EFFECT OF CERAMIC ADDITIVES ON HYDROPHOBIC LAYER ELECTRODEPOSITION

VPLYV KERAMICKÝCH ADITÍV NA ELEKTROLYTICKÚ PRÍPRAVU HYDROFÓBNYCH VRSTIEV

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Summary

The main topic of this paper is effect of ceramic powders addition to electrolytes based on myristic acid, polyvinylidene fluoride and fluorinated polyhedral oligomeric silsesquioxane for hydrophobic surface deposition. Alumina and tungsten carbide were introduced to decrease surface roughness and porosity of deposits.

Complementary diagnostics using confocal microscopy, scanning electron microscopy with energy dispersive spectroscopy, X-ray computed tomography, infrared spectroscopy, contact angle and surface free energy calculation provided complex methodology for hybrid superhydrophobic deposit observation and optimization od electrolytic process.

As a result, superhydrophobic electrodeposits with water contact angle up to 164°, surface free energy under 20 mJ/m^2 were prepared. Addition of ceramic powders, especially tungsten carbide, had positive effect on surface roughness decrease.

Key words

Electrolysis, superhydrophobic, polyvinylidene fluoride, silsesquioxane, alumina, tungsten carbide

Introduction

With respect to the type of material, hydrophobization of surfaces can be realized via numerous methods [1–3]. Effective modification of metal substrates can be managed by electrolysis. Depending on demanding wettability, tribological or chemical properties, three main approaches are usually used. The first one is based on fabrication of suitable surface roughness, followed by chemical modification to reach non-wettability. Secondly, direct electrodeposition of liquid repellent product combines two subsequent steps of the first approach. Lastly, production of composite deposits can be used as one-step method for modulation of numerous desired properties like wettability, chemical or mechanical resistance [4].

In our work, we present experimental deposition of superhydrophobic surfaces on stainless steel using electrolytes based on myristic acid with nickel chloride. To emphasize the non-wettability, polyvinylidene fluoride and polyhedral oligomeric silsesquioxane acted as hydrophobization additives enabling the repellency for liquids with lower surface tension than water, due to fluorine content. Furthermore, ceramic powders were added to observe possible differences in layer roughness, homogeneity, wettability and possible reinforcement. For this purpose, alumina and tungsten carbide were tested. Surface free energy and contact angle calculation, surface structure imaging and roughness measurement (scanning electron microscopy, confocal microscopy), chemical analysis (energy dispersive X-ray spectroscopy, infrared spectroscopy) and computed tomography observation provided complex way for evaluation of deposits. Combination of polyvinylidene fluoride and tungsten carbide addition showed promising results by producing layers with reduced surface roughness, increased homogeneity and water contact angle over 160°.

Experimental

Sample preparation

Stainless steel plates were used as substrates for electrodeposition. Firstly, steel was cleaned using detergent and washed in distilled water followed by mechanical wiping using isopropyl alcohol. Specimens were dried at ambient air, taped to have a constant area of 0.1 dm^2 for electrodeposition and weighed. Secondly, DC deposition of hydrophobic layer took place in centrifuge tube with continual agitating using small magnetic stirrer (400 rpm) with 1 cm distance between electrodes. Electrolytes contained

agents for hydrophobization (myristic acid (MA; 98 %; Alfa Aesar); polyvinylidene fluoride (PVDF; Alfa Aesar); polyhedral oligomeric silsesquioxane (POSS; cage mixture; Hybrid Plastics)), conductivity (nickel(II)chloride hexahydrate ($NiCl_2.6H_2O$; Penta)) and ceramic material (alumina (Al_2O_3; 110 nm; Taimei Chemicals Japan,), tungsten carbide (WC; 50 nm; Nanografi Nanotechnology Co. Ltd.,) dispersed or dissolved in ethanol. List of electrolytes and deposition details for selected samples are in Tab. 1. Lastly, samples were immersed in ethanol, remained to dry at ambient air and weighed before tape removal.

Methods

Surface wettability measurement was realized by AdvexInstruments SEE System device and software providing contact angle (CA) measurement and surface free energy (SFE) evaluation using 2 µl droplets and 6-liquid Owens-Wendt regression model for calculation (deionized water, glycerol, ethylene glycol, formamide, a-bromonaphthalene, diiodomethane).

Confocal microscope Olympus LEXT OLS4000 3D Laser Measuring Microscope (CLM) was used to obtain information about surface macroscopic topography and roughness. Snapshots were created via multilayer image composition using magnification 20x while roughness was measured with magnification 50x for 1 mm length at three different locations on each specimen. Rq was calculated by LEXT software and averaged.

For detailed insight to presence of surface structures and formations, scanning electron microscope (SEM) Tescan Mira3 equipped with energy dispersive spectroscopy (EDX) provided images in high magnification and elemental composition of deposits. Prior to SEM imaging, samples were covered by 30 nm of metal using sputtering of Au/Pd target to prevent charging.

To observe presence of defects and porosity of deposits, X-ray computed tomography (CT) RIGAKU Nano 3DX device was used. This method is complementary to surface analysis, providing valuable information about the bulk material.

Furthermore, attenuated total reflectance Fourier transformation infrared spectroscope (ATR-FTIR) Bruker VERTEX 80v revealed the presence and qualitative representation of functional groups in deposit. Measurement was specified by spectral range from 600 to 4 000 cm^{-1}, resolution 4 cm^{-1}, averaging from 50 scans on three locations for each sample.

Results and discussion

For demonstration, three groups of samples using the same electrolyte base (PVDF, MA, $NiCl_2$) with variation of ceramic powder addition and deposition working conditions are described and depicted Tab. 1: Specification of electrolyte composition, deposition conditions, surface free energy and fluorine content for selected samples below. Details concerning deposition, presence of ceramic additives, calculated surface free energy values and fluorine content are summarized in Tab. 1. Starting with SFE, in majority of experiments, addition of ceramic powders led to enhancement of complex liquid repellency. Furthermore, significant increase of CA for water > 160° occurred mainly for specimens produced from electrolytes combining PVDF and WC with highest calculated value 164 ± 3° for sample T38. Graph on Fig. 1 plots the development of water CA and Rq for selected samples. Roughness increase with applied current density/voltage during the deposition. WC addition contributes to surface smoothening when compared to samples prepared without the ceramic powder or with alumina. The lower roughness is unexpected, as WC containing electrolytes usually had higher conductivity and therefore the slightly higher current density within sample groups. The surface structure from macro and microscopic point of view in Fig. 2 supports the roughness evolution. In case of reference samples, layers are extensively cracked. Although the addition of alumina did not completely inhibit the crackling, providing in many cases roughness increase, aggregates formed denser structures composed of nanoparticles analogous to [5]. Decidedly, WC presence in electrolyte led to denser and more homogeneous layer production with positive effect on the liquid repellency. The shape of formations comparable in [6] and W content up to 16 at % confirm the successful WC particles embedment. EDX revealed the presence of fluorine on all samples, however due to high accelerating voltage used for proper detection of elements like tungsten, values are informative. Presence of hydrophobization agents is confirmed by detection of functional groups by ATR-FTIR.

Tab. 1: Specification of electrolyte composition, deposition conditions, surface free energy and fluorine content for selected samples

Sample	T18	T19	T20	T24	T25	T26	T36	T37	T38
Electro-lyte	1 g PVDF + 0.2g MA + 0.5g $NiCl_2$	1 g PVDF + 0.2g MA + 0.5g $NiCl_2$	1 g PVDF + 0.2g MA + 0.5g $NiCl_2$	1 g PVDF + 0.2g MA + 0.5g $NiCl_2$	1 g PVDF + 0.2g MA + 0.5g $NiCl_2$	1 g PVDF + 0.2g MA + 0.5g $NiCl_2$	1 g PVDF + 0.2g MA + 0.5g $NiCl_2$	1 g PVDF + 0.2g MA + 0.5g $NiCl_2$	1 g PVDF + 0.2g MA + 0.5g $NiCl_2$
	100 ml EtOH	100 ml EtOH	100 ml EtOH	100 ml EtOH	100 ml EtOH	100 ml EtOH	100 ml EtOH	100 ml EtOH	100 ml EtOH
		1 g Al_2O_3	1 g WC		1 g Al_2O_3	1 g WC		1 g Al_2O_3	1 g WC
Deposi-tion	t = 8 min	t = 8 min	t = 8 min	t = 8 min	t = 8 min	t = 8 min	t = 8 min	t = 8 min	t = 8 min
	U = 10 V	U = 10 V	U = 10 V	U = 5 V	U = 5 V	U = 5 V	U = 7.5 V	U = 7.5 V	U = 7.5 V
	J = 0.4 A/ dm^2	J = 0.4 A/ dm^2	J = 0.5 A/ dm^2	J = 0.1 A/ dm^2	J = 0.1 A/ dm^2	J = 0.15 A/ dm^2	J = 0.25 A/ dm^2	J = 0.25 A/ dm^2	J = 0.3 A/ dm^2
SFE [mJ/m^2]	23	18	21	29	24	19	21	20	18
F content [at %]	1.6	1.7	2.0	2.7	1.3	0.8	10.1	1.2	2.5

Fig. 1: Average WCA and Rq roughness for selected samples

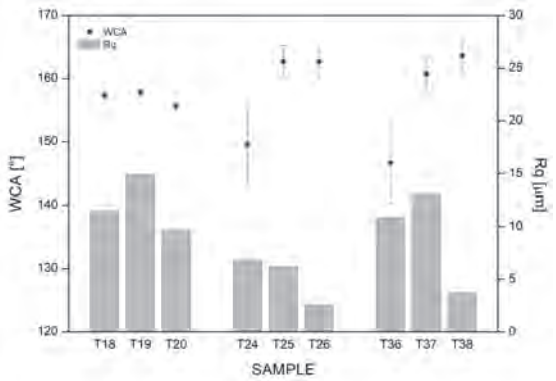
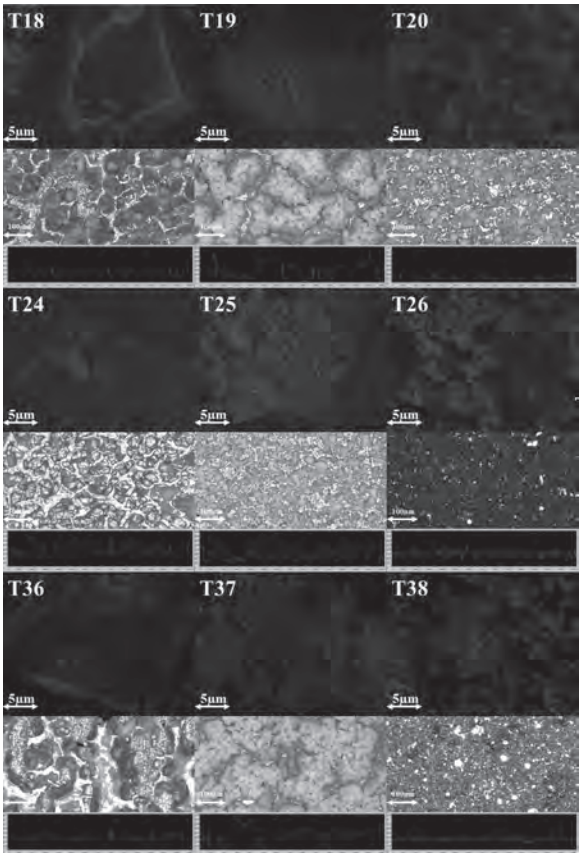


Fig. 2: SEM micrograph (mag. kx), CLM snapshot (mag. 20x) and roughness profile for selected samples T18 (upper left); T19; T20; T24; T25; T26; T36; T37 and T38 (bottom right)



Conclusion

Electrodeposition of thick layers on stainless steel substrate using electrolytes containing hydrophobization agents (myristic acid, polyvinylidene fluoride, polyhedral oligomeric silsesquioxane) and ceramic powders (alumina, tungsten carbide) provided promising outputs. As a result of tungsten carbide addition, majority of specimens showed significant increase of water contact angle and all specimen exhibited surface roughness decrease. In particular, electrolyte composed of myristic acid, nickel chloride, polyvinylidene fluoride and tungsten carbide using both current densities 0.15 and 0.3 A/dm^2 for 8 min deposition resulted in deposits with average water contact angle 163 and 164°, surface free energy 19 and 18 mJ/m^2 and RMS roughness decrease of more than 60 % to 2.56 and 3.72 µm, respectively. Furthermore, ceramic introduction could have positive effect on mechanical properties and therefore hardness and wear measurements would be next phase to validate this hypothesis.

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