A Study on Preparation of Copper Powder without an External Electrical Current Source

NIZAMETTIN DEMIRKIRAN*
Department of Chemical Engineering, Faculty of Engineering, Inonu University, 44280, Malatya, Turkey

In this study, copper powder has been synthesized via cementation and electroless deposition methods, which do not require an external source of current. Zinc was used as the reductant metal in cementation method while ascorbic acid was used as chemical reducing agent in electroless deposition. The copper powders prepared by these methods were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Based on results from these analytical techniques, it was determined that copper powder was successfully synthesized using both methods. Autocatalytic or electroless method seems more advantageous from some ways according to cementation method. Copper powder can be prepared using these two methods that are more economical according to other methods in the literature.

Keywords: ascorbic acid, copper powder, displacement reactions, electroless deposition, zinc

Copper is one of the most prevalent and valuable metals used by industry because of its electrical, thermal, optical and catalytic properties among the various conductive materials. Copper is mainly used in the electrical and electronics industries due to its high electrical conductivity [1]. Because the production of metal pieces using powder metallurgy technique has gained importance in recent years, the synthesis of metal powders with different morphology has attracted considerable attentions of the researchers depending on this importance [2].

In order to produce the copper powder having the desired shape and morphology for purpose of use in many scientific and industrial applications, various synthesis methods, such as thermal decomposition [1], thermal reduction [3], polyol method [4], micro emulsion method [5], solvothermal method [6], microwave heating [7], vacuum vapor deposition [8], and electrochemical deposition [9,10] have been performed by researchers. Nanometer-sized copper powder with uniform and controllable dimensions has been synthesized using these techniques. But, these methods required the specific instruments or harsh synthesis conditions, and they can be expensive for large-scale production [11].

In addition to these syntheses methods, copper powder can be also produced via electrochemical techniques, which do not require an external source of current. Generally, two deposition methods that do not require a current source can be applied. The electrons required for the deposition in these two processes are supplied either by charge exchange reactions or derived from chemical reducing agents [12,13]. The first of these processes is cementation method. Cementation process can be described as chemical reduction of metal ions by galvanic interaction between noble metal ions and a more active metal in an aqueous solution medium without an external source of electrical current [14-16]. This method has been used to produce the copper power [17-21]. However, cementation process has been intensively used to purify the leach liquor or to separate the impurities from solution in the hydrometallurgical processing of ores. For example, the resulting solutions after the leaching of copper and zinc ores contain high levels of contaminants depending upon the structure of the ore and the type of solvent used. In electrolytic production of copper and zinc, these contaminants should be removed from the leach liquor before the electrolysis process because they cause decreasing in the current efficiency, the rate of metal production, and the purity of the deposited metal [22-26]. For this aim, cementation process can be effectively used to remove some impurities in the leach solution. This process is one of the most effective and economical techniques used to recover the metallic values from industrial solutions because of its relative simplicity, ease of control, and low energy consumption [27-29].

Recovery of copper from various solutions containing copper (II) ions by metal displacement reactions has been investigated by researchers. In these studies relating to copper cementation, iron has been generally used as sacrificing metal because of its cheapness. However, zinc and aluminum have been also used as precipitant or reductant metals [17-22, 30-43]. In most of these studies, the kinetics of copper cementation has been generally examined.

The second process applied without an external electrical current source is known as electroless deposition process. Electroless metal deposition method can be described as chemical reduction of metal ions from an aqueous solution containing a metal salt and chemical reducing agent without an external source of electrical current [13, 44]. In this method, the electrons required for the deposition of metal ions are supplied by a suitable chemical compound (reducing agent). During the process, the reducing agent is oxidized. Such processes are usually referred as autocatalytic or electroless plating process [12, 13]. The deposition of metals by this technique has been widely used to produce the films of metal, alloy and composite on conductive or non-conductive substrates surfaces [13, 44-50].

In order to prepare the metallic copper powder particles using electroless deposition method, various reducing agents, like sodium borohydride [51], hydrazine [52], hypophosphite [53] and ascorbic acid [54] have been

* email: nizamettin.demirkiran@inonu.edu.tr; Tel:+904223774760

applied. The copper powder obtained by this method have been used for various applications, mainly in the electronics industry and powder metallurgy [19,55,56].

Two methods mentioned above are simple, effective, reproducible, easily controllable and low cost approaches that do not require expensive and specialized equipment. A study comparing these two techniques has not been found in the literature. Thus, this paper describes an introductory study made to compare the metal displacement and electroless deposition methods.

Experimental part

Metal displacement reaction (cementation) between copper (II) ions and metallic zinc was performed in a 500 mL glass reactor. The stock solutions containing Cu^{2+} ions were prepared using $CuCl_2.2H_2O$. The *p*H of the reaction solution was adjusted using diluted HCl and NaOH. The solution in the glass reactor was mixed using a mechanical stirrer. During the reaction, the reaction temperature was kept constant using a constant temperature circulator. The experimental procedure and full details of cementation study are noted in previous works [40,43], and briefly noted here. After placing 250 mL of the solution containing Cu^{2+} (0.25 mol/L) into the reactor and bringing it to 45°C, 5.1 g of granular zinc particle (1.3 times of stoichiometrically required) was added to the reactor, and the reactor content was stirred at 500 rpm for 60 min. During the experiment, the *p*H of the reaction solution was 3. At the end of the reaction, it was determined complexometrically that all of the copper in the solution had precipitated. After the metal precipitate separated by filtration from the solution was washed by distilled water and ethyl alcohol, it was dried at 50°C in air.

Electroless deposition experiment was conducted using ascorbic acid as chemical reducing agent. This experiment was performed as similar to the cementation experiment. Metallic copper via this experiment was prepared as follows: After putting 250 mL of a $CuCl_2.2H_2O$ solution (0.25 mol/L) into the glass reactor and bringing it to 60°C, ammonia solution was added dropwise to the solution containing copper (II) ions to adjust the *p*H value. The solution *p*H was 6 after adding ammonia. Ammonia was used as a complexing agent. Then, solid ascorbic acid was added to this solution in small portions. The experiment was performed for 30 min of reaction time. At the end of the experiment, the copper precipitate separated from the solution was washed by distilled water and ethyl alcohol, it was dried at 50°C in air.

The morphological analyses of the solid products were carried out using a LEO-EVO 40 XVP model scanning electron microscope. The mineralogical analyses of the samples also were carried out using a Rigaku RadB-DMAX II model X-ray diffractometer.

Results and discussions

Metal displacement reactions require the transfer of electrons between the dissolving and the precipitating metals. Due to the difference between the standard electrode potential of two metals, metal ions in the solution are easily reduced to its metallic state on the reductant metal surface. The reaction between copper ions and zinc metal occurs according to the reaction in eq. (1):

$$Cu^{2+}_{(aq)} + Zn^{\circ}_{(s)} \rightarrow Cu^{\circ}_{(s)} + Zn^{2+}_{(aq)} \quad (1)$$

The standard reduction potential of copper and zinc are 0.34 and -0.76 V, respectively. ΔE° of the cementation reaction is positive (+1.1 V), and the standard free energy ΔG° is to be negative ($\Delta G^{\circ} = -n\Delta E^{\circ}$). The negative value of the standard free energy indicates that this process is favorable thermodynamically, and thus a spontaneous heterogeneous reaction takes place through the galvanic cell. As can be seen from eq. (1), copper ions in the solution precipitate in the form of metal while metallic zinc passes into the solution by dissolving. As a result of this reaction, copper powder can be produced with high-efficiency.

Copper powder obtained in the reaction conditions in this study was in the red-brown color, and its purity was determined to be 94% by complexometric titration method. In addition, the EDX analysis of the powder was also carried out. Figure 1 shows the result of EDX analysis of the produced copper powder. The EDX spectrum in figure 1 indicates the presence of copper and oxygen in the precipitated product.

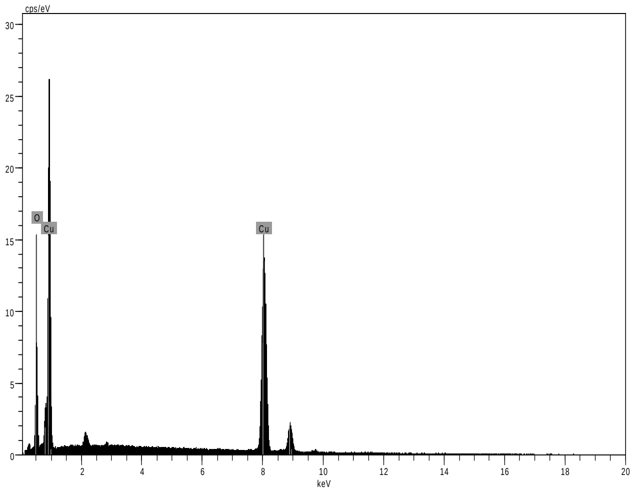

Fig.1.EDX spectrum of copper powder synthesized by cementation method

The X-ray pattern in figure 2 shows the mineralogical analysis of the copper powder. The major diffraction peaks in this figure correspond to copper while the minor peaks indicate the cuprous oxide (Cu_2O) phase. Figure1 and figure 2 show that oxygen exists in the powder product obtained, and it is in the form of compound with copper. Cuprous oxide is likely formed during the drying of wet cement copper. In the literature, it has been expressed that cuprous oxide can form even at low temperatures like room temperature [57,58].

The SEM image of copper powder is given in figure 3. This figure shows that cubic copper (I) oxide is formed on the surface of copper powder precipitated by cementation technique.

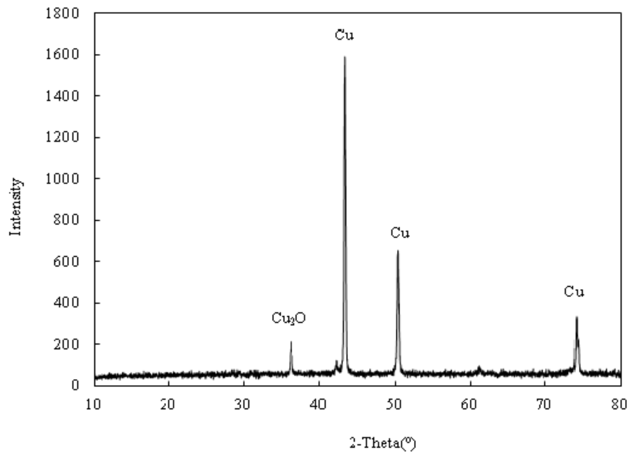

Fig.2.XRD pattern of copper powder synthesized by cementation method

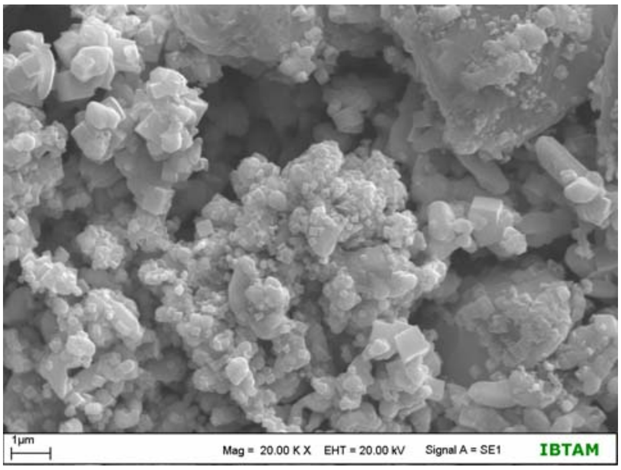

Fig.3.SEM image of copper powder synthesized by cementation method

In electroless or autocatalytic deposition, metal ions in the solution are reduced using the electrons released by the oxidation of the reducing agent. Ascorbic acid used as reducing agent in this study produces the electrons by oxidation reaction represented in the eq. (2).

$$C_6H_8O_6 \rightleftarrows C_6H_6O_6 + 2H^+ + 2e \qquad (2)$$

When ammonia solution is added to solution containing copper ions, the copper amine complex occurs according to the following reaction.

$$Cu^{2+} + 4NH_3 \rightleftarrows Cu(NH_3)_4^{2+} \qquad (3)$$

The electrons formed in the above oxidation reaction (eq. 2) are utilized to reduce the copper ions in solution according to the reduction reaction in the eq. (4).

$$Cu(NH_3)_4^{2+} + 2e \rightarrow Cu + 4NH_3 \qquad (4)$$

Consequently, the total reaction occurred in this process to obtain copper powder can be written as shown in the eq. (5).

$$Cu(NH_3)_4^{2+} + C_6H_8O_6 \rightleftarrows Cu + C_6H_6O_6 + 4NH_3 + 2H^+ \qquad (5)$$

Copper powder obtained by electroless deposition in this study was in the red color, and its purity was determined to be 96.5% by complexometric titration method. Figure 4 shows the result of EDX analysis of the copper powder produced by autocatalytic deposition. The EDX spectrum in figure 4 indicates the presence of copper and oxygen in the powder product. The XRD pattern of the copper powder obtained by reduction of the copper ions using ascorbic acid is given in figure 5. In this figure, the major diffraction peaks relate to metallic copper while the minor peaks indicate the copper (I) oxide (Cu_2O) phase as in the cementation process. The formation of this oxide product can be due to reason mentioned for cementation process. That is, cuprous oxide probably is formed during the drying wet metallic product.

The morphology of the copper powder prepared by electroless deposition method was examined by scanning electron microscope. From the SEM photograph shown in figure 6, it can be seen that the copper powder particles are non-agglomerated polyhedral structure.

According to the findings obtained from the experiments, in both methods have been reached similar

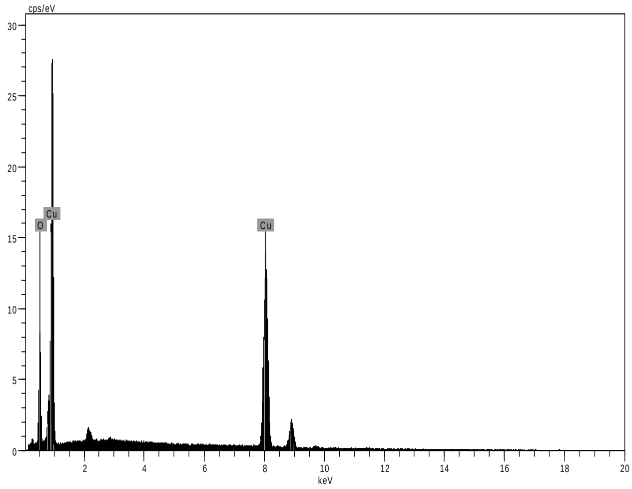

Fig.4.EDX spectrum of copper powder synthesized by electroless deposition method

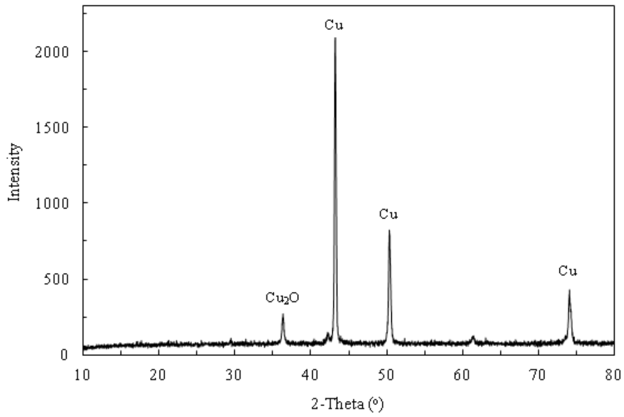

Fig.5. XRD pattern of copper powder synthesized by electroless deposition method

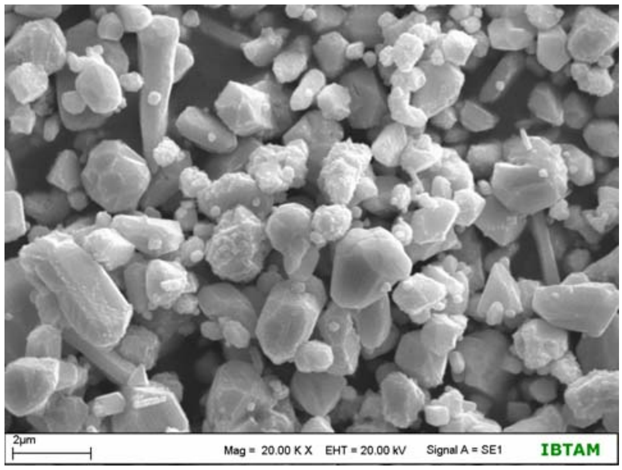

Fig.6. SEM image of copper powder synthesized by electroless deposition method

conclusions. However, autocatalytic or electroless deposition process among two methods seems to be more advantageous from the standpoint of the formed product homogeneity. In addition, more pure product by electroless deposition method can be obtained, and the reaction happens in a much shorter period of time. In this method, the product morphology can be controlled easier through the use of different complexing agents. But, autocatalytic method can be slightly more expensive according to the cementation method due to the cost of chemical substances used in the process.

In the cementation method, the reaction occurs on the reductant metal surface, and a product layer covers the reductant metal surface as the reaction progresses. If the deposit formed on the reductant metal surface is coherent, then the reaction rate can excessively decrease since the diffusion of ions through the deposit layer would be difficult. In this case, for completion of precipitation can need longer reaction times. In addition, the pH of reaction medium should be well controlled to prevent precipitation of hydroxides during the reaction. The formation of hydroxides may cause a decreasing the yield and purity of the precipitated product. In practice, the purity of the copper product obtained by cementation method is not high, and usually is around 80-90%. Nevertheless, cementation is a more economical method.

While the cementation method is generally performed to purify the leach liquor or to separate the impurities from solution in the hydrometallurgy, electroless deposition method is extensively used to form the films of metal, alloy and composite on conductive or non-conductive substrates surfaces. Depending on the purpose of their use, there can be advantages or disadvantages of these methods.

Conclusions

In this introductory study examined synthesis of copper powder without an external electrical current source, it was determined that copper ions in the solution were completely precipitated using metallic zinc and ascorbic acid as precipitation agents. Copper powder was recovered with high-efficiency in both methods. It was detected that copper powder obtained by electroless method was more pure. It was determined that the powder product obtained by both methods contained cuprous oxide formed due to oxidation of metallic copper in air. To produce the copper powder, both cementation and electroless procedure are simple, effective, reproducible, easily controllable and low cost techniques that do not require expensive and specialized equipment.

References

1.SALAVATI-NIASARI, M., DAVAR, F., Mater. Lett., **63**, 2009, p.441.
2.POÇO, J.G.R., GUARDANI, R., SHIMMI, C.S., M. GIULIETTI, Mater. Res., **9**, 2006, p.131.
3.DASH, N.A., RAJ, C.P., GEDARKEN, A., Chem. Mater., **10**, 1998, p.1446.
4.PARK, B.K., JEONG, S., KIM, D., MOON, J., LIM, S., KIM, J.S., J. Colloid Interf. Sci., **311**, 2007, p.417.
5.PILENI, M.P., NINHAM, B.W., GULIK-KRZYWICKI, T., TANORI, J., LISIECKI, I., FILANKEMBO, A., Adv. Mater., **11**, 1999, p.1358.
6.TANG, X.L., REN, L., SUN, L.N., TIAN, W.G., CAO, M.H., HU, C.W., Chem. Res. Chinese U., **22**, 2006, p.547.
7.ZHU, H., ZHANG, C., YIN, Y., Nanotechnology, **16**, 2005, p.3079.
8.LIU, Z., BANDO, Y., Adv. Mater., **15**, 2003, p.303.
9. KUMAR, S., SAINI, D., LOTEY, G.S., VERMA, N.K., Superlattice Microst., **20**, 2011, p 698.
10.MAKSIMOVIC, V.M., PAVLOVIC, L.J., PAVLOVIC, M.G., TOMIC, M.V., J. Appl. Electrochem., **39**, 2009, p.2545.
11.ZHANG, D.W., CHEN, C.H., ZHANG, J., REN, F., J. Mater. Sci., **43**, 2008, p.1492.
12.SIMON, F., Gold Bull., **26**, 1993, p.14.
13.POPOV, K.I., DJOKIC, S.S., GRGUR, B.N., Fundamentals Aspects of Electrometallurgy, Kluwer Academic, New York, 2002.
14.WADSWORTH, M.E., Trans. Metallugy Soc. AIME, **245,** 1969, p.1381.
15.POWER, G.P., RITCHIE, I.M., Aust. J. Chem., **29**, 1976, p.699.
16.SEDZIMIR, J.A., Hydrometallurgy, **64**, 2002, p.161.
17.KANUNGO, M., MISHRA, K.G., DAS, S.C., Miner. Eng., **16**, 2003, p.1383.
18. KARAVASTEVA, M., Hydrometallurgy, **76**, 2005, p.149.
19.FOUAD, O.A., ABDEL-BASIR, S.M., Powder Technol., **159**, 2003, p.127.
20.HONG, H.S., KONG, M.S., GHU, J.K., LEE, J.K., SUK, H.G., J. Mater. Sci. Technol., **24**, 2008, p.141.
21.ABDEL-AZIZ, M.H., Hydrometallurgy, **109**, 2011, p.161.
22.ZAGHLOUL, A.A., EL-SUBRUITI, G.M., AHMED, A.M., J. Mater. Sci. Technol., **12**, 1996, p.41.
23.BOCKMAN, O., OSTVOLD, T., Hydrometallurgy, **54**, 2000, p.65.
24.NELSON, A., DEMOPOULOS, G.P., HOULACHI, G., Can. Metal. Q., 39, 2000, p. 175.
25.BOYANOV, B.S., KONAREVA, V.V., KOLEV, N.K., Hydrometallurgy, **73**, 2004, p. 163.
26.DIB, A., MAKHLOUFI, L., Miner. Eng., **20**, 2007, p.146.
27.NOSIER, S.A., SALLAM, S.A., Sep. Purif. Technol., **18**, 2000, p.93.
28.NOUBACTEP, C., J. Hazard. Mater., **181**, 2010, p.1170.
29.KUNTYI, O., ZOZULYA, G., SALDAN, I., KREE, V., KORNIY, S., STEL'MAKHOVYCH, B., Cent. Eur. J. Chem., **9**, 2001, p.180.
30.KU, Y., CHEN, C.H., LEE, K.C., J. Chinese Inst. Environ. Eng., **4**, 1994, p.275.
31.CHEN, H.J., LEE, C., Langmuir, **10**, 1994, p.3880.
32.MASSE, N., PIRON, D.L., J. Electrochem. Soc., **141**, 1994, p.664.
33DJOKIC, S.S., J. Electrochem. Soc., **143**, 1996, p.1300.
34.STEFANOWICZ, T., OSINSKA, M., STEFANIA, N.Z., Hydrometallurgy, **47**, 1997, p.69.
35. DÖNMEZ, B., SEVIM, F., SARAÇ H., Hydrometallurgy, **53**, 1999, p.145.
36. KANUNGO, M., CHAKRAVARTY, V., MISHRA, K.G., DAS, S.C., Hydrometallurgy, **61**, 2001, p.1.
37.STANKOVIÇ, V., SERBULA, S., JANCEVA, B., J. Min. Metall. Sec.B: Metallurgy, **40B**, 2004, p.21.
38. DIB, A., MAKHLOUFI, L., Chem. Eng. Process., **43**, 2004, p.1265.
39. HUNG, Y.P., MOHAMED, N., DARUS, H., J. Appl. Sci., **5**, 2005, p.1328.
40. DEMIRKIRAN, N., EKMEKYAPAR, A., KÜNKÜL, A., BAYSAR, A., Int. J. Miner. Process., **82**, 2007, p.80.
41.TURONOVA, A., GALOVA, M., GERNATOVA, M., Particul. Sci. Technol., **26**, 2008, p.126.
42.AMIN, N.K., EL-ASHTOUKHY, E.S.Z., Can. J. Chem. Eng., **89**, 2011, p.609.
43.DEMIRKIRAN, N., KÜNKÜL, A., T. Nonferr. Metal Soc., **21**, 2011, p.2778.
44.MISHRA, K.G., PARAMGURU, R.K., African J. Pure Appl. Chem., **4**, 2010, p.87.
45.OSKAM, G., LONG, J. G., NATARAJEN, A., SEARSON, P.C., J. Phys. D: Appl. Phys., **31**, 1998, p.1927.
46.XU, X., LUO, X., ZHUANG, H., LI, W., ZHANG, B., Mater. Lett., **57**, 2003, p.3987.
47.PINTO, N.J., CARRION, P., QUINOSEN, J.X., Mater. Sci. Eng., **A366**, 2004, p.1.
48.YANAGIMOTO, H., DEKI, S., AKAMATSU, K., GOTOH, K., Thin Solid Film, **491**, 2005, p.18.
49.BALARAJU, J.N., RAJAM, K.S., Int. J. Electrochem. Sci., **2**, 2007, p.747.
50.RUDNIK, E., KOKOSZKA, K., LAPSA, J., Surf. Coat. Tech., **202**, 2008, p.2584.
51.SINHA, A., DAS, S.K., KUMAR, T.V.V., RAO, V., RAMACHANDRARAO, P., J. Mater. Synt. Process., **7**, 1999, p.373.
52.WU, S., MENG, S., Mater. Lett., **60**, 2006, p.2438.
53.TOUIR, R., LARHZIL, H., EBNTOUHAMI, M., CHERKAOUI, M., CHASSAING, E., J. Appl. Electrochem., **36**, 2006, p.69.
54.WU, S., Mater. Lett., **61**, 2007, p.1125.
55.XUE, J., WU, Q., WANG, Z., YI, S., Hydrometallurgy, **82**, 2006, p.154.
56.WU, X.C., BITTNER, A.M., KERN, K., Langmuir, **18**, 2002, p.4984.
57. COCKE, D.L., SCHENNACH, R., HOSSAIN, M.A., MENCER, D.E., MC WHINNEY, H., PARGA, J.R., KESMEZ, M., GOMES, J.A.G., MOLLAH, M.Y.A., Vacuum, **79**, 2005, p.71.
58.KEVIN, M., ONG, W.L., LEE, G.H., HO, G.W., Nanotechnology, **22**, 2011, p.235701.

Manuscript received: 22.10.2012