KEEMIA- JA MATERJALITEHNOLOOGIA TEADUSKOND
MATERJALIUURINGUTE TEADUSKESKUS
TEADUS- JA ARENDUSTEGEVUSE AASTAARUANNE 2014

1. Struktuur

Materjaliuuringute teaduskeskus, Centre for Materials Research
Keskuse juhataja Urve Kallavus

- Materjaliuuringute õppetool, Chair of Materials Research, Urve Kallavus

Materjaliuuringute teadus- ja katselaboratoorium, Laboratory for Materials Research

2. Teadus- ja arendustegevuse (edaspidi T&A) iseloomustus

2.1 Struktuuriüksusesse kuuluvad uurimisgrupid *(kõik uurimisgrupid näidatakse aruandes eraldi, järgides alltoodud ülesehitust).*
Uurimisgrupi nimetus *(eesti ja inglise keeles)* **ja juhi nimi**

- uurimisgrupi teadustöö kirjeldus *(inglise keeles*);
- uurimisgrupi aruandeaastal saadud tähtsamad teadustulemused *(inglise keeles);*
- uurimisgrupi kuni 5 olulisemat publikatsiooni aruandeaastal.

Main research directions and results:

1. Investigation of hard sintered materials, their formation and structural characterization, metallographic structures, computer-aided feature analysis. Optimization and production of ceramic-based composites, coatings and multi-materials systems for application in extreme conditions – severe wear, high temperatures, complex mechanical loads, oxidative/corrosive media. (Mart Viljus, M.S.Nat.Sci. PhD.Nat.Sci).

Focus is on the recycled hardmetal reinforced composite hardfacings with iron based matrixes, produced by plasma transferred arc welding (PTAW) and by powder metallurgy (PM) route (liquid phase sintering; LPS). The size of the reinforcement varied from 0.15 to 0.30 mm in the PTAW-hardfacing and from 0.35 to 1.0 and 1.0 to 2.5 mm in the PM-hardfacings. Microstructure of the hardfacings was studied by scanning electron and optical microscopy; energy dispersive spectroscopy was applied to determine a possible dissolution of the hardmetal particles in the matrix. Wear mechanisms are described, and the results of the wear tests are discussed. The hardfacings studied generally demonstrated higher resistance to abrasive wear than the reference material, especially in the rubber wheel wear test (11.7 times lower wear in the case of the PTAW-hardfacing and up to 9.9 times lower wear in the case of the PM-hardfacings). The PTAW-hardfacing exhibited 3.6 times and 2.4 times lower wear at the abrasive erosive wear conditions at the low and normal impact angles, respectively, and 3.6 times lower wear at the abrasive impact wear conditions. The PTAW-hardfacing also showed up to 2.1 times lower wear in the rubber wheel wear test, up to 3.6 times lower wear in the

abrasive erosive wear test and up to 1.7 times lower wear in the abrasive impact wear test than the PM-hardfacings.

The formation of nanoscopic ripple patterns on top of material surfaces has been reported for different materials and processes, such as sliding against polymers, high-force scanning in atomic force microscopy (AFM), and surface treatment by ion beam sputtering. In this work, we show that such periodic ripples can also be obtained in prolonged reciprocating sliding against nanocrystalline diamond (NCD) films. NCD films with a thickness of 0.8 lm were grown on top of silicon wafer substrates by hot-filament chemical vapor deposition using a mixture of methane and hydrogen. The chemical structure, surface morphology, and surface wear were characterized by Raman spectroscopy, scanning electron microscopy (SEM), and AFM. The tribological properties of the NCD films were evaluated by reciprocating sliding tests against Al2O3, Si3N4, and ZrO2 counter balls. Independent of the counter body material, clear ripple patterns with typical heights of about 30 nm induced during the sliding test are observed by means of AFM and SEM on the NCD wear scar surfaces. Although the underlying mechanisms of ripple formation are not yet fully understood, these surface corrugations could be attributed to the different wear phenomena, including a stress-induced micro-fracture and plastic deformation, a surface smoothening, and a surface rehybridization from diamond bonding to an sp2 configuration. The similarity between ripples observed in the present study and ripples reported after repeated AFM tip scanning indicates that ripple formation is a rather universal phenomenon occurring in moving tribological contacts of different materials.

Green alumina porcelain samples containing kaolin (27 %), Al2O3, grog (50 %) and feldspar (23 %) were fired at temperatures between 300 °C and 1250 °C with a heating and cooling rate of 5 °C/min. The Shore hardness and the Vickers hardness of the fired samples were measured at room temperature. Both hardnesses of the green alumina porcelain samples are low and remain approximately constant up to 400 °C when dehydroxylation begins. Between 400 °C and 700 °C both hardnesses slightly increase. Above 700 °C, they increase exponentially. This is explained by sintering and high-temperature reactions in metakaolinite. The dependencies between both hardnesses, Shore and Vickers, and the firing temperature are very similar, i.e., the Shore hardness and the Vickers hardness reflect changes in the sample in the same manner. The Vickers hardness is much more sensitive to the firing temperature. Its values after firing at 1250 °C are 130 times higher than those measured at room temperature. However, the values of the Shore hardness are only four times higher. The relationship between the Young's modulus and the Shore hardness and the Vickers hardness can be fitted by power-regression functions.

To solve the problem, that in some cases the SFAs alone can't provide the required wear resistance a co-deposition of a NiCrSiB alloy and a hard phase, mostly a tungsten carbide-based material, is usually attempted. It has been shown that coatings of such a composition demonstrate lower wear due to the combination of the relative toughness of the SFA and the hardness of the hardmetal [9–11]. In their turn, TiC- and Cr_3C_2-based cermets proved to be suitable alternatives for the WC-based hardmetals due to their high

wear and corrosion/oxidation resistance, especially at elevated temperatures [12–17]. It was formerly shown that the application of the TiC-NiMo and Cr_3C_2-Ni cermets as a reinforcement in the high velocity oxy-fuel sprayed (HVOFS) NiCrSiB coatings allowed to increase their resistance to abrasive wear by up to 1.6 times at the room temperature in comparison with the unreinforced coating [18]. Analogously, the composite NiCrSiB/Cr_3C_2-Ni HVOFS coating demonstrated 1.6 times lower abrasive wear than the steel C45 at the room temperature [19]. Still, to authors' best knowledge, no research concerning the high temperature wear of a TiC- or Cr_3C_2-based cermet particles reinforced thermal sprayed coating with a SFA matrix has been conducted yet. In the present paper, authors concentrate on the high temperature erosion wear of the TiC-NiMo and Cr_3C_2-Ni particles reinforced HVOFS coatings with the NiCrSiB matrix and compare the wear values to the other widespread wear resistant materials (steels AISI 304 and HARDOX 400 and WC-15Co hardmetal).

2. Investigation of lignocellulosic materials (wood, cellulose, paper, structure timber), natural and man-made stone, and their degradation by natural and artificial causes; objects of cultural heritage, archaelogy, art and their conservation problems (Urve Kallavus, Dr.Habil.Chem.).Investigation of the indoor climate influence to the biodeterioration of materials.

Supercritical carbon dioxide extraction ($scCO_2$) is chosen to a treatment to remove lignin and to peel off outer cell wall layers to expose S2 layer of aspen wood fibres. The aim is to find an effective and environmentally friendly method to advance the fibrillation of the BCTMP pulp. The effects of the treatment are analysed by using scanning electron microscopy (SEM). The chemicals used together with $scCO_2$ extraction include 1:1 ethanol: water co-solvent, isopropyl alcohol, and dimethyl sulfoxide (DMSO) with urea. The results show that supercritical CO_2 extraction helps to peel the fibres of mechanical pulp. Best results are gained with 1:1 ethanol: water co-solvent.

In this study an attempt to further refine aspen BCTMP is reported. The aim is to find an energy effective and environmentally friendly way to affect the surfaces of BCTMP fibres, in other words, to peel and fibrillate the pulped aspen wood cells. Agitation in a bag mixer and supercritical carbon dioxide (scCO2) extraction were selected as methods to treat the fibres. The effects of the treatment were analysed by the surface charge measurement and scanning electron microscopy (SEM). The surface charge of pulp fibres is important as it influences interfibre and fibre-additive interactions in the pulping process, as well as in other applications. In this work, the effect of mechanical treatment scCO2 extraction on the surface charge of aspen BCTMP was evaluated. Dried and ground BCTMP was dispersed in water, treated with a BagMixer (BM) with a nylon separator, extracted with scCO2 with and without ethanol-water co-solvent. The influence of 1% sodium hydroxide was also studied. Polyelectrolyte titration was used to measure the surface charge. The processes were carried out at various times and in different order of succession. A relatively high surface charge was gained by a gentle mechanical and chemical treatment. SEM analysis showed the relation of surface fibrillation to the surface charge of the fibres. Washing with sodium hydroxide removed

both the fibrils from the surfaces and the surface charge. The results can be used as a guide to further fibrillation of aspen BCTMP for various applications. Fibrillated intermediates are aimed for processing to, for instance, aerogels and other nanostructured materials.

In this part of the work an attempt to fibrillate aspen BCTMP fibre in an environmentally friendly way is reported. The effects of various NaOH, KOH, urea and ethanol aqueous solutions at lowered temperature were tested for pre-treatment. The pre-treatment was followed by vibration milling aiming to peel off outer cell wall layers and to fibrillate S2 layer of the aspen wood fibre. The effects of the treatments were evaluated by scanning electron microscopy (SEM). The results show that it is possible to fibrillate BCTMP aspen fibres by using alkaline aqueous solutions at low temperatures followed by a mechanical treatment. A strong dependence of fibrillation of cellulose on temperature, time and alkali concentration was established.

In Estonia a number of medieval churches has been preserved but not in the proper meaning of this word. Churches under survey are located in remote areas and even there is no substantial air pollution form urban or industrial activity they bear breakdown of structures of vital importance. Particularly it concerns finishing layers of the stone walls. These churches are mostly unheated and built with massive stone walls. Therefore indoor climate is mainly determined by the outdoor climate which is not very favourable in Estonia. Multiple microorganisms take advantage from that and drastically alter the original mineral composition and structure of plaster layers. Building material for these medieval churches is porous sedimentary carbonate rock Kaarma dolostone (dolomite rock) and other local dolostones, quarried from the local stone-pits nearby of the each church. Finishing layers, particularly lime plaster, have been produced from the same crude dolostone and in essence have very good adhering properties. Being a low density and soft material it turns harder in time due to the carbonisation and redeposition of primary minerals in plaster. But similar chemical transformation may occur also due to the microbial activity. The aim of this work is to determine the redistribution and re-precipitation of altered crystalline phases onto the solid surface area of finishing plaster of dolostone. Optical microscopy, scanning electron microscopy, qualitative microanalysis and X- ray diffraction analysis appeared to be useful tools to locate microbial activity and redeposition of vital chemical elements as well as discovering formation of microbiologically induced new crystal phases. This provides valuable information upon physical state of aged dolostone walls and allows making suggestions for the development of conservation strategies.

The next study analyses the indoor climate that creates risk of damages in naturally ventilated churches in the cold climate of Estonia. Indoor temperature and humidity were measured over a one-year period and the results were analysed on the basis of damage functions: mould growth, risk of cracking and fracturing of wooden objects and delamination of the gesso layer of panel paintings. In unheated churches, one of the most dominant problems was very high relative humidity throughout the year, creating a high risk for mould and algae growth. Churches may need background heating to avoid freezing during a long cold winter that causes low surface temperatures of massive walls

during the spring-summer period. It was found that mould risk was significantly lower in heated churches than in unheated or intermittently heated churches. The risk of mould growth was not decreased by the use of intermittent heating. In heated churches, overheating (room temperature >+10 ºC) causes a RH below 50% during cold periods, and the favourable period for irreversible response of panel paintings was significantly longer, so there is a higher risk that the gesso may crack or delaminate. From the point of view of the cracking and fracturing of wood, indoor climate conditions are in the safe range for most of the year.

2.1.1 Paremad publikatsioonid

Kärner, K.; Elomaa, M.; Kallavus, U. (2014). Study of the effect of mechanical treatment and supercritical CO2 extraction on aspen BCTMP by surface charge measurements and SEM. Cellulose Chemistry and Technology, 48(5-6), 535 - 544.

Jõeleht, M.; Pirso, J.; Juhani, K.; Viljus, M.; Traksmaa, R. (2014). The formation of reactive sintered (Ti,Mo)C-Ni cermet from nanocrystalline powders. International Journal of Refractory Metals and Hard Materials, 41, 284 - 290.

2.2 Loetelu struktuuriüksuse töötajate rahvusvahelistest tunnustustest.

2014.a. rahvusvahelisi tunnustusi ei saadud.

2.3 Loetelu struktuuriüksuse töötajatest, kes on välisakadeemiate või muude oluliste T&A- ga seotud välisorganisatsioonide liikmed.

Urve Kallavus - Kaunas University of Technology, Academy of Sciences of Lithuania "Materials Science - Medziagotyra" Ediorial Board, liige.

Urve Kallavus - HORIZON 2020 individual expert, projects' reviewer.

2.4 Soovi korral esitatakse aruandeaastal saadud T&A-ga seotud tunnustused (va punktis 2.3 toodud tunnustused), ülevaade teaduskorralduslikust tegevusest, teadlasmobiilsusest ning hinnang oma teadustulemustele.