tribology*, which includes topics related to wear, friction and lubrication. It has been difficult to study the wear process because it occurs at the interface between interacting bodies and is thus usually hidden from investigators by the wearing components. It becomes visible in malfunctions and on the damaged surfaces of worn parts when they are replaced. Traditionally, the wear processes have been investigated mainly experimentally by a large variety of wear testing devices and with a trial-and-error approach. There is typically a large scatter in wear test results reported today due to the large number of influencing parameters, including material, design, input energy and environmental parameters, and also due to the difficulty to control the testing conditions well. The results may be conflicting and are often difficult to analyse and interpret.

A NOVEL PPSP METHOD

VTT has taken a pioneering role in developing a novel concept for the development of wear resistant materials. The novel PPSP method (Performance-Properties-Structure-Processing) is a systematic approach starting from product lifetime and reliability requirements, transferred to requirements in terms of wear performance. The wear rate of the defined contact system is directly influenced by the material properties of the surfaces which are determined by the microstructure of the materials. The microstructure again is a result of the material processing which includes a large variety of influencing parameters (figure 1a).

A better understanding of the links from material processing to surface microstructure, from microstructure to surface properties and from the properties to wear performance opens completely new possibilities to optimised surface design and to tailor surfaces for specific low wear applications. Each tailored product surface is related to the estimated prevailing wearing conditions that might

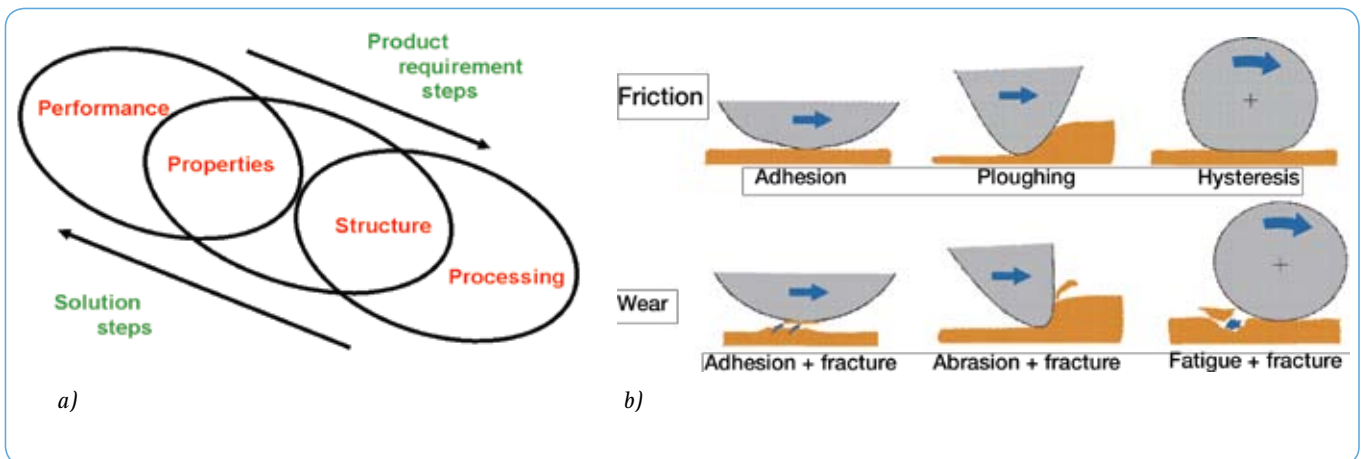


Figure 1. The required lifetime defines the required wear performance, the material properties, the microstructure at the surface and the surface processing methods that are linked to each other by interactions to be modelled (a). A tribological contact analysis defines the dominating wear and friction mechanisms for the chosen application (b).

include adhesive, abrasive, fatigue and chemical wear or a combination of these (figure 1b).

The choice of different surface designs may include bulk surfaces with optimised microstructure, thick lamellar coatings, thin surface films with, e.g., nanocomposite, multilayer, gradient or lattice structures (figure 2a).

COMPUTER SIMULATION ASSISTED DEVELOPMENT

Wear testing is today not the only way to increase our knowledge of prevailing wear mechanisms. The rapidly increasing computer capacity, the new material modelling tools and the improved micro- and nanolevel characterisation techniques makes it possible to perform computer simulations where the stresses, strains and deformations are calculated for a defined contact with defined surface properties. The calculated loading conditions can then be compared with the strength of the material and the risk for deformation, cracking, fracture and wear can be estimated. The simulations show the interaction between the different influencing parameters and help to find the dominating parameters to be optimised.

Depending on the studied contact conditions the modelling and simulation may be relevant to perform either on macro-, micro- or nanolevel (figure 2b, Olsson, 1997; Holmberg et al., 2007). The advantage with the holistic modelling and simulation approach is that it supports a logical fundamental understanding of the influencing parameters and the effect of different parameters can be precisely calculated without any problem of scatter and repeatability.

The computer modelling and simulation approach is believed to be the future route to better understand and control the wear process. It is supported by the rapid development of the last few decades, which has brought about several new techniques and possibilities, such as:

- the continuous increase in computer capacity makes it possible to run very complex material models and simulations and get results out in a reasonable time frame,
- new computer modelling and simulation tools have been developed that make it possible to model the surface material response to loading in a wear situation and to simulate the generated stresses, strains and deformations that form the conditions for crack initiation and crack growth with wear particle detachment as result; such tools are:
 - 1) *continuum methods* (1 μm - 1m): FEM (Finite Element Method),
 - 2) *meso-, damage and fracture mechanics* (1 - 100 μm): FEM, EFG (Element Free Methods), X-FEM (Extended FEM),
 - 3) *dislocation dynamics* (100 nm-100 μm): FEM, DDD (Discrete Dislocation Dynamics), and CDD (Continuum Dislocation Dynamics),
 - 4) *molecular dynamics* (0.1nm - 1 μm): MDS (Molecular Dynamic Simulation), and
 - 5) *first principles methods* (0.1 - 10 nm): DFT (Density Functional Theory),
- there is an increasing understanding of the fundamental wear mechanisms that result in material removal from the surface and the interactions related to the macrolevel as well as microlevel, and now also to some extent, the nanolevel, and

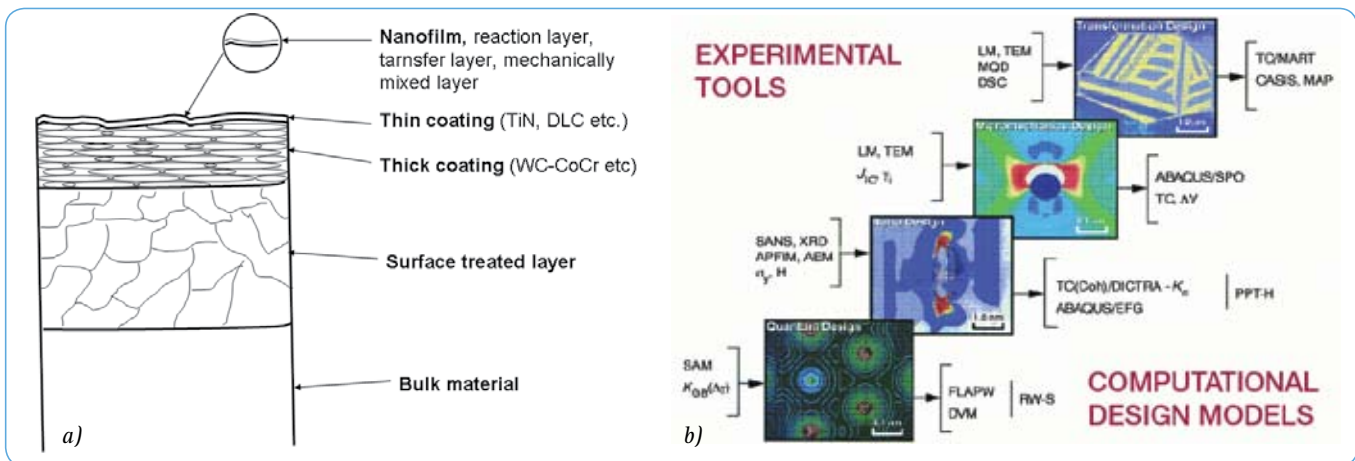


Figure 2. A variety of different surface modification techniques are available for the optimal tailored surface solution that may be a simple or a more complicated surface design including various material structures (a). Computational surface design models are developed at different scale levels and verified by experimental tools (b) (Olsson, 1997).

- new material characterisation techniques give the possibility to characterise the surface properties and their changes at the surface and very close under the surface with great precision; such techniques are, e.g., SEM and TEM (Scanning and Transmission Electron Microscopy), Raman Spectroscopy, SIMS (Secondary Ion Mass Spectrometry), AES (Auger Electron Spectroscopy), AFM (Atomic Force Microscopy), nanoindentation, etc.

Figure 1a shows that the following three links are needed to be modelled for a holistic modelling of the wear performance of a surface:

- 1) the interactions between the manufacturing process of the surface and the surface microstructure,
- 2) the interactions between the surface microstructure and the surface material properties, and
- 3) the interaction between the material properties and the wear process.

The modelling and simulation approach has been used in contact mechanics (Wriggers, 2002) and in fracture mechanics of structures (Andersson, 2004). The same FEM-based approach has successfully been used for improved understanding of the wear process of a sliding contact with one of the surfaces coated by a thin surface coating (Gong and Komvopoulos, 2004a,b; Holmberg et al., 2003, 2007; Holmberg and Mathews, 1994, 2009). Precise measurements of the elastic (elastic modulus), plastic (yield strength) properties at and close under the surface and the contact geometry made it possible to simulate stress and strain conditions, deformations and calculate fracture behavior and evaluate the

wear performance of the coated surface and the effect of influencing parameters.

The modelling approach is fairly laborious and requires a good fundamental understanding but when a good model has been developed the information is very generic and can be used for different applications. A requirement is always that the validity of the model must be tested by comparing the results with some suitable empirical test.

RESULTS

This approach has successfully been used by VTT researchers that have modelled the link from surface material mechanical properties to the surface fracture and wear performance for steel surfaces covered by a thin, 1-5 μm thick, hard ceramic titanium nitride coating (TiN), diamond-like carbon coating (DLC) and molybdenum disulphide coating (MoS₂). In experimental studies these coatings have excellent wear resistance and low friction properties. The stresses, strains and deformations in a loaded contact were simulated. The crack initiation effects and the crack growth mechanisms were studied and the fracture toughness of the surfaces was calculated. The influence of coating hardness, coating elasticity, coating thickness, bond layer thickness and Young's modulus between coating and substrate, as well as residual stresses have been reported (Holmber et al., 2003, 2007). Figure 3 shows the dominating effects of bond layer parameters on surface first principal stresses in a 2 μm thick coating on a steel surface with a rigid 500 nm thick bond layer between the coating and the substrate.

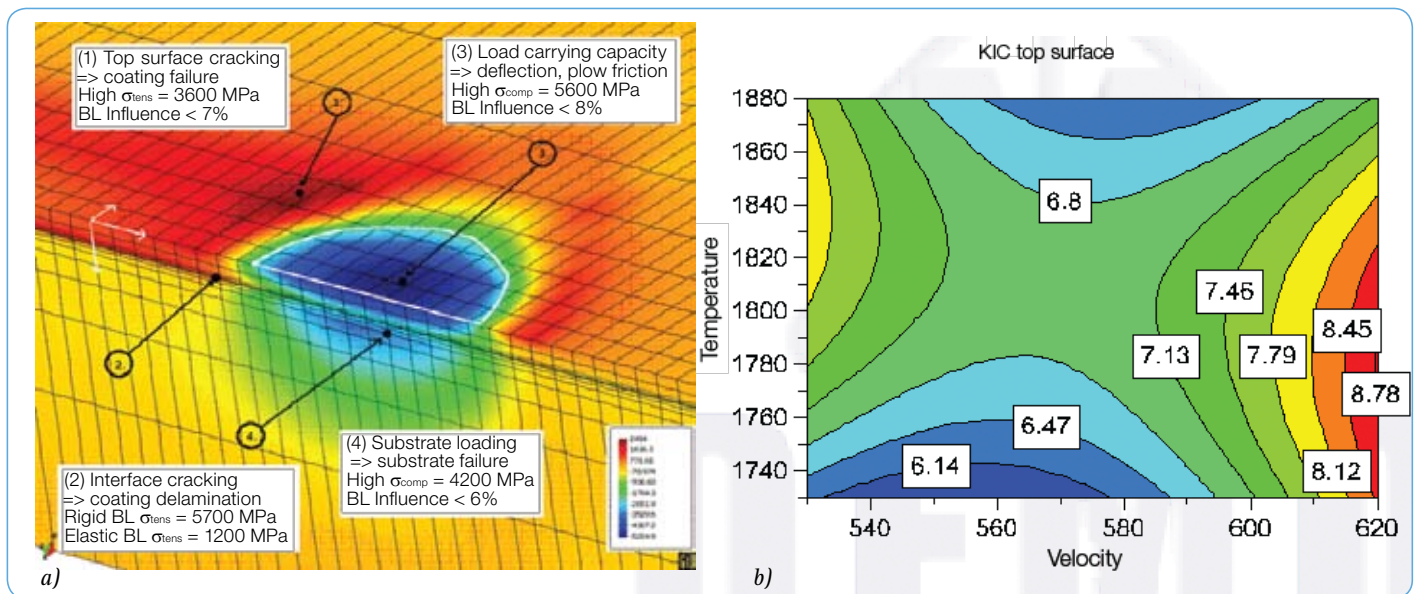


Figure 3. First principal stresses resulting in cracking and wear initiation on top surface and at a depth section in the symmetry plane of sliding when a diamond ball is sliding on a $2 \mu\text{m}$ thick TiN coating on steel with a 500 nm thick rigid bond layer. The major failure mechanisms and the influencing parameters are indicated (a). Variation in fracture toughness of a WC-CoCr coating in the T - v plot obtained from thermal spraying Process Mapping (b).

VTT researchers have developed a Process Mapping concept (Turunen, 2005; Turunen et al., 2005, 2006) that links the processing parameters to surface microstructure and residual stress and further to material properties in thermal sprayed coatings. With this systematic approach a complex multi-variable thermal spray process has been simplified and logical cause and effect interactions demonstrated. This is an important step for introduction of the thermal spray process into the PPSP-method.

CONCLUSIONS

The new PPSP (Performance - Properties - Structure - Processing) method is a holistic and systematic approach to developing wear resistant and low friction materials. It opens possibilities to find new material solutions for energy efficient and well controlled machines, production tools and consumer products. VTT has successfully used this technique for optimising the surface properties of very thin and hard TiN, DLC and MoS_2 coatings and somewhat thicker WC-CoCr thermally sprayed coated surfaces.

ACKNOWLEDGEMENTS

The financial support of TEKES (the Finnish Funding Agency for Technology and Innovation), Taiho Kogyo Tribology Research Foundation (Japan) and Savcor Coatings (Finland) is gratefully acknowledged.

REFERENCES

- Anderson, T.L., Fracture mechanics. Fundamentals and applications. Third edition. CRC Press LLC, London, UK, 2004, 700 p.
- Gong, Z.Q., Kompopoulos, K., Mechanical and thermomechanical elastic-plastic contact analysis of layered media with patterned surfaces, *Trans. ASME, J. Tribology*, 126 (2004a) 9–17.
- Gong, Z.Q., Komvopoulos, K., Surface cracking in elastic-plastic multi-layered media due to repeated sliding contact, *Trans. ASME, J. Tribology*, 126 (2004b) 655–663.
- Holmberg, K., Laukkanen, A., Ronkainen, H., Wallin, K., Varjus, S., A model for stresses, crack generation and fracture toughness calculation in scratched TiN-coated steel surfaces, *Wear*, 254 (2003) 278–291.
- Holmberg, K., Matthews, A., *Coatings Tribology*, Elsevier, Amsterdam, The Netherlands, 1st ed., 1994, 442 p. and 2nd ed. in press, 2009, 650 p.
- Holmberg, K., Ronkainen, H., Laukkanen, A., Wallin, K., Friction and wear of coated surfaces - scales, modelling and simulation of tribomechanisms, *Surface and Coatings Technology*, 202 (2007) 1034–1049.

Olsson, G.B., Designing a new material world, Science, 288 (1997) 5468, 993–998.

Turunen E., Diagnostic tools for HVOF process optimization, Doctoral Thesis 2005. VTT Industrial Systems, Espoo. 66 p. + app. 92 p. VTT Publications: 583, ISBN 951-38-6677-7; 951-38-6678-5

Turunen E., Varis T., Hannula S-P., Kulkarni A., Gutleber J., Vaidya A., Sampath S., Herman H., On the role of particle state and deposition procedure on mechanical, tribological and dielectric response of high velocity oxy-fuel sprayed alumina coatings, Materials Science and Engineering: A, Volume 415, Issues 1-2, 15 January 2006, Pages 1–11

Turunen E., Varis T., Keskinen J., Fält T., Hannula S-P., Improved mechanical properties by nanoreinforced ceramic composite HVOF coatings, Advances in Science and Technology Vol. 45, Trans Tech Publications, Switzerland 2006 pp. 1240–1245

Wriggers, P., Computational Contact Mechanics, John Wiley & Sons, Chichester, UK, 2002, 441 p.



CONTACTS

Kenneth Holmberg
Dr, Research Professor
kenneth.holmberg@vtt.fi
Tel. +358 20 722 5370

NANOSTRUCTURED THERMAL SPRAYED COATINGS

Tomi Suhonen, Erja Turunen, Tommi Varis

Improved mechanical properties have widely been demonstrated for bulk nanocrystalline materials. A decrease in grain size has been found to be favourable for a wide range of ceramic and metallic materials. Nanocrystalline materials can offer better strength, toughness, thermal shock resistance, lower thermal conductivity and better wear resistance than their conventional counterparts. Typically, ceramic materials have good mechanical and corrosion properties even at high temperatures, but the main obstacle to their wider technical use is their inherent brittleness. For nanostructured bulk composites with nanosized metal or ceramic precipitations in the nanocrystalline ceramic matrix, improved fracture toughness properties have been reported. An increasing effort has been made to transfer such improvements into thermal sprayed ceramic coatings. In this paper we describe the development of HVOF sprayed nanocrystalline Al₂O₃ composite coatings, where the grain size of Al₂O₃ has been decreased and a few percent of alloying elements has been added in order to toughen the coating. The benefits of decreasing the carbide size in WC-CoCr-composite coatings are also presented.

INTRODUCTION

In thermal spraying, material is partially or fully melted, usually in the form of a powder in a flame. These molten droplets are accelerated in the flame and hit the surface of the component to be coated. The droplets solidify on the surface and a laminated structure is formed. In Figure 1a) an HVOF spray gun and a process diagnostic sensor are shown. Figure 1b) shows a typical thermal sprayed ceramic coating cross-section, and in Figure 1c) a schematic representation of a nanocomposite powder is presented. Due to the fast heating and cooling of the particles, the nanostructure is also preserved in the coating (Fig. 2). Table 1 gives an overview of typical applications and materials of thermal sprayed coatings.

METHODS

Five different alumina-based coatings were produced by HVOF-spraying. The reference material was a pure Al₂O₃ coating with a conventional grain size (>1 μm). In other coatings the alumina grain size was 200 nm, and the precipitate size was <50 nm. The produced nano-coatings were n-Al₂O₃, n-Al₂O₃-5%Ni, n-Al₂O₃-5vol%ZrO₂ and n-Al₂O₃-5vol%SiC. The effect of alumina grain size refinement and precipitate strengthening was studied by mechanical property measurements and an abrasive wear test (ASTM G 65 rubber wheel).

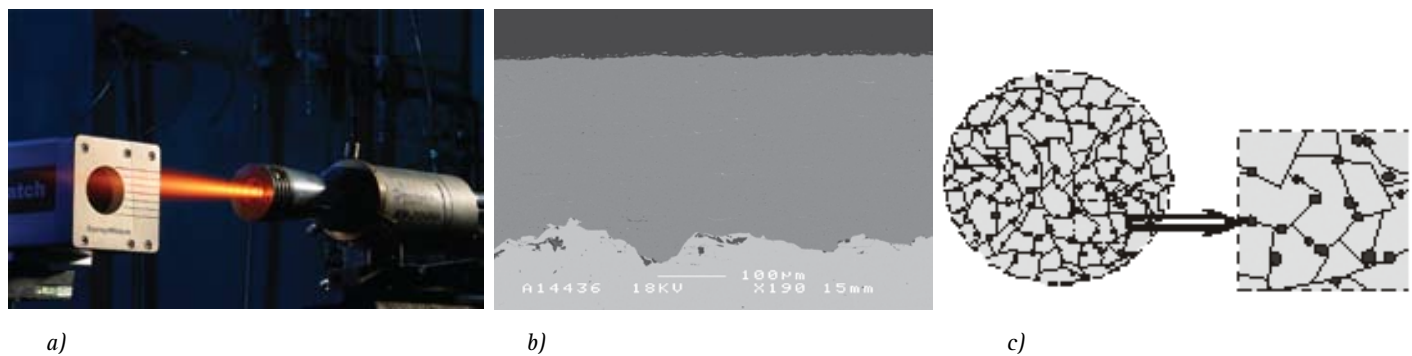


Figure 1. a) HVOF spray gun and diagnostic sensor monitoring the particle temperature and velocity, b) Cross-section of ceramic coating on top of sand blasted steel and c) agglomerated nanocomposite powder particle.

Table 1. Typical thermal sprayed coating applications and spray materials:

Wear resistance	WC-Co, Cr ₃ C ₂ -NiCr, Amorphous metals, Al ₂ O ₃ -TiO ₂ , Cr ₂ O ₃
Corrosion resistance	Superalloys, NiCr, Al, Zn, polymers
Oxidation resistance	NiCrAlY, superalloys
Electrical insulation	Al ₂ O ₃
Non-stick coatings	Quasicrystals, fluoropolymers, TiO ₂
Thermal insulation	YSZ, PSZ (ZrO ₂ -Y ₂ O ₃)
Electrical conductivity	Cu, Al
Biomedical applications	Hydroxylapatite, Ti, NiTi, CoCr, CoCrMo

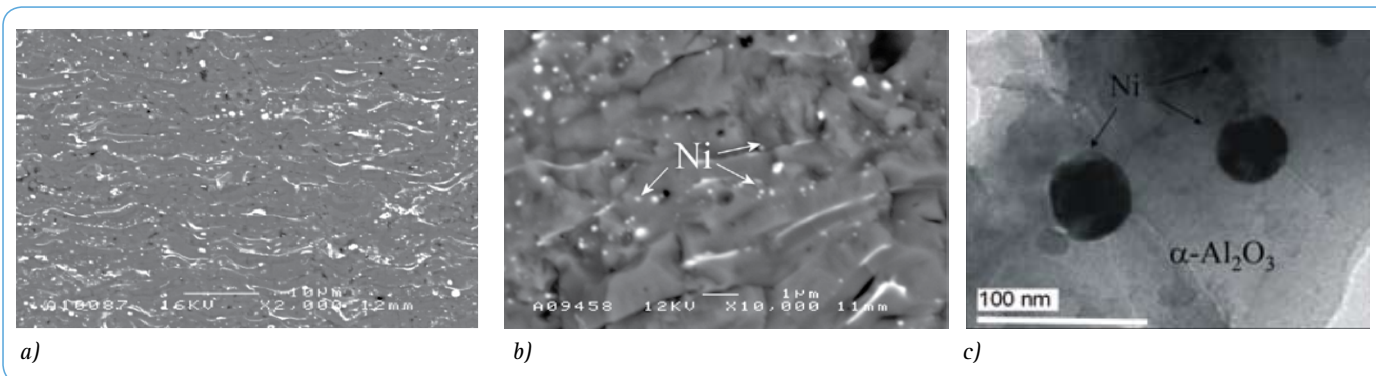


Figure 2. Nano-Al₂O₃-Ni-composite coating a) and b) SEM-images showing nano-sized nickel precipitates in alumina matrix and c) TEM-image revealing the nano-grain size.

Two carbide coatings with different carbide sizes were also produced by the HVOF method. The produced coatings were WC-10%Co4%Cr, with average carbide sizes of 1 μm and 400 nm. In this study the ASTM G 65 rubber wheel test was modified for fine particle slurry abrasion testing of coatings.

RESULTS AND DISCUSSION

Clear benefits were obtained by introducing a nanostructure to the alumina-based coatings. Table 2 presents the abrasive wear and hardness results for the coatings. Fracture toughness was also increased in all of the nanostructured coatings, compared to the conventional grain size (a 100% increase in toughness with n-Al₂O₃-5vol%Ni and -5vol%ZrO₂). The wear resistance was greatly improved with all of the nanostructured coatings, except the softer 5vol%Ni-coating.

One potential approach to improve the wear performance of an HVOF-sprayed WC-CoCr-coating in micro wear ap-

plications (such as paper machines or other process industry applications) is to reduce the carbide size. The mechanism for micro abrasion wear is believed to begin with the wear of the softer metal matrix, causing pull-out of carbides. Therefore, the advantage of using fine, evenly distributed carbide particles is assumed to derive from the smaller free path of the matrix between carbides, re-

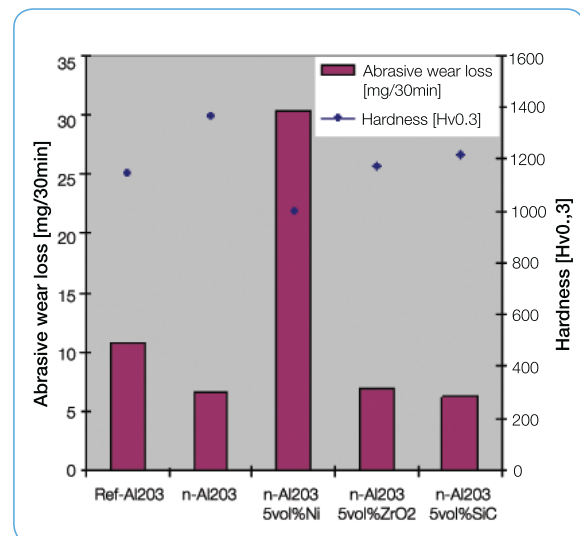
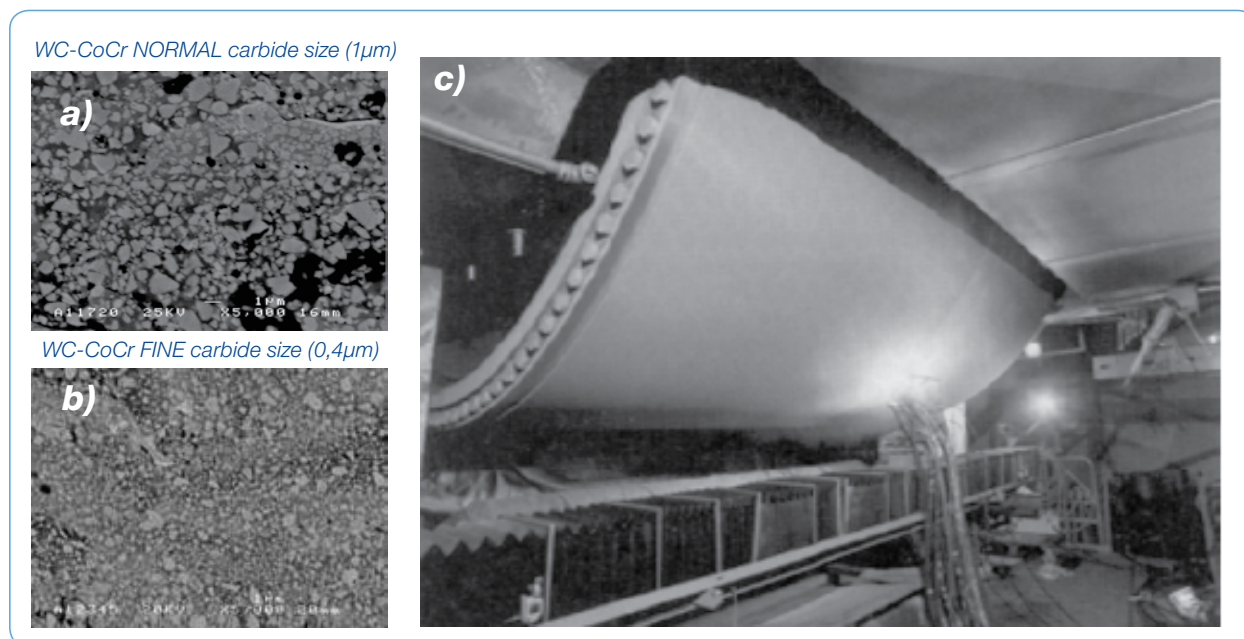


Table 3. Abrasion wear losses and hardness values for alumina coatings.



Figures 3 a) and b) showing the microstructures of the studied coatings, and c) WC-CoCr-coating being applied to paper roll by two HVOF spray guns.

sulting in lower surface roughness of wear track. The effect of sub-micron (400 nm) and conventional (>1 μ m) carbide size on the wear performance of coatings was studied. By studying the wear track with SEM and a 3D-optical profilometer, the wear mechanism in the test was revealed to be fine particle wear of the soft matrix, pull-out of carbides or lamellas, as well as wear induced by corrosion.

The wear rate of the sub-micron carbide coating was reduced by almost 100% compared to a conventional carbide size. Corrosion was observed to have an effect on the surface degradation on the lamella scale. The results also show a much smoother worn surface for the finer carbide at the micron scale, due to the smaller pull-out size, meaning that, for example, in paper rolls the desired polish is preserved throughout the coating service life. Figure 3 shows the difference in microstructure of the studied coatings as well as the in-site spraying process of a paper roll.

CONCLUSIONS

The refinement of alumina grain size and introduction of nano-sized precipitates to the structure was shown to increase the mechanical properties of the coating, as well as the abrasion wear resistance of the coatings. Carbide size reduction in WC-CoCr-coatings resulted in a huge improvement in fine particle slurry abrasion resistance. HVOF-spraying was shown to be suitable in the produc-

tion of nano grain-sized coatings, due to the fast heating and cooling rates. In more conventional fabrication techniques, such as sintering or hot pressing, there are problems in preserving the nano-sized structure because of the slower cooling rates.

ACKNOWLEDGEMENTS

These studies were mainly funded by Tekes and VTT.



CONTACTS

Tomi Suhonen
Research Scientist
tomi.suhonen@vtt.fi
Tel. +358 20 722 5436

TAILORED PROPERTIES FOR CAST SURFACE BY USING EXOTHERMIC REACTION

Tapio Ritvonen

Using exothermic reactions to reinforce cast components provides some benefits. It is possible to produce a locally reinforced cast component with improved wear properties using a cast material which is well known and risk free. Tailored surface properties make it possible to exchange a stainless steel cast for a cheaper steel cast. In experiments, hardness values 1.5 times higher were obtained in reinforced areas compared with white cast iron, and wear resistance was 2 to 4 times better with the reinforced cast component. Many foundries could utilize this method to improve wear resistance.

INTRODUCTION

The conventional solution to improve the wear resistance of a cast component is to reinforce it with a hardening component throughout the structure. Particles could be carried along due to melt flow rate and then the component is no longer locally reinforced. This means higher costs if the whole component is made of the same “expensive composite material”. Such practices are usable only for special products, not for mass production. The manufacturing industry really needs locally reinforced cast components to decrease expensive raw material costs. They also want a cast material that is well known and risk free. User-friendliness and short installation time

are important goals. Some solutions, for example coating and the addition of reinforcement particles in the mould have already been experimented with. Plasma, laser and other coating methods need an extra step at the production line. This means that both time and money are wasted. Additionally thermal spray methods can produce only thin – up to 0.5 mm – coatings; laser and welded coatings can be somewhat thicker but temperature of the coating process is quit high. Coating is a feasible method if the application is a special component and the price is not the most important factor. The addition of reinforcement particles, such as TiC, (Ti, W)C and WC to the mould to a specific location where the better wear resistance is needed is a potential method, but some problems have been observed related to poor wettability and porosity.

METHOD

The process performance is rather simple. The reactive powder mixture is added into the mould. Metal melt is poured into the mould, the reaction is started in-situ and the component cooled down as usual. There are many benefits when the exothermic reaction is integrated with casting. Local reinforcement can be controlled. However, the detailed mechanisms are currently under investigation. Reinforcement areas and functional graded structures are denser when reactive reinforcement particles are used, due to the melting of the matrix metal by exothermic reaction. Tailored reinforcement compositions and controlled thickness of reinforcement layers are very important benefits. An interesting additional benefit is to utilize the ambient high temperature to postpone solidification in critical areas.

The new solution is to use an exothermic reaction to form a locally reinforced area in situ.

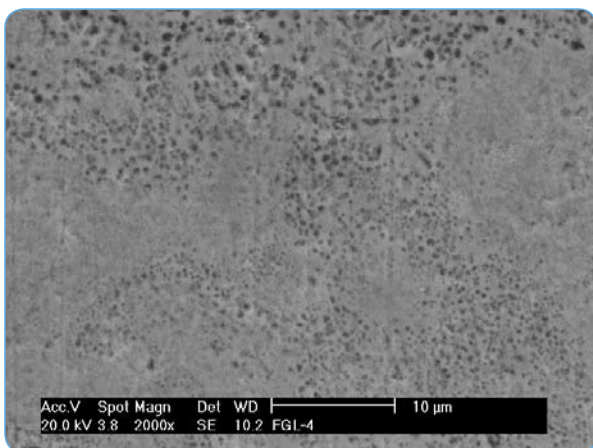


Figure 1. Typical reinforcement particle size is under 1 μm .

Some articles have been written, but we are not aware of any industrial manufacturers who use exothermic reactions to reinforce cast components. VTT has long, practical experience in exothermic reactions, which assists in achieving good quality products. Powder preparation, addition methods and functional graded materials are core competencies of our research group. The method has already been demonstrated and its applicability for industrial components is shown and further developed

An exothermic reaction has common basic principles. The original mixed powder materials react and form a new compound; for example titanium and carbon react to form titanium carbide. If the powder mix is located in a casting mould, metal melt poured into the mould ignites the reaction. If the reaction is strongly exothermic, it is self-propagating and proceeds without external energy at a speed of 1-100 mm/s. The speed of the exothermic reaction is controlled by the amount of matrix metal or other additives, for example titanium carbide. The speed of the exothermic reaction with pure titanium and carbon was twenty times faster than in powder where titanium and carbon were diluted to 50% with the matrix metal powder. Exothermic heat of the compound formation helps the reinforcement to adhere to the cast part – this is not the case with an already formed compound. Adhesion and densification does not occur as the temperature of the melt does not have enough energy to melt the binder phase of the reinforcement. However, the detailed mechanisms of adhesion, densification and placement accuracy are currently under investigation.

Commonly, an exothermic reaction has a few important benefits. The process is fast and energy efficient and the production line does not need any extra steps, such as heating. Impurities are evaporated during the process due to the high temperature, and gases and impurities are assumed to evaporate into the sand mould and make pure reinforced regions. A fine grain size was achieved due to the short time at high temperatures. The typical grain size of the reinforcement particles was under 1 μm (Figure 1). The composition can be easily tailored to each application, which is a very important benefit.

Functional graded structures are an important goal of further development, because then it would be possible to avoid sharp composition changes which tend to cause stresses, tensions and propagate cracks due to different coefficients of heat expansion (Figure 2). The content of

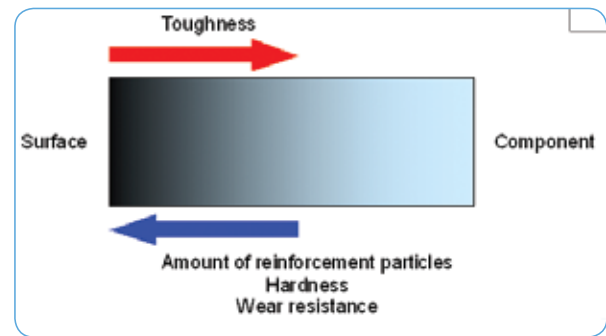


Figure 2. Benefits of functional graded structures.

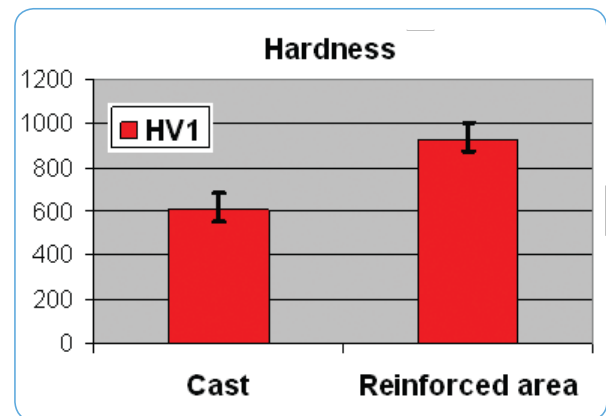


Figure 3. Hardness of reinforced area is 1.5 times higher than hardness of cast steel.

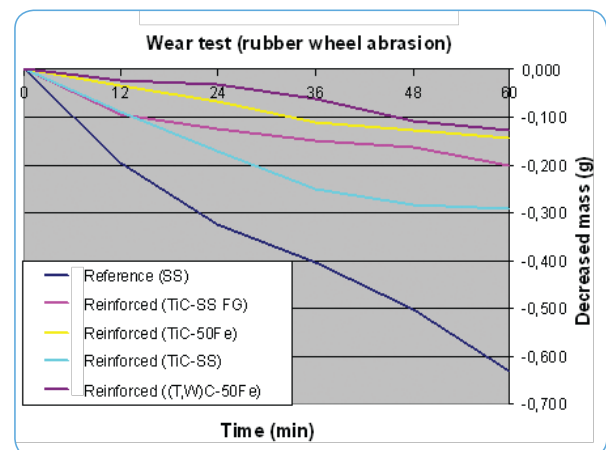


Figure 4. Wear resistance of reinforced cast stainless steel is 2 to 4 times better than cast stainless steel.

the reinforcing particles should be highest at the outer surface and decreases smoothly inside the component. Stresses and failures are minimized due to the smooth composition change. Toughness also increases inside the component. Hardness and wear resistance are decreased inside the component; however, these properties are still better than in the initial cast material.

RESULTS AND DISCUSSION

Locally reinforced cast components have improved hardness and wear resistance properties. In the example, the hardness of the cast white iron was about 600 HV, whereas in reinforced areas the average hardness was about 900 HV, figure 3. The hardness was thus increased 1.5 times. White cast iron is usually considered as the best wear resistant cast alloy. The wear resistance of reinforced cast stainless steel was 2 to 4 times better than that of cast stainless steel without reinforcement, tested with a rubber wheel abrasion test (Figure 4).

There are many possibilities to utilize exothermic reactions. It is possible to prepare a locally reinforced component with any cast material, geometry and thickness of reinforced area. Tailored properties can be produced for cast surfaces, such as wear resistance, strength, stiffness and thermal properties. The spectrum of materials is wide: ceramics (TiC, WC, SiC, B₄C, Cr₃C₂, TiB₂, etc.), compositions of ceramics ((Ti, W)C) and matrix metals (iron, steel, stainless steel, super alloys, Al, Cu, etc.). It is possible to add special materials, e.g. low-friction materials. Using an exothermic reaction it is possible to create totally new material compositions on the cast surface. An important possibility is to substitute a costly cast bulk material with an inexpensive material, for example to use carbon steel instead of stainless steel, but maintaining the material properties – for example corrosion resistance – unchanged on and near the component surface by matrix selection.

CONCLUSION

The goal of ongoing project is the development of a new process to produce locally reinforced cast components with tailored surface properties, to find possibilities to build functional graded structures and to change costly cast materials to less expensive materials with improved surface properties. Properties of the reinforced casts will be tested in order to give guidelines for industrial applications. It is hard to estimate the potential markets, but in the eventual applications the component size can vary from kilograms to tons. Foundries can develop new competitive products which have improved properties at near the same cost but better turnover. This gives the foundry industry a new way to produce tailored special products which can replace more expensive products made by other methods.

ACKNOWLEDGEMENTS

Many thanks for co-operation to the partners, and Tekes for funding.



CONTACTS

Tapio Ritvonen
Customer Manager
tapio.ritvonen@vtt.fi
Tel. +358 20 722 3003

ADDED VALUE FOR ALUMINIUM SURFACES USING HYBRID SOL-GEL COATINGS

Juha Nikkola, Anne Pahkala, Juha Mannila, Riitta Mahlberg, Jarmo Siivinen, Reima Lahtinen, Tom E. Gustafsson and Amar Mahiout

Aluminium is mainly utilized in the construction, transportation, packaging and electronics industries, where surface quality is one of the most important criteria. In order to produce added value for aluminium products, different hybrid sol-gel coatings suitable for pure aluminium, aluminium alloys and anodized aluminium were developed. The sol-gel coatings improved the hydro- and oleophobic properties of aluminium substrates. By improving the repellence properties of a non-sealed aluminium surface, the easy-to-clean properties of the aluminium were also remarkably enhanced.

Keywords: Sol-gel, hybrid, coating, aluminium, easy-to-clean

INTRODUCTION

Applications for aluminium are structures where qualities such as lightness, strength, weatherproofness, formability, ecological solutions and electric conductivity are required. Therefore, aluminium is mainly utilized in the construction, transportation, packaging and electronic industries. Aluminium surfaces can be vulnerable to

acidic and alkaline corrosive solutions, abrasive wear and contamination. In order to increase the durability of aluminium surfaces, different protective treatments are used. [1] The potential of multifunctional nanocoatings, for example an inorganic-organic hybrid sol-gel coating as a novel protective surface treatment for metal surfaces, has been studied worldwide during the last ten years. The synthesis of sol-gel coatings involves an evolution of inorganic networks in a continuous liquid phase through the formation of colloidal suspension and the following gelation of the sol. [2, 3]. Recently, the corrosion-resistance, wear resistance and easy-to-clean properties of sol-gel coatings on metal substrates, e.g. stainless steel [4,5,6] and copper [7], have been studied by the authors.

MATERIALS AND METHODS

The protective properties of sol-gel coatings on two different aluminium plates, Al6060 and pure aluminium (Al99.5), were investigated. Some of the aluminium plates were anodized before deposition of sol-gel coatings. Three types of sol-gel coatings were investigated. Coating 101 consisted of an alumina-silica-epoxide (Al_2O_3 - SiO_2 -epoxide) base matrix. The 300-series coatings 301 and 302 consisted of hydrocarbon and fluorocarbon additives along with the base matrix. Ethanol and water were used as solvents. The coatings were spray-coated on anodized 99.5% pure aluminium and Al6060 aluminium alloy substrates. After the deposition the coatings were thermally cured at 130°C for half an hour.

The surface structure of the sol-gel coating on anodized aluminium was studied with SEM scanning electron microscopy (JEOL LSM-6400). The repellence properties of the deposited sol-gel coatings were studied by measuring the contact angles of water (distilled) and oleic acid droplets on the surfaces (CAM 200 Optical Contact Angle Me-

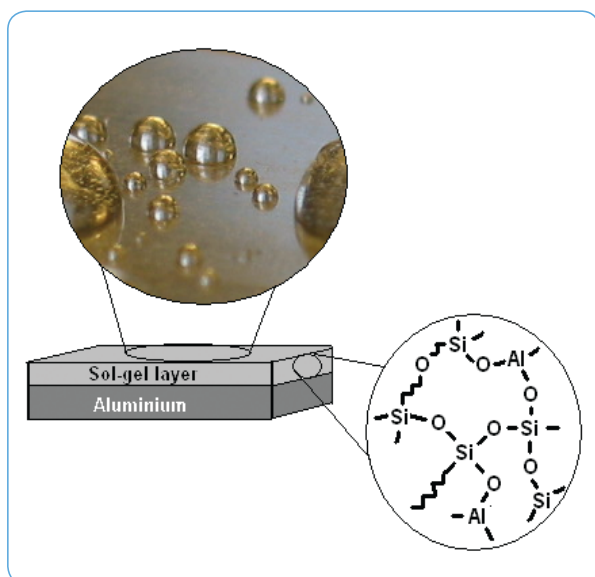


Figure 1. Functionalization of aluminium surface by sol-gel coating.

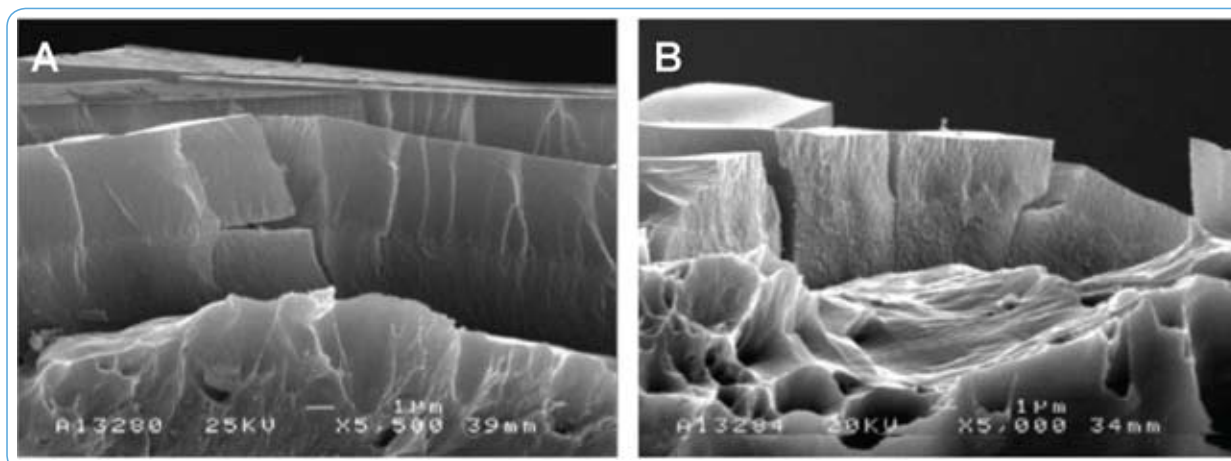


Figure 2. Cross-section figure of sol-gel coatings 101 (A) and 301 (B) on anodized non-sealed Al6060 substrate.

ter, KSV Instruments Ltd.). The easy-to-clean properties were studied via the infrared spectroscopy method (Bio-Rad FTS 6000, Shadow Pro Mapping Software). The abrasion resistance of the sol-gel coatings was tested with a standard paint scrubbing test apparatus (modified standard DIN 53778).

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM) characterisation was used to study the surface structure of the sol-gel coating on anodized aluminium with and without sealing. Figure 2 presents cross-sections of sol-gel coatings 101 (A) and 301 (B) on an anodized non-sealed Al6060 substrate. The cross-section figure indicates that an interface between anodized non-sealed aluminium and the sol-gel coating can be seen. In order to study more exactly the bonding of sol-gel on anodized non-sealed aluminium, a line analysis over the cross-section was done. The line analysis confirmed that the sol-gel penetrated into the porous structure of anodized non-sealed aluminium.

The hydro- and oleophobic properties of uncoated and sol-gel-coated pure aluminium (Al99.5) were studied with contact angle measurements. Figure 3 shows that the two-layer spray deposition with coatings 302 and 301 increased the contact angle of water (the black bar). Based on the contact angle measurements, coating 101 did not have a significant effect on water contact angle values. Furthermore, the contact angle of oleic acid was measured in order to investigate the oleophobic behaviour of the surfaces. When comparing the contact angle results between the uncoated and sol-gel-coated aluminium, it can be observed that the contact angle of oleic acid was clearly increased by coating 302. With coating 301 the contact angle of oleic acid was increased only

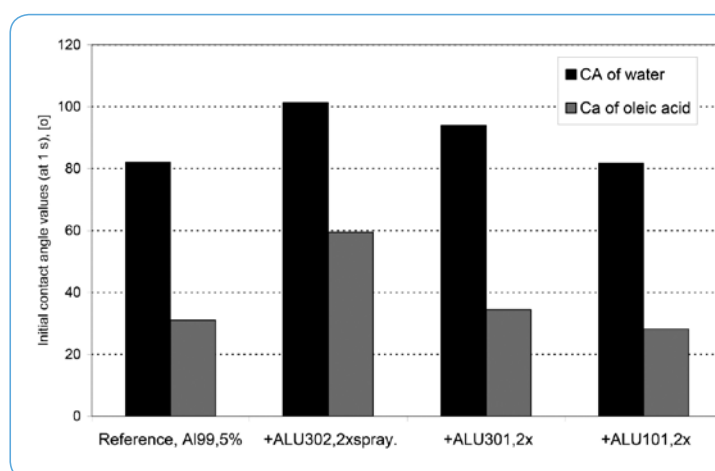


Figure 3. Contact angle of water and oleic acid for uncoated and sol-gel-coated aluminium surfaces.

slightly. Based on these results, the surface chemistry of aluminium can be tailored with sol-gel coatings.

The results of the FTIR mapping of uncoated and 302-coated aluminium 6060 alloy are seen in figure 4. The colour maps and bars indicate traces of oleic acid on the sample surface. The blue colour indicates that there are no traces of oleic acid on the surface. Respectively, the red and orange colours indicate that there is a lot of oleic acid on the surface. Based on the results it can be concluded that even after cleaning there is still a lot of oleic acid left on the surface of the anodized non-sealed aluminium alloy 6060. Sol-gel coating 302 seemed to improve the easy-to-clean properties of the aluminium surface.

CONCLUSIONS

Three different sol-gel coatings were developed and deposited on aluminium plates with and without anodiz-

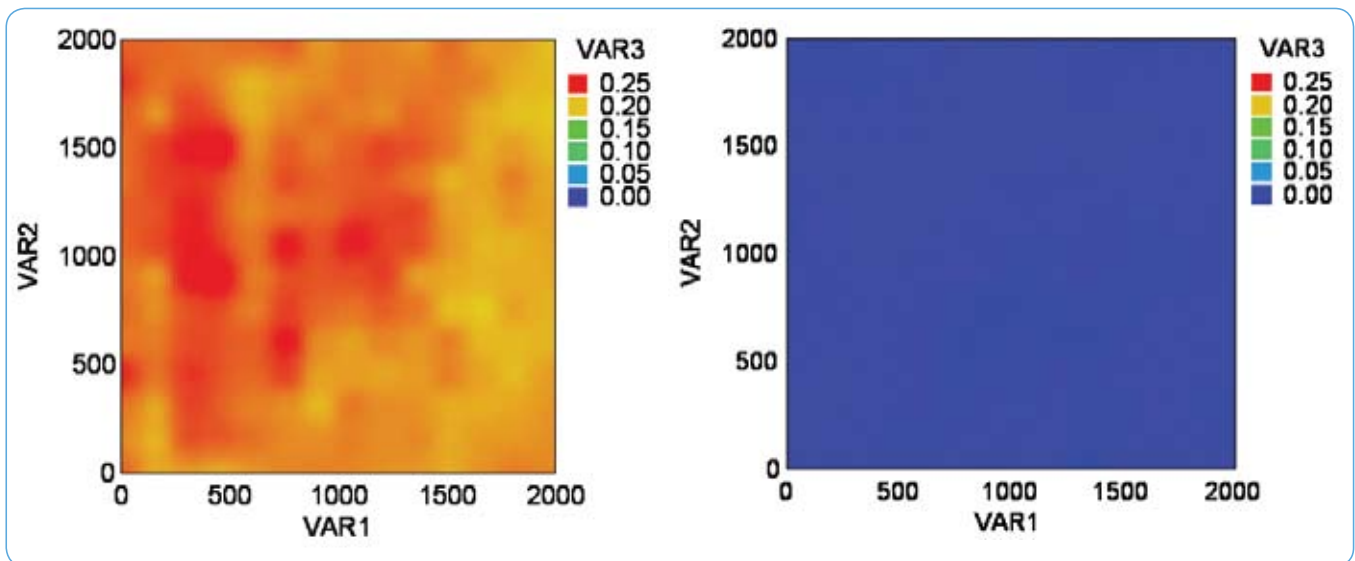


Figure 4. Cleanability of aluminium alloy 6060 (left) was improved by sol-gel coating 302 (right).

ing. Based on the results, it can be concluded that sealing of the porous anodized structure could be done with sol-gels. Eventually, it can be said that added value for the aluminium surfaces can be obtained by using sol-gel coatings. The easy-to-clean property of aluminium was remarkably improved.

ACKNOWLEDGEMENTS

The financial support of the Finnish Funding Agency for Technology and Innovation (TEKES), VTT and the Finnish metal industry is acknowledged.

REFERENCES

1. Nikkola, J., Mahlberg, R., Siivinen, J., Pakkala, A., Lahtinen, R. & Mahiout, A. VTT Tiedotteita - VTT Research Notes 2431, 49 s., 2008.
2. Sanchez C. et al., Applications of Hybrid Organic-Inorganic Nanocomposites. Journal of Materials Chemistry 15, 3559-3592, 2005.
3. Brinker, C.J. and Scherer, G.W. Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing. Academic Press, Inc., 1990.
4. Mahlberg R, Mannila J., Romu J., Nikkola J., Ilola R., Söderberg O., Koskinen J., Hannula S.-P. & Mahiout A., 6th European Stainless Steel Conference, ESSC 2008. Helsinki, 10 - 13 June 2008.
5. Vuorio, T., Jaakkola, J., Kolari, M., Mannila, J., Nikkola, J., Liu, X.W., Söderberg, O., Mahiout, A. & Hannula, S.-P., Wear and Chemical Resistance of Sol-Gel Coatings on Stainless Steel, 6th European Stainless Steel Conference, ESSC 2008. Helsinki, Finland, 10 - 13 June 2008 (2008), 6 p.
6. Nikkola J., Mannila J., Kallio M., Pakkala A., Kolari M., Mahlberg R., Posti O. & Mahiout A. The effects of chemical parameters and surface topography on the properties of the sol-gel-coatings. VTT Symposium on applied materials, June 8, 2006, Dipoli Espoo, Finland.
7. Nikkola J., Mannila J., Mahlberg R., Siivinen J., Kolari M. & Mahiout A. Sol-gel based protective coatings for copper products, Journal of Coatings Technology and Research Vol. 5 (2008) No: 3, 335 - 344.



CONTACTS

Juha Nikkola
Research Scientist
juha.nikkola@vtt.fi
Tel. +358 20 722 3672

VTT Technical Research Centre of Finland is the largest multitechnological applied research organisation in Northern Europe. VTT provides high-end technology solutions and innovation services. From its wide knowledge base, VTT can combine different technologies, create new innovations and a substantial range of world class technologies and applied research services thus improving its clients' competitiveness and competence. Through its international scientific and technology network, VTT can produce information, upgrade technology knowledge, create business intelligence and value added to its stakeholders. VTT is a non-profit-making research organisation.

VTT TECHNICAL RESEARCH CENTRE OF FINLAND

Vuorimiehentie 5, Espoo

P.O.Box 1000, FI-02044 VTT

Tel. +358 20 722 111, Fax +358 20 722 7001

www.vtt.fi