Jurnal Mekanikal
December 2013, No 36, 34 - 41

Evaluating the Effect of Pretreatment Parameters on Co-Cr-Mo Alloy Prior to Physical Vapor Deposition Coating

S. Hamtaiepour, S.Izman*, H. Hessam

Faculty of Mechanical Engineering,
Universiti Teknologi Malaysia,
Skudai 81310, Malaysia

ABSTRACT

Surface morphology and surface roughness of substrate are important parameters that determine the quality of physical vapor deposition (PVD) coating. Various methods are adopted to address this issue and one of them is by using chemical pretreatment. In the present work, an attempt is made to study the effect of pretreatment parameters, namely temperature and time, using two types of acids on surface morphology of Co-Cr-Mo alloy. The surface roughness Ra is the independent response variable. Experimental results show that higher surface roughness was obtained at temperature of 50˚C and time of 30 seconds when etched using HCl + HNO_3 *+ Acetic acid +* H_20*. However, temperature of acids and time of etching are involving, to obtain the optimum situation of substrate surface prior to PVD coating.*

Keywords: *Pretreatment, PVD, CoCrMo alloy, Surface roughness, Surface morphology*

1.0 INTRODUCTION

Co-Cr-Mo alloys are commonly used for surgical implants since more than 70 years ago [1]. This is due to their biocompatibility and specific properties, such as excellent wear resistance, corrosion resistance, high strength and fatigue resistance, and low creep [2-7]. Co-Cr-Mo alloys spontaneously form a protective thin passive film on their surface, mostly composed of Cr_2O_3 as well as some Co-oxide and Mo-oxide [5].

There have been some concerns about the mechanical properties and potentially harmful effects of metal ions (Cr^6 for example) released from Co-Cr-Mo when used as implants [8,9]. To address this, surface modification techniques can be used to produce desirable properties on the surface of the material. Physical vapor deposition (PVD) is one of the techniques where coating a thin film on the surface can improve the mechanical and chemical properties of material. Surface coating of TiN for example [10], is able to significantly reduce this metal ion release.

Pretreatment is an important stage affecting the performance of PVD coating. All activities employed to reduce the level of contamination on the substrate quality prior to PVD coating are called cleaning processes. Polishing and chemical etching chosen to be appropriate to the material in question, can usually remove the contaminants and smoothing the surface to have better adhesion between coating film and substrate. Chemical etching efficiency is mainly governed by types of acid and etching time and temperature. Smooth surface roughness of coating is important to reduce friction. Adhesion strength of coated layer on substrate must be sufficiently high to aviod failure during implantation. Nevertheless, there is not many studies investigating the effect of these parameters on Co-Cr-Mo alloys.

*Corresponding author: izman@fkm.utm.my

In this present work effect of etching parameters on Co-Cr-Mo alloy using two different acids was investigated. Temperature, etching time and surface roughness were varied in the experimental work.

2.0 EXPERIMENTAL METHODS AND MATERIALS

2.1 Material and Sample Preparation

Sample of a biomedical Co-Cr-Mo alloy (ASTM 1537) in disc shape of 13mm in diameter and 2 mm in thickness were cut from as received bar. The main elemental composition is shown in Table 1. The sample was cut form as received disc, mounted by hardener/epoxy and was then fixed to grinding machine fixture in order to do 4-step mechanical polishing.

Table 1: Specification for Cobalt Chromium alloy (wt %)

Type[a,b]	Cr	Ni	Mo	Si	C	Fe	Ti	W	N	P	S
Wrought alloy											
F1537	26-30	<1.0	5-7	<1.0	<1.0	<0.35	-	-	<1.0	-	-

[a] Balance of composition is cobalt (Co).
[b]ASTM specification F1537 standard specification for Wrought Cobalt-28 Chromium-6 Molybdenum Alloy for surgical implants (R31537-9). FHS vitallium, GADS Zimaloy Micrograin, Protasul^{TM} - 20 ,CMM Plus^{TM}

Polishing is used mainly to make the substrate surface smooth and to remove the contaminants which subsequently enhanced the adhesive strength. After the polishing, the surface roughness and surface morphology was evaluated. The polishing in this research is mechanical polishing that includes 4 step which are described below as follows:

i. Grinding with running water and SiC paper #320, force 15 N, speed of upper spindle 150 rpm, speed of lower spindle 150 rpm, both spindle rotate counter clock wise and the time is 1 minute.
ii. Grinding with running large diamond suspension (9 µm size) and MD-largo disc with 250 mm diameter, force 15 N, speed of upper spindle 150 rpm, speed of lower spindle 150 rpm, both spindle rotate counter clock wise and time is 2 minutes.
iii. Grinding with running small diamond suspension (3 µm) and MD-Dac disc with 250 mm diameter, force 15 N, speed of upper spindle 150 rpm, speed of lower spindle 150 rpm, both spindle rotate counter clock wise and time is 2 minutes.
iv. Polishing with running silica suspension and MD-chem disc with 250 mm diameter, force 20 N, speed of upper spindle 150 rpm, speed of lower spindle 150 rpm, upper spindle rotate counter clock wise and lower spindle rotate clock wise, time is 2 minutes.

Chemical etching was carried out after polishing process. This process was performed with two types of acids, i.e. HF + HNO_3 + Ethanol and HCl + HNO_3 + Acetic Acid + H_2O. Temperature was varied in sequence of 30 ^oC and 50 ^oC. Durations of etching for HF + HNO_3 + Ethanol were 2 minutes and 4 minutes and for HCl + HNO_3 + Acetic Acid + H_2O were 10 and 30 seconds. Replications in center point were done three times. Chemical etching was carried out under ultrasonic condition. After etching, the substrate was rinsed in deionized water, cleaned and dried with compressed air flow. Surface roughness and surface morphology were analyzed after chemical etching.

2.2 Surface Image Observation

Field Emission Scanning Electron Microscope (FESEM) used was a SUPRA 35VP for analyzing the surface morphology of substrate after pretreatment. This machine is equipped with energy dispersive X-ray analysis.

2.3 Surface Roughness Measurement

The surface roughness of the substrates was measured using Mitutoyo CS.5000 surface roughness tester. The average Ra values were taken as an indicator of the surface roughness values. A total of four measurements were taken on each sample before calculating the average values. Quantitative analysis such as surface roughness measurement sometimes giving misleading information on the surface quality. It depends largely on the cut-off length and sampling size during measurements. Cut-off length of 0.25mm with five sampling length is typically used for polished surface. However, the total measured length is too short (1.25mm) to produce conclusive results. In this work, a total measurement length of 2mm was used to measure the surface roughness of the etched substrates. This decision was made with the reason to increase the measurement area.

3.0 RESULTS AND DISCUSSION

3.1 Surface Roughness

Surface roughness values before and after etching using both acids 1 and 2 are summarized in Figure 1 and 2 respectively. For acid 1, there is not much different in Ra when the substrates were etched at 40°C for 3 minutes. Similar phenomenon happens when etching at 30°C for 2 and 4 minutes. It seems that acid 1 has a little attack on removing peaks and valleys of surface roughness at low temperature. However, when the temperature is increased to 50°C, the acid shows a little bit aggressive to attack the peaks and valleys roughness profile which resulting a smoother surface finish. The higher etching time shows the smoother surface finish. It is believed that the roughness peaks get the highest amount of heat and easy to be eroded as compared to the roughness valley which is considered as cooler area. The flatten peaks reduce the Ra value. At low temperature (30 °C and 40 °C), acid 2 also illustrates similar behavior with acid 1. Acid 2 performs differently at 50°C where the surface roughness is getting rougher.

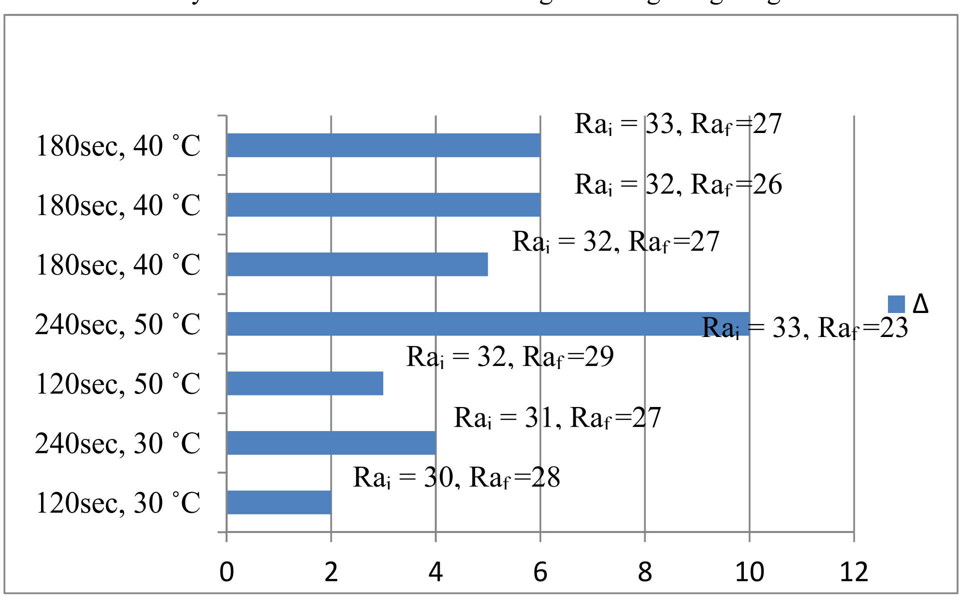


Figure 1: Differences of surface roughness after etching using acid type 1

Subsequently, the effect of etching process on the surface roughness are analyzed based on their differences in Ra value before (polished) and after etching process. The highest surface roughness reduction in acid 1 is run (50 °C at 4 minutes). While for acid 2, the highest increment in surface roughness is run (50 °C at 30 seconds). In acid 1, etching temperature and time influence the amount of surface roughness reduction. As temperature and time increase, the amount of smoothing of roughness peaks also increases. A reversed behaviour was shown in acid 2 where increasing in temperature results in increasing the surface roughness. Acid 2 seems more aggressive than acid 1 at high temperature. Acid 2 appears attacking both roughness peaks and valleys that results rougher surface. However, varying etching time from 10 sec to 30 sec demonstrates insignificantly influence the increment in surface roughness.

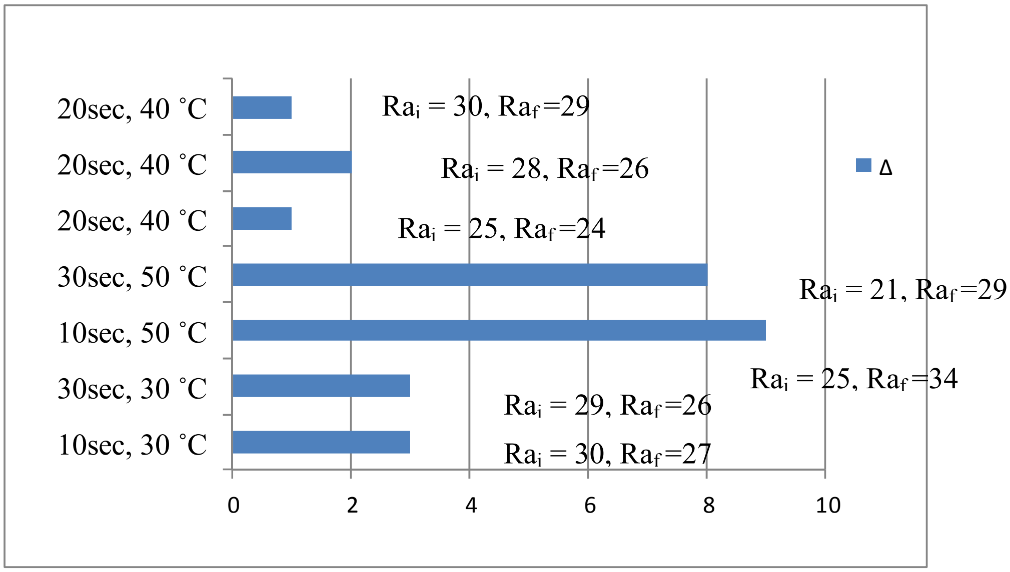


Figure 2 : Differences of surface roughness after etching using acid type 2 Surface Morphology

Since the Ra measurements were taken based on a straight line, it was still unable to provide the overall behavior of the surface. To complement, qualitative analysis on surface morphology using FESEM is still required to conclude the surface integrity after the etching process. Figure 3 and 4 show the surface morphology observed under FESEM of the selected etched samples of acid 1 and acid 2 respectively.

Under acid 1, time and temperature play major roles in attacking the substrate surface during etching. As can be seen in Figure 3, micro pitting starts to develop on the substrate at temperature as low as 30˚C at 4 minutes. Surprisingly, no pitting occurs at 40˚C with etching time 3 minutes. At higher temperature of 50˚C, pitting phenomenon is more obvious with larger and deeper holes.

Under acid 2, effect of temperature from 30˚C to 50˚C is distinctly demonstrated in Figure 4. At low temperature, it was hardly noticed any pit holes on the substrate surface. In contrast, at higher temperature the acid seems to be more aggressive in attacking the substrate surface. Massive tiny pit holes can be observed on the surface which later merge together to develop bigger pitting holes. Figure 5 shows clearly these tiny holes at higher magnification.

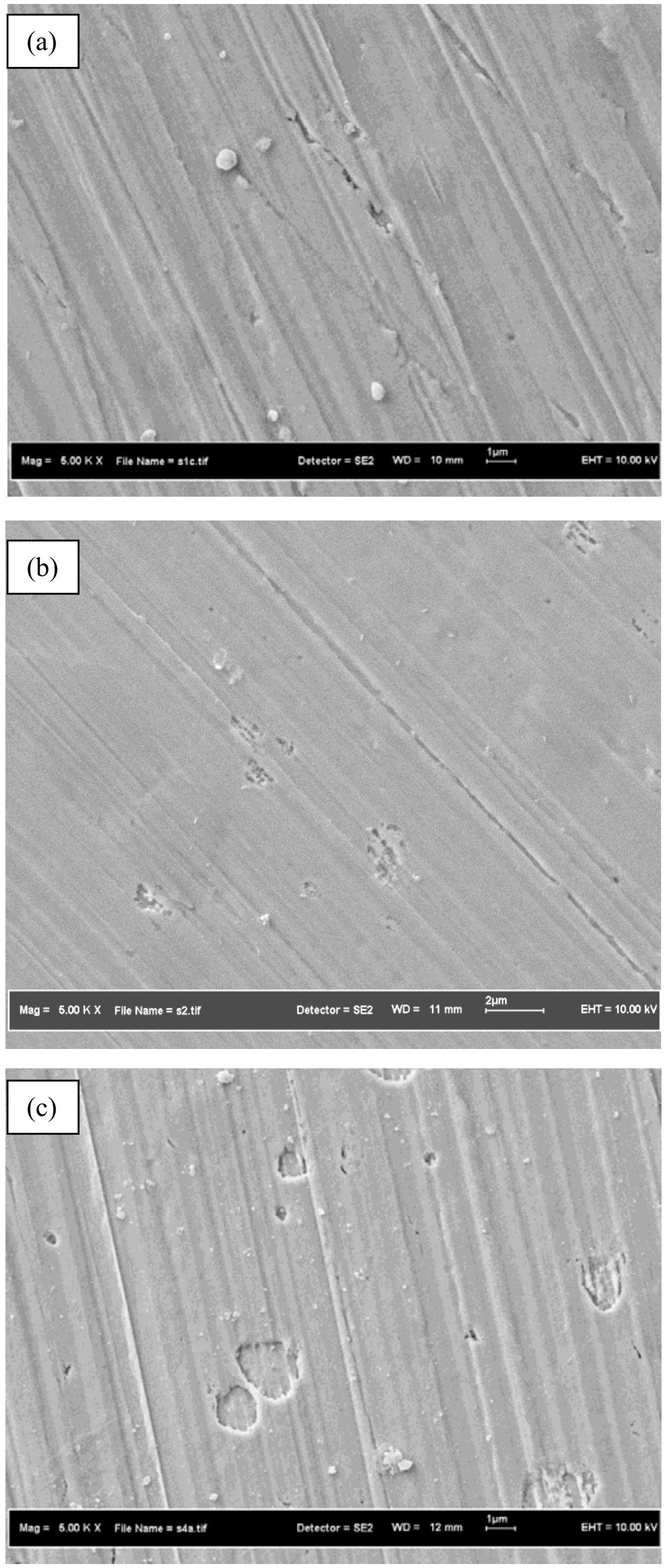


Figure 3 : Surface morphology after etching with acid 1: a) 3 min 40 ˚C, b) 4 min, 30 ˚C and c) 4 min, 50˚C

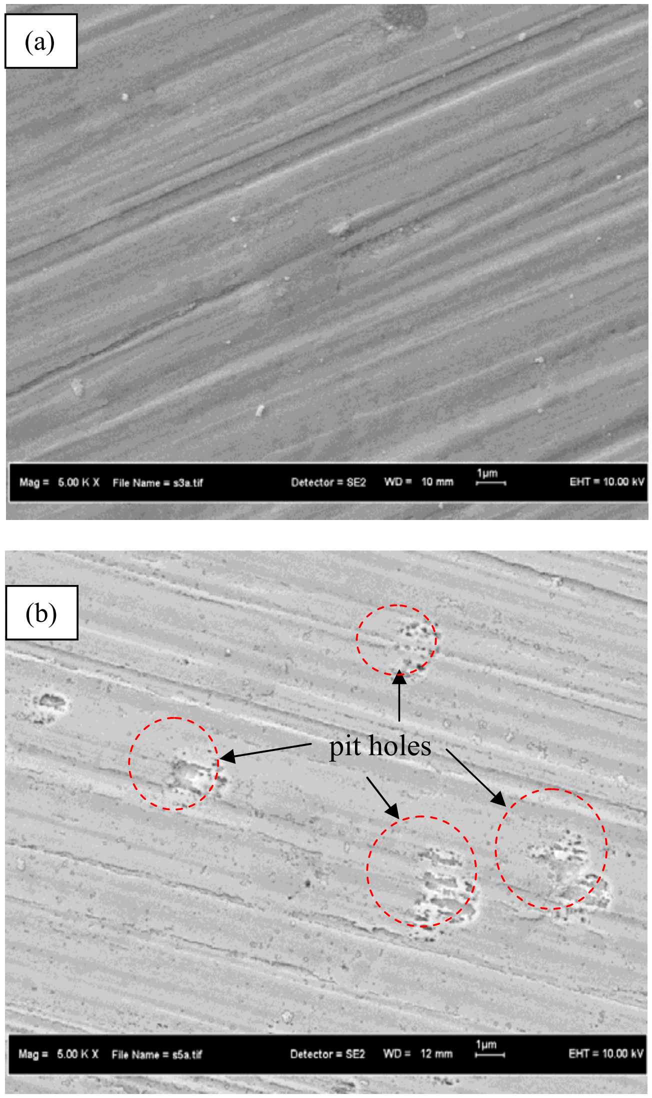
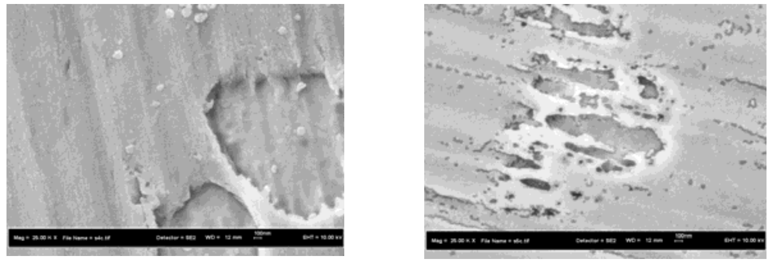


Figure 4 : Surface morphology after etching with acid 2: a) 30 sec, 30 ˚C and b) 30 sec, 50 ˚C

Figure 5 and 6 show the comparison of surface morphology after the substrates were etched at different times and temperatures under acid 1 and acid 2. As mentioned earlier, acid 1 is less aggressive than acid 2 due to factor of time. Acid 2 reacts in a fraction of less than 1 minute to develop micro pits on Co-Cr-Mo substrate at 50˚C. In contrast, acid 1 requires four times longer to develop a similar size of pit on the substrate. Another interesting phenomenon is the different type of pit shape produced by two different acids. Pit shapes produced by acid 1 appears to have undercut edge which has potential to provide good anchorage for coating material as compared to thin blister-like surface produced by acid 2 at 50˚C etching temperature.



Enlargement of X   Enlargement of Y

Figure 5 : Enlargement of pit holes

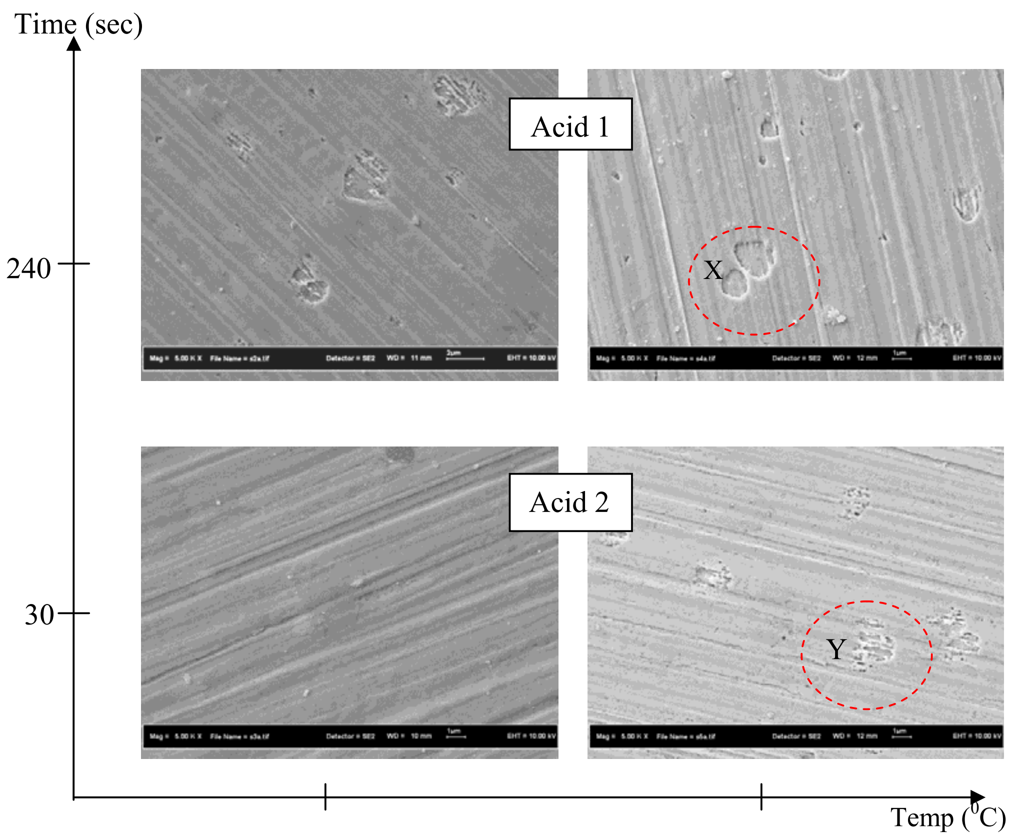


Figure 6 : Comparison of surface morphology after acid etching at different time and temperature

Micro pits produced on the etched surface seem to have good potential to increase adhesion strength of coating material without sacrificing the smoothness of the substrate. Fine finishing of the substrate is necessary for maintaining low friction between mating surface. In order to confirm this hypothesis, an actual PVD coating on the etched surface should be carried out. Scratch test on the coated material will finally certify this hypothesis.

4.0 CONCLUSIONS

The following conclusions can be drawn from this preliminary study on the effect of pre-treatment parameters on cobalt chrome molybdenum substrate:

a) Time and temperature of acid pretreatment has significant influence in determining the final surface roughness of substrate.
b) Micro pits were produced on the etched surface at higher temperature using both acids. Massive pits on the etched substrate surface are seen as a good phenomenon for better adherence of coating material on the substrate. This phenomenon occurs at low temperature with longer etching time of acid 1. Larger pit size develops at higher temperature as a result of merging of tiny pits.

ACKNOWLEDGEMENTS

Authors would like to express highest gratitude to Ministry of Higher Education(MOHE), Malaysia and faculty of Mechanical Engineering, UTM for funding via project vote nos. 78611 & Q.J130000.7124.02H60 and providing their facilities for conducting this research respectively.

REFERENCES

1. Bettini E., Eriksson T., Boström M., Leygraf C., Pan J., 2011. Influence of metal carbides on dissolution behavior of biomedical CoCrMo alloy: SEM, TEM and AFM studies, *Electrochimica Acta 56,* 9413– 9419
2. Davis J.R. 2003. ASTM International, Medical Applications: Metallic Materials, *Handbook of Materials for Medical Devices,* 21. American Society for Metals
3. Black J., 1999. Biological Performance of Materials, *Fundamentals of Biocompatibility,* 245. 3rd ed. New York: Marcel Dekker
4. Savio III J.A., Overcamp L.M., Black J., 1994. Size and shape of biomaterial wear debris, *Clin Mater 15*, 101.
5. Valero Vidal, C., Igual Munoz, A., 2008. Electrochemical characterisation of biomedical alloys for surgical implants in simulated body fluids, *Corrosion Science 50*, 1954-1961.
6. Martinelli, K.A, Lemaitre, D.T, Lee T.J. 2001. Orthopedic Industry, *Update and Company Models*, 11. 1st ed. New York: MerrillLynch
7. Lorenz, M., Semlitsch, M., Panic, B., Weber, H. and Willert, H.G., 1980. Properties of implant alloys for artificial hip joints, *Medical and Biological Engineering and Computing, 18(4)*:511-520.
8. Dobbs, H.S. and Robertson, J.L.M., 1983. Heat treatment of cast Co-Cr-Mo for orthopaedic implant use, *Material Science 18*: 391- 401.
9. Woodman, J.L., Black, J. and Nunamaker, D.M., J. 1983. Release of cobalt and nickle from a new total finger joint prosthesis made of vitallium, *J. Biomed. Mater. Res., 17*: 655-668
10. Mears D.C., 1979. Materials and orthopaedic surgery, *Williams and Wilkin, Baltimore, MD.*