UDK 533.9
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 46(1)43(2012)

PLASMA-ENHANCED CHEMICAL VAPOUR DEPOSITION OF OCTAFLUOROCYCLOBUTANE ONTO CARBONYL IRON PARTICLES

PLAZEMSKO KEMIČNO NAPARJANJE OKTAFLUOROCIKLOBUTANA NA KARBONILNO ŽELEZO V PRAHU

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Prejem rokopisa – received: 2011-06-08; sprejem za objavo – accepted for publication: 2011-08-02

Conformal films of fluoropolymer have been made onto carbonyl iron microparticles by plasma-enhanced chemical vapour deposition of octafluorocyclobutane in this study. RF plasma reactor with a frequency of 40 kHz and rotating barrel fixed between the two discharge electrodes arrangement was used to achieve a uniform surface modification of particles. The samples were treated for different times and various RF powers. Chemical changes in the surface composition after plasma modifications were, subsequently, determined using high-resolution X-ray photoelectron spectroscopy, while the surface texture was analyzed via scanning electron microscopy. The results revealed successful fluorination of carbonyl iron particles with a maximum of fluorine content of 2.9 %. The fluoropolymer film fabricated onto particles generally improves the corrosion protection and friction properties resulting in possible use of such magnetic particles in magnetorheological suspensions.

Keywords: carbonyl iron, functionalization, fluoropolymer, octafluorocyclobutane, modification, plasma, surface

Za namen tega dela je bila opravljeno plazemsko kemično naparevanje fluoropolimera na karbonilno železo v prahu. Enakomerno modifikacijo površine smo dosegli z uporabo RF plazemskega reaktorja s frekvenco 40kHz in z rotirajočim bobnom, ki je bil postavljen med razelektritveni elektrodi. Vzorci so bili obdelani pri različnih časih in pri različnih RF močeh. Spremembe kemijske sestave po obdelavi so bile določene z visokoločljivostno rentgensko fotoelektronsko spektroskopijo, morfološke spremembe površine pa smo določili iz slik vrstičnega elektronskega mikroskopa. Površina karbonilnega železovega prahu je bila uspešno flurinirana, saj smo na površini dosegli maksimalno 2.9 % fluora. Z nanosom fluoro polimernega filma na prašnate delce načeloma izboljšamo njihovo korozijsko odpornost in trenje ter jih naredimo primerne za uporabo v magnetnoreoloških suspenzijah.

Ključne besede: karbonilno železo, funkcionalizacija, fluoropolimer, oktafluorociklobutan, modifikacija, plazma, površina

1 INTRODUCTION

Magnetic particles have attracted increasing interest recently due to their novel applications. For example, magnetorheological (MR) fluids consisting of magnetic particles dispersed in carrier liquid can controllably change their rheological properties such as viscosity, yield stress and viscoelastic moduli according to the external magnetic field applied. These smart fluids can be used with benefit in applications utilizing adjustable control of the applied damping/force.[1] The corrosion, oxidation, and abrasive properties of iron and iron alloys frequently used as optimal magnetic agents in MR fluids are, however, obstacles for their wider commercial usage. To overcome this problem, modification of particle surface chemical composition has proven to be efficient.[2]

Recently, there is growing interest in using low-temperature plasma to modify the surface of various materials.[3–7] This interest has developed for two reasons. First, plasma can produce a unique surface structure and modification, and, second, the extent of modification can be easily controlled by treatment conditions.[7–14] Moreover, plasma treatment method is a non-polluting technique, which is not negligible for industrial fabrication, and only short reaction times are required.[15,16] Although there are several methods employed for film deposition onto iron, including sputtering, arc-plasma spray deposition, or various wet chemistry methods such as sol-gel deposition, the formed films are not uniform many times. Instead of the plasma reacting with and etching the substrate surface, plasma-enhanced chemical vapour deposition employs the conversion of gaseous monomer into reactive radicals, ions and neutral molecules and subsequent deposition of these precursors onto the substrate surface. Films formed in this way afterwards exhibit strong adhesion, low pinhole density and high surface uniformity.[17] Choice of proper plasma reactor type is another important factor for obtaining of conformal deposited film. Hence, fluidized bed or rotary plasma reactors with constant particles recirculation resulting in optimal fluid-solid contact and increased heat transfer coefficient have to be used for three-dimensional materials such as powders.

As mentioned above, the corrosion and oxidation protection as well as friction properties have to be improved in order to use iron and its alloys in MR applications. For these purposes fluorocarbon plasma seems to be an efficient tool to improve the substrate hydrophobicity and frictional properties, since the produced Teflon-like surface film possess chemical inertness, low surface energy (non-wettable), excellent frictional properties, lower permeability, and relatively good thermal stability.[18–20] In addition, the relative amount of functional groups can be profitably controlled upon parameters adjustment during fluorocarbon plasma treatment.

The objective of this work is plasma-enhanced chemical vapour deposition of octafluorocyclobutane (OFCB) onto carbonyl iron (CI) particles using rotary plasma reactor. Effects on surface functionalization after variation of RF power and plasma treatment time were investigated by XPS, while surface morphology was determined from SEM images.

2 EXPERIMENTAL

2.1 Plasma modification

The main material characteristics of CI particles (SL grade, BASF, Germany) are following: spherical shape of particles, non-modified surface, and content of α–iron in a bulk > 99.5 %. Plasma treatment of CI particles was carried out with Diener Femto (Diener Electronic, USA) plasma reactor. The reactor, designed for powder treatment, is equipped with a 250 ml flask which is kept rotating during the treatment for a uniform modification, as schematically shown in **Figure 1**. The plasma is created inside the discharge chamber with an inductively coupled RF generator, operating at a frequency of 40 kHz. A controlled flow of OFCB gas (purity ≥ 99.998, Linde AG, Germany) diluted with argon gas (purity ≥ 99.998, Messer Industriegase GmbH, Germany) in the ratio of 1:1 was introduced inside the chamber. The resulting gas flow rate was 45 ccm and operating pressure of approx. 30 – 40 Pa. Treatment time (60 – 600 s) and RF power (33 – 100 W) were used as experimental variables. All samples were kept under the atmosphere of processing gas for next 2 minutes after the plasma was quenched.

2.2 Scanning electron microscopy

Visual observation of fabricated films was carried out using a scanning electron microscopy (SEM, VEGA II LMU, Tescan Ltd., Czech Republic) operated at 30 kV with 30 kx magnification. Samples were coated with a thin layer of gold using a polaron sputtering apparatus before the observation.

2.3 XPS characterization

In order to determine the surface chemical changes after the plasma treatments, XPS measurements (X-ray photoelectron spectroscopy, TFA XPS, Physical Electronics, USA) were used. To avoid dispersion of the sample during the pumping, investigated particles were compressed with a laboratory press at 250 kN to obtain the test pellets. The base pressure in the chamber was about 6×10^{-8} Pa. The samples were excited with X-rays over a 400–μm spot area with a monochromatic Al $K_{\alpha 1,2}$ radiation at 1486.6 eV. Survey spectra were performed at two different spots on the surface of CI particles (pellet). Photoelectrons were detected by hemispherical analyzer positioned at the angle of 45° with respect to the sample surface. Survey-scan spectra were made at pass energy of 187.85 eV and an energy step was 0.4 eV. The concentration of individual elements was determined using MultiPak v7.3.1 software from Physical Electronics, which was supplied with the spectrometer.

3 RESULTS

A thin film suggesting a possible formation of fluoropolymer onto CI particles can be observed in **Figure 2**. Clearly from SEM images, OFCB plasma treatment does not change markedly surface morphology or roughness of modified samples. This is in good correlation with previously polymerized fluoropolymer

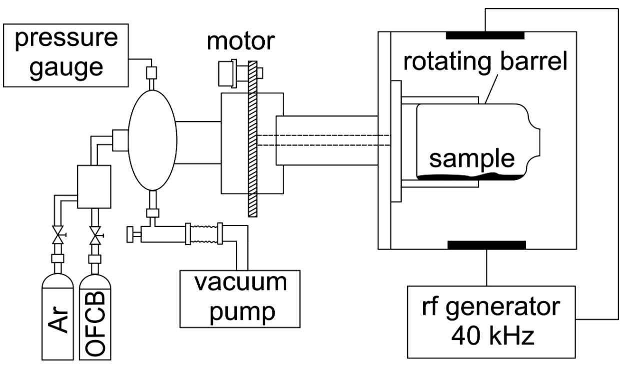

Figure 1: Rotary plasma reactor used for the treatment of CI particles
Slika 1: Rotirajoči plazemski reaktor za obdelavo CI prašnatih delcev

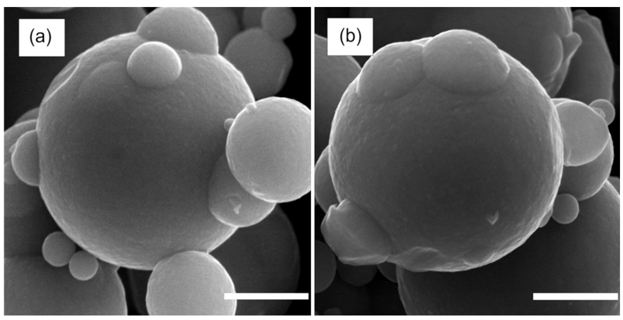

Figure 2: SEM images of mere CI particles (a) and plasma-treated (600 s, 100 W) CI particles (b); bar length 2 μm
Slika 2: SEM slika neobdelanih prašnatih delcev (a) in plazemsko obdelanih (600 s, 100 W) CI prašnatih delcev (b); dolžina merila 2 μm

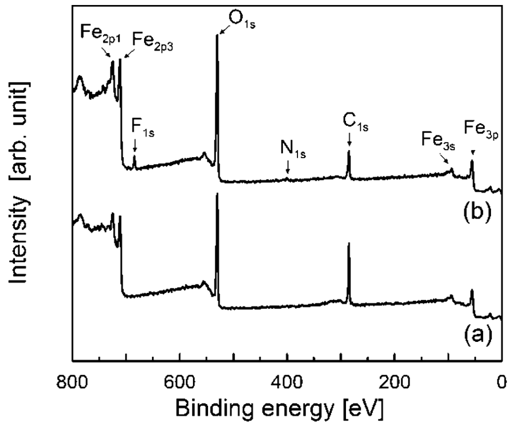

Figure 3: XPS survey spectra recorded on mere CI particles (a) and on plasma-treated (600 s, 100 W) CI particles (b)

Slika 3: Pregledni XPS-spekter neobdelanih CI prašnatih delcev (a) in plazemsko obdelanih (600 s, 100 W) CI prašnatih delcev (b)

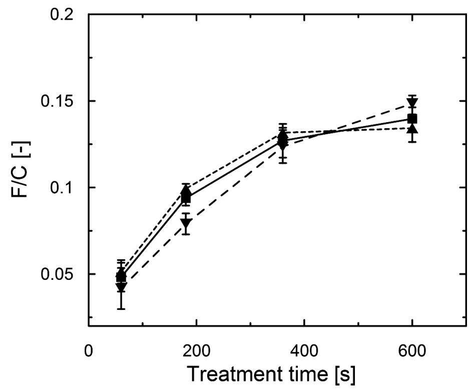

Figure 4: Dependence of the F/C atomic ratio versus the treatment time under an applied RF power of 33 W (■), 66 W (▼), and 100 W (▲)

Slika 4: Odvisnost atomskega deleža F/C glede na čas obdelave pri RF moči 33 W (■), 66 W (▼), in 100 W (▲)

films on various substrates in which extremely smooth interfaces and structures that were uniform through the thickness of the film have been demonstrated.[21]

Figure 3 shows the XPS survey spectra of the CI particles recorded before and after the plasma treatment. The peaks attributed to C_{1s}, O_{1s}, and Fe orbitals are observed in both spectra. Nevertheless, two new peaks are observed in the XPS spectrum recorded after OFCB plasma treatment. A peak near 684.3 eV suggests the formation of covalent C–F bond and hence, effective grafting of fluorine on the CI surface while a weak peak near 400.7 eV attributed to nitrogenated species is probably due to the post-plasmatic reaction ongoing in the air.

The surface composition of untreated and treated particles is listed in **Table 1**. It is worth noting that standard deviation of atomic concentration of elements was below 10 % in all cases.

As can be seen in **Figure 4**, the efficiency of fluorine bonding is affected by treatment time. The F/C atomic ratio on the CI surface firstly increased with treatment time for all RF powers used and then reached more less equilibrium value.

Furthermore, the effect of the plasma power on the fluoropolymer formation was examined. The treatment power was varied from 33 W to 100 W under the same pressure. The obtained F/C atomic ratio dependence on RF power in various treatment times is shown in

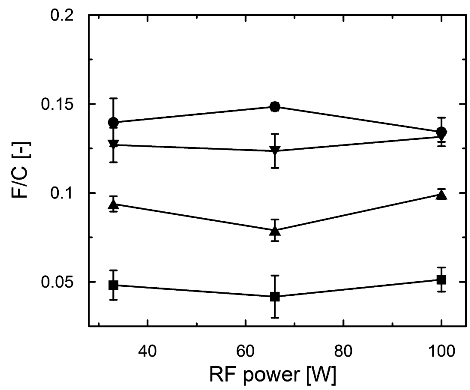

Figure 5: Dependence of the F/C atomic ratio versus the plasma power under 60 s (■), 180 s (▲), 360 s (▼), and 600 s (●) treatment time

Slika 5: Odvisnost atomskega deleža F/C glede na RF moč pri času obdelave 60 s (■), 180 s (▲), 360 s (▼) in 600 s (●)

Figure 5. The F/C atomic ratio is almost independent on the RF power used for treatment times until 360 s. However, the highest fluorine bonding efficiency for 600 s treatment time is reached at 66 W plasma power.

4 DISCUSSION

From the XPS results shown in **Table 1**, it is obvious that certain amount of fluorine covalently-bonded to the CI particles surface is present after the OFCB plasma-

Table 1: Surface composition of CI particles at different treatment times and RF powers

Tabela 1: Kemijska sestava površine CI prašnatih delcev, obdelanih pri različnih časih in RF moči

Power [W]	0	33				66				100			
Time [s]	0	60	180	360	600	60	180	360	600	60	180	360	600
C [%]	42.3	26.1	15.2	22.7	17.4	15.1	20.2	17.9	15.2	19.8	15.1	15.9	21.9
O [%]	39.5	49.1	47.3	47.0	43.9	44.1	49.2	49.9	42.6	49.3	41.5	44.4	48.4
N [%]	0	1.3	0.7	1.6	1.6	0.7	0.5	1.3	1.5	0.9	0.7	0.5	1.2
F [%]	0	1.3	1.4	2.9	2.4	0.6	1.6	2.2	2.5	1.0	1.5	2.1	2.9
Fe [%]	18.2	22.2	35.5	25.1	34.7	39.5	28.5	28.8	38.2	29.0	41.3	37.0	26.6

enhanced chemical vapour deposition in a rotary plasma reactor. Fluorine atomic concentration on the surface of CI particles grows with the treatment time. However, the increase in fluorine content is getting slower at higher treatment times probably due to the saturation of surface reactive sites. The atomic concentration of bonded fluorine does not increase significantly with RF power used as could be expected. This is supposedly caused by the degradation of formed surface layer which takes place under severe conditions of plasma treatment. In other words, the etching phenomenon will occur and remove the surface atoms along with the functionalized groups at higher plasma powers. Above mentioned statements, which are furthermore in good correlations with dependencies shown in **Figure 4** and **Figure 5**, suggest that the parameters of OFCB plasma for optimal fluoropolymer film formation onto CI particles are lower power (33 or 66 W) and higher treatment time (360 or 600 s).

5 CONCLUSIONS

A successful plasma-enhanced chemical vapour deposition of OFCB as precursor and argon mixture was used to deposit ultrathin fluoropolymer films onto CI particles in a rotary plasma reactor. The fluorine atomic concentrations on the plasma treated CI particles surface increased with increasing treatment time until approximately 400 s while remained almost constant afterwards. The concentration of fluorine did not significantly increase with higher RF power and thus, lower plasma powers are preferred from economical point of view. Since plasma treatment is a non-polluting method with shorter treatment time compared with chemical modifications, this study provides a new way for the Teflon-like surface modification of CI particles to improve their corrosion, oxidation, and abrasive properties for MR applications.

Acknowledgements

The authors wish to thank to the Ministry of Education, Youth and Sports of the Czech Republic (MSM7088352101) and the Czech Science Foundation (project 104/09/H080) for financial support.

This article was written with support of Operational Programme Research and Development for Innovations co-funded by the European Regional Development Fund (ERDF) and national budget of the Czech Republic, within the framework of the project Centre of Polymer Systems (reg. number: CZ.1.05/2.1.00/03.0111).

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