



Preparation of Nanohydroxyapatite-Carbon Nanotube Composite Coatings on 316L Stainless Steel Using Electrophoretic Deposition

M. Nabipour¹, S. Rasouli², A. R. Gardeshzadeh^{3*}

¹. M. Sc., Islamic Azad University, Sciences and Research Branch, Hesarak, P.O. Box: 14778938552, Tehran, Iran.

². Associate Professor, Department of Nanomaterials and Nanocoatings, Institute for Color Science and Technology, P.O. Box: 16765-654, Tehran, Iran.

³. M. Sc., Department of Nanomaterials and Nanocoatings, Institute for Color Science and Technology, P.O. Box: 16765-654, Tehran, Iran.

ARTICLE INFO

Article history:

Received: 29-08-2011

Revised: 13-12-2011

Accepted: 14-12-2011

Available online: 14-12-2011

Keywords:

Nanohydroxyapatite

Electrophoretic deposition

Nanocomposite

Carbon nanotubes

316L stainless steel.

ABSTRACT

Nanohydroxyapatite-carbon nanotube composite coatings were deposited via electrophoretic deposition (EPD). AISI 316L stainless steel and ethanol were used as substrate and dispersing medium, respectively. 5%wt carbon nanotube (CNT) was used as reinforcing phase. Uniform and macrocrack-free coatings were obtained both for hydroxyapatite (HA) and HA-5%wt CNT coatings. Scanning electron microscopy (SEM) revealed that most of microcracks in HA coating has eliminated after introducing CNT as reinforcing phase. The variation of deposit weight by time and voltage was measured both for HA and HA-5%wt CNT coatings. Thickness measurements revealed that for both coatings, the thickness increases with deposition voltage. X-ray diffraction patterns indicated that HA has not decomposed after sintering at 850 °C for 2 hr in argon atmosphere. Prog. Color Colorants Coat. 5(2012), 47-53. © Institute for Color Science and Technology.

1. Introduction

Electrophoretic deposition (EPD) is a simple and low cost coating method which can be used for thick film deposition of ceramic materials [1,2]. Recently, this technique has been used for deposition of hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (HA) coatings on biocompatible metals such as AISI 316L stainless steel [3-5], Ti [6,7] and Ti-6Al-4V [8,9] alloys for orthopedic applications. Wei et al [10] deposited hydroxyapatite (HAp) coatings on substrates such as metallic biomaterials (Ti, Ti-6Al-4V,

and 316L stainless steel) by electrophoretic deposition. They reported that metallic substrates tend to react with HA coatings at temperatures below 1050 °C, while decomposition for pure HA normally occurs above 1300°C. Therefore, densification of these coatings needs to be conducted at temperatures lower than 1050 °C, and this necessitates the use of high-surface-area HA nanoprecipitates. They also showed that the less equiaxed the nanoparticles, more cracks initiate in the coatings obtained by the electrophoretic deposition technique.

The remarkable high mechanical strength and

*Corresponding author: amirrg60@yahoo.com

nanoscale morphology of CNTs make them attractive for biomedical applications, particularly for developing nanofibrous bioactive surfaces in combination with HA or bioactive glasses [11]. So, Carbon nanotubes (CNT) are added to HA coatings to use mechanical properties of CNTs to reinforce HA layers obtained by EPD.

Both plasma spraying and laser surface treatment have been applied to produce HA/CNT composite layers on Ti-6Al-4V alloys [12,13]. These two techniques however are cost-intensive coating technologies and it is also difficult to control the coating parameters and thickness during processing [12]. Kaya [14] deposited ultra-fine (20nm) hydroxyapatite powders-reinforced with multi-walled carbon nanotubes on Ti-6Al-4V medical alloy using electrophoretic deposition. He reported that the addition of carbon nanotubes increases hardness, elastic modulus and inter-laminar shear strength of monolithic hydroxyapatite layers.

All of the investigations on electrophoretic deposition of CNT/hydroxyapatite coatings focused on Ti and especially Ti-6Al-4V as deposition substrate and to our knowledge, there is not any report on electrophoretic deposition of CNT/hydroxyapatite coatings on 316L stainless steel substrates.

The electrophoretic deposition of carbon nanotubes and its kinetic behavior in order to obtain a uniform coating as a cold cathode electrode in field emission devices is reported elsewhere [15,16]. In this work, we investigated the deposition of nanohydroxyapatite and its carbon nanotube composite (HA- CNT) on 316L stainless steel substrates using EPD. The variation of deposit weight by deposition time and voltage as well as

variation of film thickness by voltage are investigated. The phase stability of the coatings is also examined for both HA and HA-5%wt CNT coatings after sintering.

2. Experimental

Hydroxyapatite and ethanol were of analytical grade (Merck, Germany). Multiwall carbon nanotube was purchased from PlasmaChem GmbH. The CNTs (purity>95%) were 1-10 micrometer in length and 5-20 nm in diameter. The SEM images of the as-received CNT and nanohydroxyapatite powders are shown in Figure 1. 10 g/L hydroxyapatite suspension was prepared after sufficient ultrasonication. Then, 0.05 %wt iodine was added to enhance dispersability and particle surface charge. HA-5%wt CNT suspensions were also prepared for nanocomposite deposition after 10 min ultrasonication. EPD was performed under constant voltage using a DC power supply. Deposit weight was measured using a 0.0001 balance. The deposition time was 3 min for all the experiments. 316L stainless steel substrates (4×4 cm²) were sand blasted, acetone washed and dried in air for subsequent deposition.

After deposition, coatings were sintered at 850 °C for 2 hr in argon atmosphere. In order to investigate decomposition of HA on the 316L substrate as well as in the presence of CNTs, the obtained coatings were characterized by X-ray diffraction (XRD) (Siemens, D500) after sintering. Scanning electron microscopy (SEM) micrographs were obtained on a LEO 1455VP scanning electron microscope. The thickness of the coatings was evaluated by Phynix digital thickness meter ($\pm 1 \mu\text{m}$).

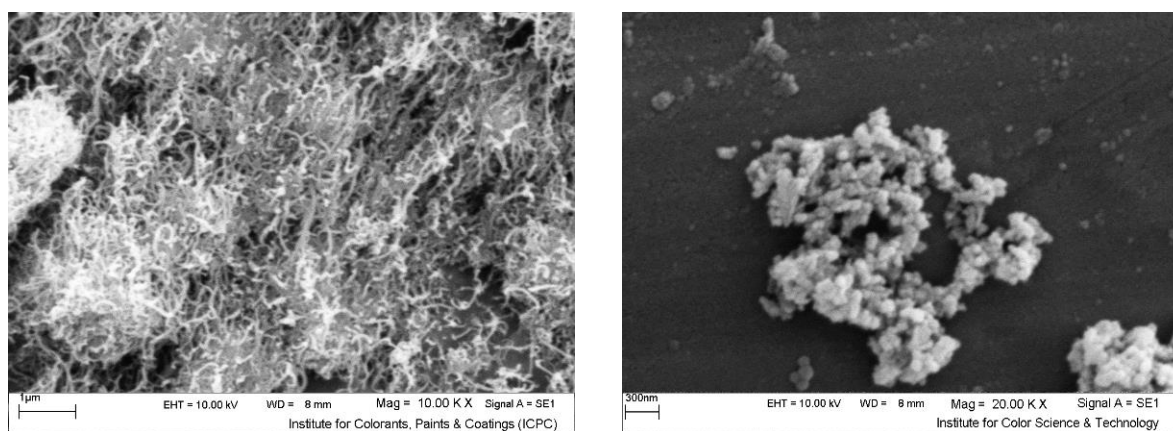


Figure 1: SEM images of the as-received CNT and nanohydroxyapatite powders.

3. Result and discussion

Figure 2 shows macroimages of the deposited coatings. It is evident that there is no macrocrack in both obtained coatings, especially for HA-5%wt CNT. Comparing Figures 2(a) and 2(b) reveals that the uniformity of the deposited coating has improved after introducing 5%wt CNT. This may be attributed to the simultaneous migration of HA and CNT particles and the ability of CNTs to fill the free spaces between HA nanoparticles, hence creating more uniform coatings after deposition. Figure 2 also shows the SEM images of the coatings after EPD. It can be seen that in contrast to HA-5%wt CNT, there exists many microcracks in HA coating which will be detrimental to mechanical properties of final coatings. The existence of CNTs within the HA nanoparticles avoids the propagation of microcracks, so providing a less-microcracked nanocomposite coating.

For investigating the electrophoretic behavior of these two coatings, the deposited weight (W) was measured at different times (t) and voltages (V). For all the samples,

the deposition area and the electrode distance were $4 \times 3 \text{ cm}^2$ and 3 cm, respectively.

For obtaining W - t curves (Figure 3(a)), the deposited weight was measured after deposition at 100 V for 0.5, 1, 2, 3, 4 and 5 minutes. The W - V curves (Figure 3(b)) were obtained after deposition at 50, 100, 200, 400 and 800 V for 3 minutes.

It can be seen from W - t curves that the deposition weight increases almost linearly with time. So it is possible to predict the deposition weight for other deposition times by either interpolation or extrapolation techniques. However, curve fitting was not successful in the case of W - V plots. It is evident from Figure 3(b) that at lower voltages, the increasing trend is nearly linear. But at higher voltages, there is a deviation from linear trend. This is because of the fact that at these voltages, more CNTs deposit on the surface at a given time, so the obtained coating has higher resistivity than those obtained at lower voltages.

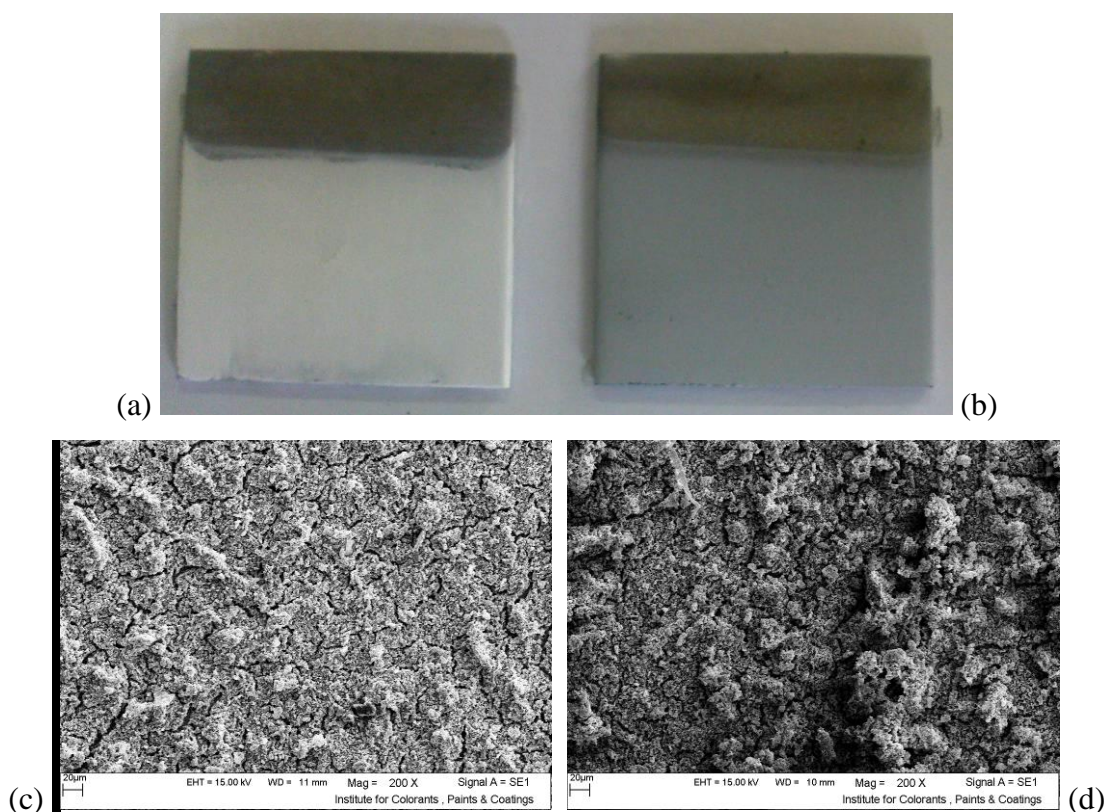
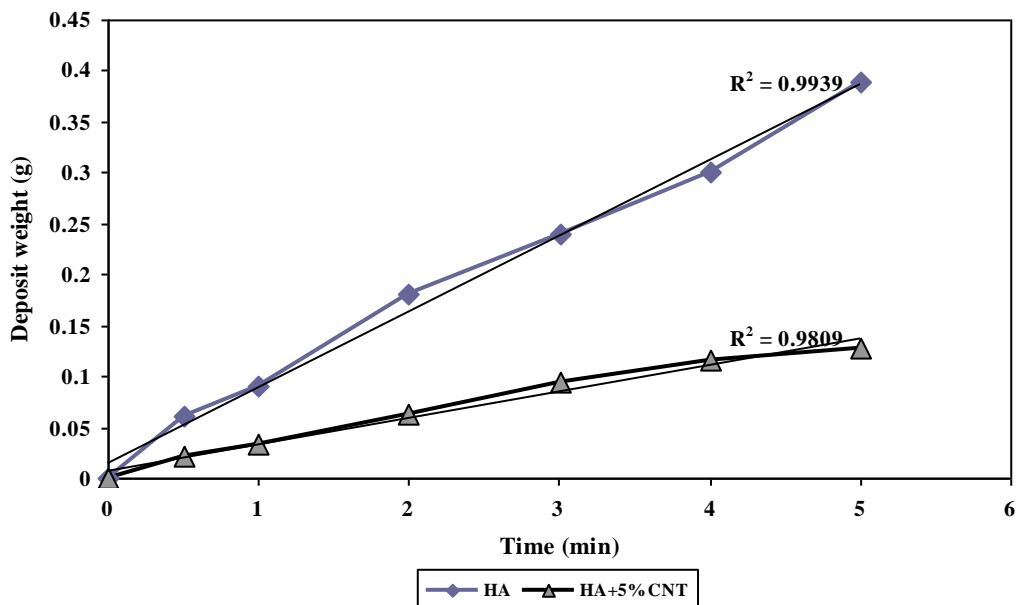


Figure 2: Macroimages of as deposited thick films: (a) HA and (b) HA-5%wt CNT coatings. Also shown SEM images of (c) HA, and (d) HA-5%wt CNT coatings.

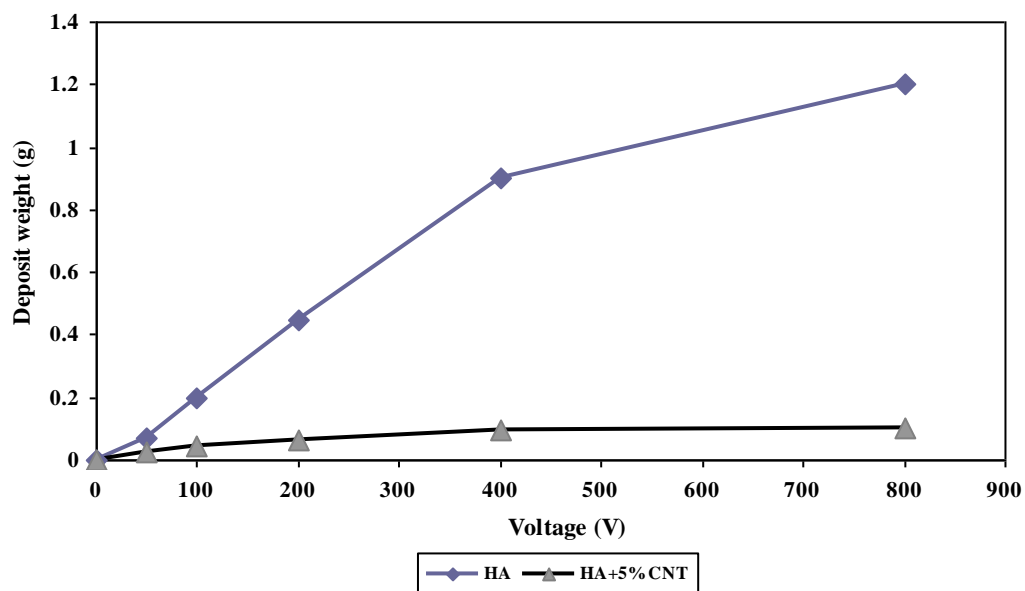
The resistivity lowers the deposition rate; hence the W-V curve deviates from the linear trend. Fluctuation and turbulence of the suspension also increases with the voltage which in turn, prevents CNTs from reaching the surface of the substrate. On the other hand, based on the observations, some of the deposited CNTs removed from the surface during drawing the sample out of the suspension. So, in this case, it is suggested to perform electrophoretic deposition at low

to medium voltages (50-200 V) in order to obtain uniform coatings.

Comparing the data obtained for HA and HA-5%wt CNT shows that in both W-t and W-V curves, the deposited weight for HA-5%wt CNT is lower than that of HA. This relates to the lower density of CNT in comparison with HA particles which results in a lightweight coating in the case of HA-5%wt CNT.



(a)



(b)

Figure 3: Variation of deposit weight by (a) deposition time and (b) electric field voltage for HA and HA-5%wt CNT coatings. The deposition area and the electrode distance are the same for all the samples (4x3 cm² and 3 cm, respectively).

These coatings are suitable for medical implants which need low weight coatings of hydroxyapatite. The thickness of the HA and HA-5%wt CNT coatings was also measured after deposition at different voltages (50, 100, 150 and 200 V) for 3 minutes. It can be seen from Table 1 that for both HA and HA-5%wt CNT coatings, the film thickness increases with deposition voltage. The obtained thickness ranges between 18-55 and 16-60 μm for HA and HA-5%wt CNT coatings, respectively. Each data is the average of five measurements on the surface of the samples.

The standard deviation of the measured values for each sample is also listed in Table 1. The data confirm the uniformity of the coatings as was claimed in Figures 2(a) and 2(b).

At a given voltage, the film thickness is approximately the same for HA and HA-5%wt CNT coatings. This shows that although HA-5%wt CNT coatings had lower weight, they exhibit the same

thickness as HA coatings. So, it can be concluded that in the presence of CNTs, the thickness of the coatings has not changed considerably. In other words, CNTs has no undesirable effect on the thickness of the electrophoretic-deposited coatings.

Cross-section view of the HA-5%wt CNT coating deposited at 100 V and 3 min is shown in Figure 4. The thickness of the coating (distance between the two dashed lines) measured at 500X is about 38.8 μm . This is in good accordance with 45.4 μm thickness value reported in Table 1. The difference arises from low accuracy of the thickness meter device.

X-ray diffraction patterns of HA and HA-5%wt CNT coatings after sintering at 850 $^{\circ}\text{C}$ for 2 hr in argon atmosphere are shown in Figure 5. The peaks correspond to hydroxyapatite composition (JCPDS 70-0795) which confirms chemical stability of the coatings on the 316L stainless steel after sintering.

Table 1: Film thickness and the standard deviation measured for HA and HA-5%wt CNT coatings.

Sample	Deposition voltage (V)	Thickness (μm)	Standard deviation
HA	50	18.6	2.2
HA	100	48.6	2.6
HA	150	54.2	4.9
HA	200	55.6	4
HA-5%wt CNT	50	16	3.1
HA-5%wt CNT	100	45.4	4.2
HA-5%wt CNT	150	52.2	2.6
HA-5%wt CNT	200	59.3	2

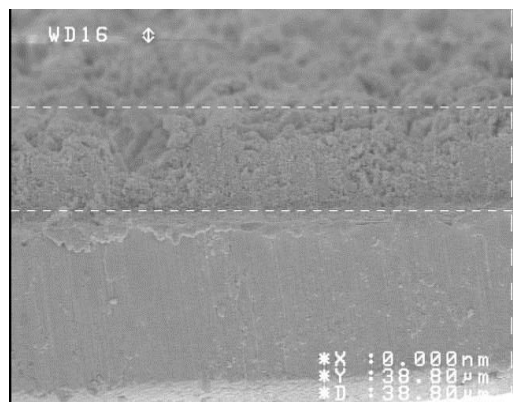


Figure 4: SEM image from cross section of HA-5%wt CNT coating deposited at 100 V and 3 min (500X).

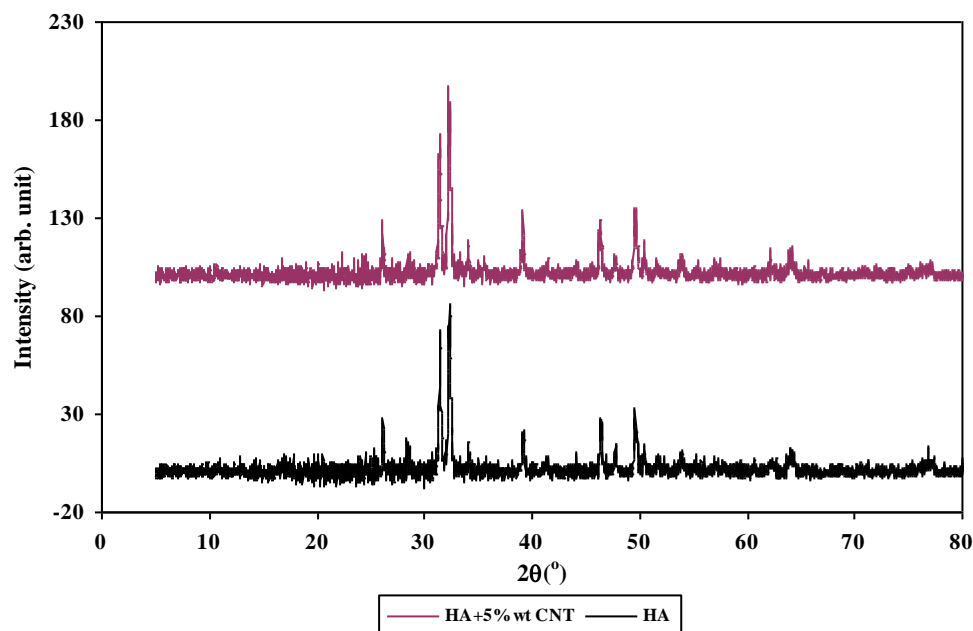


Figure 5: X-ray diffraction patterns of HA and HA-5%wt CNT coatings after sintering at 850 °C for 2 hr in argon atmosphere.

It is well known that a typical carbon structure exhibits a XRD pattern consisting of a few broad bands located near the (002), (100), (110) and (112) reflections of graphite and that the prominent peak about $2\theta = 26^\circ$ can be attributed to the (002) reflection of carbon [17]. However, in the case of HA-5%wt CNT sample, it seems that the peaks corresponding to CNT may either be overlapped by HA peaks or are not sufficiently intense. This is also reported by Najafi et al [18] who investigated the inclusion of multi-walled carbon nanotubes as the second phase in the hydroxyapatite matrix via the sol-gel process.

They pointed out that peaks at $2\theta = 26^\circ$ which were diverted to two branches, confirming the presence of CNT. XRD results also show that the HA phase is stable in the presence of CNTs, i.e. CNTs has no detrimental effects on the HA matrix.

4. Conclusions

HA and HA-5%wt CNT nanocomposites were deposited successfully using EPD technique. It was shown that introducing 5%wt CNT into the HA results in more uniform thick films with less microcracks which would improve the mechanical properties of the coatings.

The deposit weight increased almost linearly by deposition time, but it deviated from linear trend at higher voltages (> 200 V). The deposit weight of HA coating was much higher than HA-5%wt CNT nanocomposites because of low density of CNTs compared with HA powder.

The thickness of both HA and HA-5%wt CNT coatings was in the range of 16-60 micrometer and increased with deposition voltage. The thickness values of HA and HA-5%wt CNT coatings were approximately the same at a given voltage. The thickness uniformity of the coatings was also desirable.

XRD analysis showed that HA was stable in the presence of CNTs on 316L stainless steel substrate after sintering.

Finally, it can be concluded that EPD is a promising technique for coating medical implants with HA and specially HA-CNT nanocomposites. As a result, uniform and lightweight coatings are attainable using low cost and simple equipments.

5. References

1. I. Corni, M. P. Ryan, A. R. Boccaccini, Electrophoretic deposition: from traditional ceramics to nanotechnology, *J. Eur. Ceram. Soc.*, 28(2008), 1353-1367.
2. A. R. Boccaccini, I. Zhitomirsky, Application of electrophoretic and electrolytic deposition techniques in ceramics processing, *Curr. Opin. Solid State Mater. Sci.*, 6(2002), 251-260.
3. M. Javidi, S. Javadpour, M. E. Bahrololoom, J. Ma, Electrophoretic deposition of natural hydroxyapatite on medical grade 316L stainless steel, *Mater. Sci. Eng.*, 28(2008), 1509-1515.
4. G. García-Ruiz, G. Vargas, N. J. Méndez, S. A. Uribe, Water versus acetone electrophoretic deposition of hydroxyapatite on 316L stainless steel, *Key Eng. Mater.*, 314(2006), 237-244.
5. T. M. Sridhar, U. K. Mudali, M. Subbaiyan, Preparation and characterisation of electrophoretically deposited hydroxyapatite coatings on type 316L stainless steel, *Corros. Sci.*, 45(2003), 237-252.
6. Z. Feng, Q. Su, Electrophoretic deposition of hydroxyapatite coating, *J. Mater. Sci. Technol.*, 19(2003), 30-32.
7. X. Meng, T. Y. Kwon, K. H. Kim, Hydroxyapatite coating by electrophoretic deposition at dynamic voltage, *Dent. Mater. J.*, 27(2008), 666-671.
8. C. Kaya, Electrophoretic deposition of carbon nanotube-reinforced hydroxyapatite bioactive layers on Ti-6Al-4V alloys for biomedical applications, *Ceram. Int.*, 34(2008), 1843-1847.
9. C. T. Kwok, P. K. Wong, F. T. Cheng, H. C. Man, Characterization and corrosion behavior of hydroxyapatite coatings on Ti6Al4V fabricated by electrophoretic deposition, *Appl. Surf. Sci.*, 255(2009), 6736-6744.
10. M. Wei, A. J. Ruys, B. K. Milthorpe, C. C. Sorrell, Precipitation of hydroxyapatite nanoparticles: effects of precipitation method on electrophoretic deposition, *J. Mater. Sci. - Mater. Med.*, 16(2005), 319-324.
11. A. R. Boccaccini, S. Keim, R. Ma, Y. Li, I. Zhitomirsky, Electrophoretic deposition of biomaterials, *J. R. Soc. Interface*, 7(2010), S581-S613.
12. A. R. Boccaccini, J. Choa, T. Subhani, C. Kaya, F. Kaya, Electrophoretic deposition of carbon nanotube-ceramic nanocomposites, *J. Eur. Ceram. Soc.*, 30(2010), 1115-1129.
13. C. Kwok, Fabrication of carbon nanotube reinforced hydroxyapatite coating on stainless steel 316L by laser surface treatment, 11th international conference on precision engineering-towards synthesis of micro/nano-systems, Tokyo, Japan, B4(2007), 261-265.
14. C. Kaya, Electrophoretic deposition of carbon nanotube-reinforced hydroxyapatite bioactive layers on Ti-6Al-4V alloys for biomedical applications, *Ceram. Int.*, 34(2008), 1843-1847.
15. A. R. Gardeshzadeh, B. Raissi, Thick film deposition of carbon nanotubes by alternating electrophoresis, *Prog. Color Colorants Coat.*, 3(2010), 27-31.
16. A. R. Gardeshzadeh, S. Rasouli, Kinetic investigation of carbon nanotube deposition by DC electrophoretic technique, *Prog. Color Colorants Coat.*, 4(2011), 51-58.
17. I. Stamatina, A. Morozan, A. Dumitru, V. Ciupina, G. Prodan, J. Niewolski, H. Figiel, The synthesis of multi-walled carbon nanotubes (MWNTs) by catalytic pyrolysis of the phenol-formaldehyde resins, *Physica E*, 37(2007), 44-48.
18. H. Najafi, Z. A. Nemati, Z. Sadeghian, Inclusion of carbon nanotubes in a hydroxyapatite sol-gel matrix, *Ceram. Int.*, 35(2009), 2987-2991.