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Characteristics of As-Cast and Forged Biodegradable Mg-Ca Binary Alloy Immersed in Kokubo Simulated Body Fluid

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Abstract. Biodegradable implant is an alternative to metallic implant and has the advantage of not being necessary to remove once the fracture has healed. Magnesium is particularly desirable since it is biocompatible and has a modulus of elasticity closer to bone. In addition, it shows ability to biodegrade in situ, when used as an implant material. In this research, different percentages of calcium were added to magnesium during melting of the alloy. A selected alloy was forged at different parameters. Both as cast and forged alloys were subjected to polarization test performed in Kokubo simulated body fluid. Immersion test in the fluid was conducted for 96 hours to investigate the formation, growth and morphology of the hydroxyapatite on the surface of the alloys. The results showed that similar electrochemical behaviour took place in the alloys regardless of the calcium content. However, an increase in corrosion rate was observed with increasing calcium content. It was also observed that forging process decreased the corrosion resistance of the alloy. Furthermore, increasing calcium content accelerated the growth of bone-like apatite in the alloy.

Introduction

There is considerable interest in the potential of magnesium alloys to replace existing materials for surgical implants. Of particular interest is the possibility of using magnesium implants as scaffolding on which new bone can grow and as fixtures to hold together bone long enough to allow natural healing to take place. This means the implant needs not remain in the body without needing extra surgery to remove it. It is reported that existance of magnesium is necessary for bone healing by absorbing calcium [1]. However, the corrosion rate of magnesium in body is very high. Decreasing the corrosion rate of magnesium can be done by processing or alloying approach [2-4]. The binary Mg-Ca alloys have recently attracted considerable interest as biodegradable implants [5-7]. Z. Li et al, reported that hot rolling and extrusion can improve corrosion resistance of Mg–1Ca in simulated body fluid [8]. Zhi-min et al, showed that hot extruded magnesium alloy exhibits better corrosion resistance [9]. Other report showed that mechanical processing such as rolling can control the corrosion properties of the magnesium alloys [10,11]. Several published reports indicated an improvement in mechanical properties of forged magnesium alloys over cast parts [12,13]. However, there is no report on the influence of forging process parameters on biodegradablity of Mg-Ca binary alloy in Kokubo simulated body (KSB) fluid. This research work is aimed at investigating the effect of calcium content on the degradable behaviour of Mg-Ca binary alloy as biodegradable implants and to study the effect of forging parameters on the properties of Mg-1Ca alloy as a selected of them.

Experimental procedure

Casting and sample preparation. Five different Mg-Ca binary alloys with various Ca percentages, i.e 0.7, 1, 2, 3 and 4% were prepared by melting pure commercial magnesium ingot (99.9%) and Mg-30%Ca master alloy in a mild steel crucible using a medium frequency induction melting furnace. Argon gas was used to create a protective environment during melting. Molten metal was poured at the temperature of 750 °C into a simple mild steel mould preheated at 200 °C (Fig. 1). The chemical composition of the as-cast Mg-Ca alloys was analyzed by energy dispersive X-ray spectroscopy as given in Table 1.

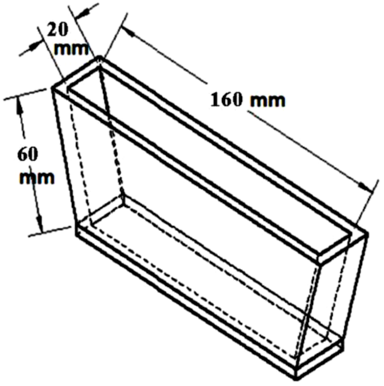


Fig. 1. The dimensions of the mild steel mould used for casting of the alloys

Table1. Calcium percentage in EDS analyzed as-cast Mg-Ca alloys

Cast Mg-Ca Alloys	1	2	3	4	5
Ca content	0.74	1.08	1.98	3.03	3.98

Forging process. Based on the analysis conducted on the samples, Mg-1Ca was found to exhibited reasonable corrosion characteristics and was selected for further processing investigation. Coupons were cut from the as-cast Mg-1Ca alloy and machined to the size of 60×25×20 mm. The samples were heated to three different temperatures; 250, 350, and 450 °C (±5 °C) before being forged. The forging force was maintained at 1080 kN and the ram speed was regulated to 40, 50, 60, and 65 stocks per minute (spm).

Sample preparation and microstructural characterization. For microstructural analysis samples sized 20×15×6 mm were cut from the as-cast and forged coupons, ground, polished and observed under optical and scanning electron microscopies (SEM) to characterize microstructural evolution of both as-cast and forged samples.

Immersion test. To investigate the corrosion products, morphology and formation of bone materials on both the as cast and forged alloy, samples, each measuring 15×10×6 mm, were prepared and ground with sand paper up to 2400 grit. The samples were immersed in Kokubo simulated body fluid (SBF) for 96 hours according to ASTM G31-72 standard. The temperature of the solution was controlled at 37 °C and the pH value of the SBF solution set at 7.7. At every 12 hours interval, the samples were withdrawn from the solution, cleaned and weighed. The surface of the samples was characterized by SEM and energy dispersive X-ray spectroscopy (EDS).

Electrochemical measurement. The as-cast and forged samples sized 1cm^2 were cut, ground with up to 2400 grit waterproof abrasive paper and subjected to electrochemical test. The electrochemical apparatus comprised of a three-electrode system; graphite, saturated calomel and the specimen act as the counter, reference and working electrodes, respectively. A potentiodynamic system set at a scan rate of 0.5 mV/sec was used to measure the electrochemical behaviour of the samples in SBF. The test was conducted according to ASTM G5-94 standard.

Results and Discussion

Microstructural characterization. Fig. 2 shows the micrographs of microstructure of Mg-Ca binary alloy with different calcium contents. As can be seen finer grain size is achieved with the increasing percentages of calcium content in the alloy which can be attributed to the precipitation of intermetallic Mg_2Ca particles in the microstructure during solidification. The micrographs also show that increasing the amount of black Mg_2Ca particles led to their precipitation at both the grains and grain boundaries due to the low solubility of Ca in Mg. The precipitates are more obvious at the interdendritic spaces where the molten metal solidifies at last.

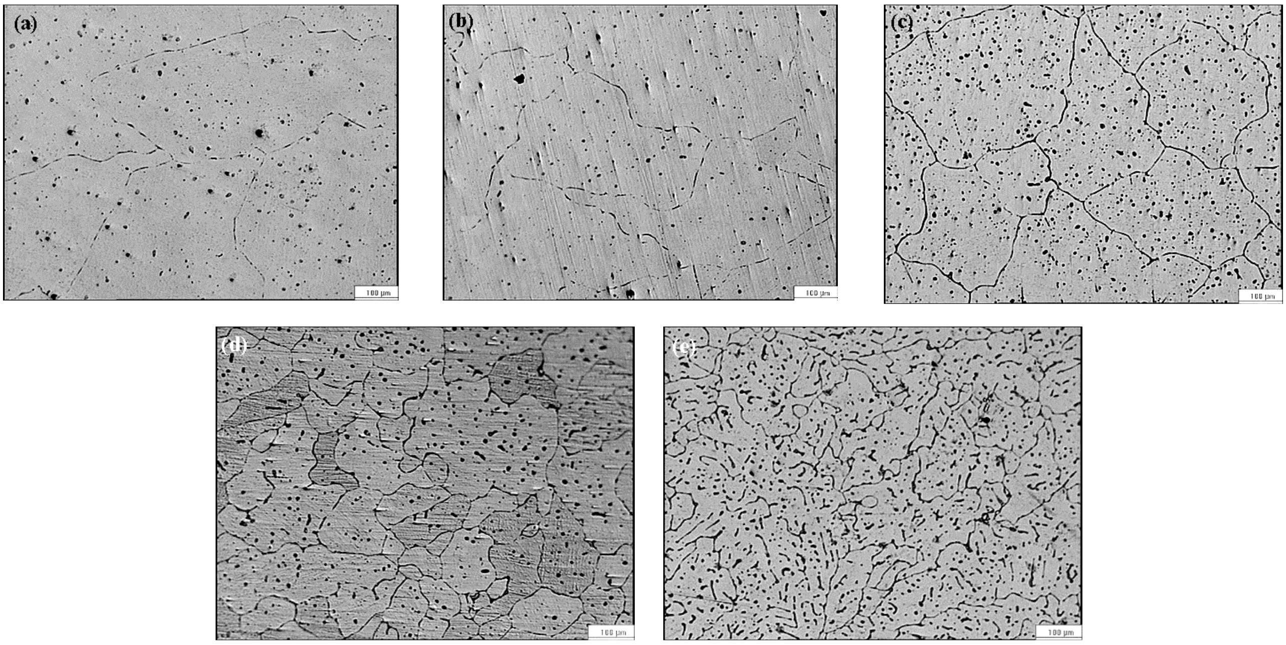


Fig. 2. Optical microstructure of Mg-Ca binary alloys with different calcium contents; (a) 0.7%, (b) 1%, (c) 2%, (d) 3% and (e) 4%.

From the optical micrograph in Fig. 3, it can be seen that for the same forging speed but with increasing forging temperature resulted in finer microstructure in Mg-1Ca alloy. This may be attributed to the higher volume of grain recrystallized at higher temperature. In addition, twinning structure, which is the dominant mechanism during the deformation of magnesium alloys can be clearly observed in the microstructures. Fig. 3 also reveals the increasing of twining planes with increasing forging temperature. It was found that no significant effect on the microstructures was observed when forging speed was regulated.

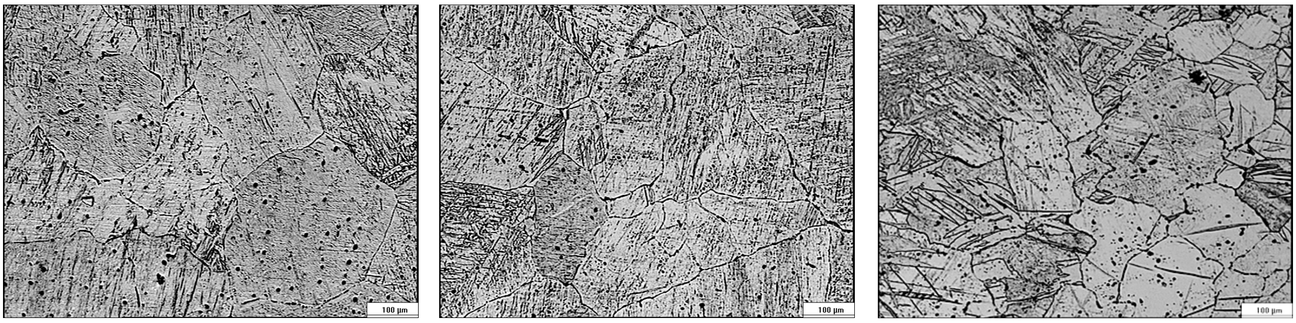


Fig. 3. Optical microstructure of Mg-1Ca binary alloy forged at the speed of 50 spm and sample temperatures of (a) 250, (b) 350 and (c) 450 °C

Immersion test. Fig. 4 shows the corrosion products of the as-cast and forged Mg-1Ca alloy immersed in SBF, after 96 hours. In general, high rate of Mg dissolution (anodic reaction) and hydroxyl anion (OH^-) formation (cathodic reaction) in SBF took place at the early stage of the immersion process followed by the formation of $Mg(OH)_2$ layer on the surface of the samples. Crackled morphology observed on the surface may be due to dehydration and shrinkage of the layer during drying.

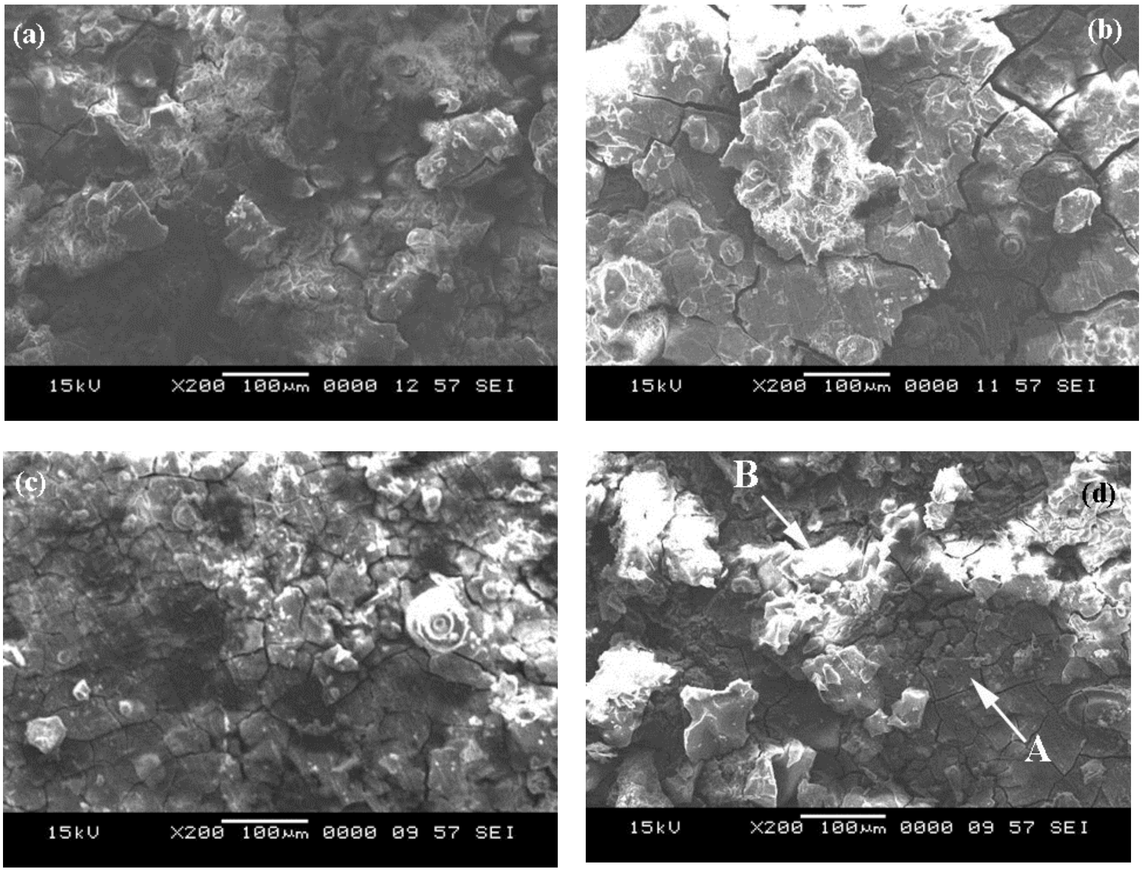
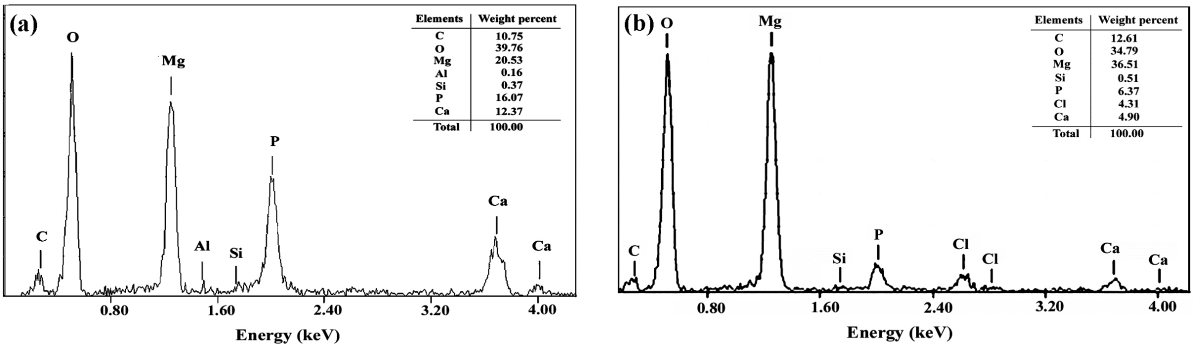


Fig. 4. SEM images of the corrosion products formed on the surface of (a) the as-cast, and the samples forged at (b) 250, (c) 350 and (d) 450 °C, and at 65 spm after immersed for 96 h in SBF

Further corrosion process developed Ca-P compound layer on the surface of the hydroxide layer. According to E. Zhang and L. Yang [14], this layer provides better corrosion resistance, which lowers corrosion rate of the alloy. On the other hand, due to the existence of considerable amount of chloride ion in the SBF, 147.8 mmol/dm^3 [15], the $Mg(OH)_2$ layer is attacked forming pits on the surface [16]. Formation of the pits accelerates the corrosion reaction and white corrosion products developed on the pits, as seen in Fig 4. The EDS analysis (Fig. 5) revealed that Mg, O, Ca and P were the dominant elements of the white products resembling formation of hydroxyapatite ($Ca_{10}(PO4)_6(OH)_2$) and magnesium phosphate ($Mg_3(PO4)_2$) [17]. These products enhanced bone healing if Mg-1Ca is used as surgical implant material. However, no significant bone-liked appetite was seen in the corrosion product. It is interesting to note that only Mg and O were the main elements found at other locations confirming the existence of $Mg(OH)_2$.

It can be seen from the SEM images in Fig. 4 that the amount of corrosion products is higher in the forged samples compared to the as-cast indicating that forging process accelerates formation of hydroxyapatite when the alloy was immersed in SBF. Similar trend was observed when Ca content was increased in the as-cast samples, as shown in Fig. 6. It can be seen that with the same immersion duration in SBF a considerable amount of bone-like apatite, the product of the corrosion process, formed on the surface of the as-cast alloys. A small amount of bone-liked apatite was found in the alloy contained lower than 3% calcium when immersed for the same duration. The increase in corrosion products can be attributed to an increase in the amount of Mg_2Ca phase in the alloys, which increased the cathode/anode ratio led to high localized corrosion risk [18]. Therefore, the more Mg_2Ca phase found in the microstructure, the higher corrosion rate observed in the alloy.



(a)

Elements	Weight percent
C	10.75
O	39.76
Mg	20.53
Al	0.16
Si	0.37
P	16.07
Ca	12.37
Total	100.00

(b)

Elements	Weight percent
C	12.61
O	34.79
Mg	36.51
Si	0.51
P	6.37
Cl	4.31
Ca	4.90
Total	100.00

Fig. 5. EDS analysis of the (a) point A and (b) Point B marked in Fig. 4

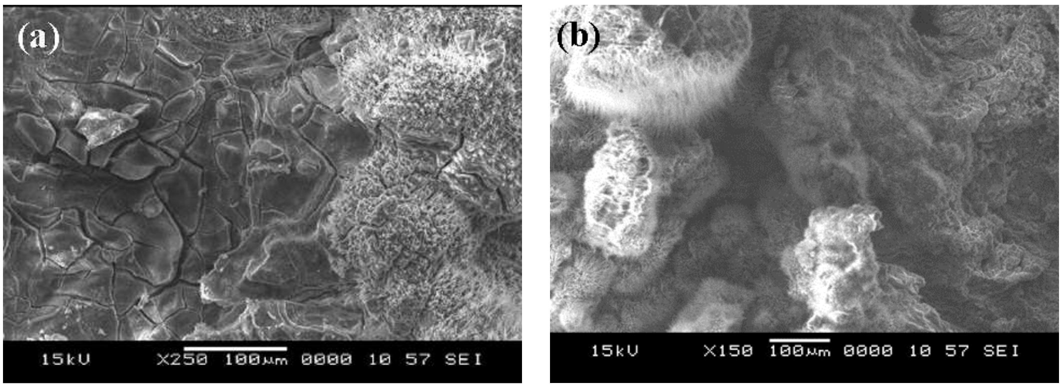


Fig. 6. SEM images of as-cast Mg-Ca samples immersed in SBF for 96 hrs; (a) 3 and (b) 4 % Ca content.

Electrochemical test. The result of the electrochemical test is derived from the potentiodynamic polarization curves are shown in Figs. 7a and b. As mentioned earlier, as the Ca content in the as-cast alloy increases, the volume percentage of Mg_2Ca phase increases, which enhanced the reactiveness of the alloy; therefore it suffers more corrosion reaction when immersed in SBF, as shown in Fig. 7a. In addition, as Fig. 7b illustrates, forging process accelerated the corrosion reaction of the Mg-1Ca alloy. This result is in disagreement with that reported by Z. Li et al. [8]. According to the results reported, hot working processes such as extrusion and hot rolling developed corrosion resistance of Mg–1Ca alloy in SBF. The increase in the corrosion rate of the forged sample may be attributed to the increase in grain boundaries; the active place in the microstructure. In addition, no other mechanism was observed based on the analyzed polarization curves of the samples. It should be added that forging speed did not show any considerable effect on the electrochemical properties of the forged samples.

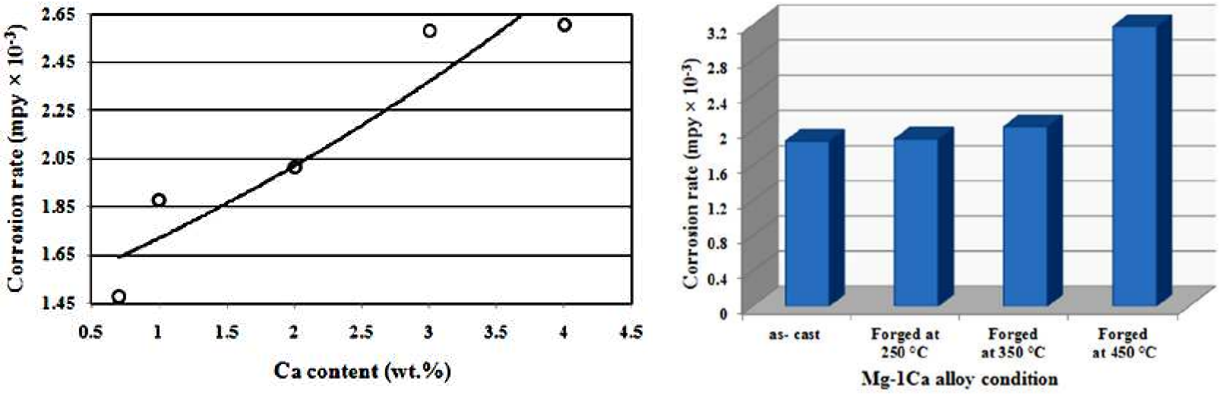


Fig. 7. Corrosion rate of (a) the as-cast Mg-Ca alloys with different Ca content and (b) the as-cast and forged Mg-1Ca alloy

Conclusion

The aim of the present study was to establish the characteristics of the as-cast and forged binary Mg-Ca alloys as biodegradable implant after immersing in Kokubo SBF. From the study, the following conclusion can be drawn:

(1) A refinement in grain size and an increase in volume fraction of Mg_2Ca precipitate were observed in the microstructure of Mg-Ca binary alloy when calcium content was increased.
(2) Increasing Ca content led to an increase in cathode/anode ratio which accelerated formation of bone-liked apatite during the immersion process in SBF due to higher corrosion rate.
(3) Increasing the forging temperature resulted in refined microstructure and increased in hydroxyapatite growth of Mg-1Ca alloy when immersed in the SBF.
(4) Forging temperature showed more pronounced effect on the properties of the Mg-1Ca alloy compared to forging speed.

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References

[1] C.M. Serre, M. Papillard, P. Chavassieux, J.C. Voegel and G. Boivin: J. Biomed. Mater. Res. Vol. 42 (1998), p. 626.
[2] Y.C. Li. M.H. Li, W.Y. Hu, P.D. Hodgson and C.E. wen: Mater. Sci.Forum Vol. 654-656 (2010), p. 2192.
[3] K. Feser, M. Kietzman, W. Bäumer, C. Krause and F.W. Bach: J. Biomater. Appl. Vol. 25 (2011), p. 685.
[4]. F. Witte, V. Kaese, H. Haferkamp, E. Switzer, A. Meyer-Lindenberg, C.J. Wirth and H. Windhagan: Biomaterials Vol. 26(2005), p. 3557.
[5] Z. Chun-yan, Z. Rong-chang, C. Rong-shi, L. Cheng-long, G. Jia-cheng: Trans. Nonferrous Met. Soc. China Vol. 20 (2010), p. s655.
[6] S.E. Harandi, M.H. Idris and H. Jafari: Mater. Design Vol. 32 (2011), p. 2596.
[7] B. Denkena, F. Witte, C. Podolsky and A. Lucas, in: Proc. of 5th Euspen International Conference, Montpellier, France (2005).
[8] Z. Li, X. Gu, S. Lou and Y. Zheng: J. Biomater. Vol. 29 (2008), p. 1329.
[9] Z. Zhi-min, X. Hong-yan, W. Qiang: Trans. Nonferrous Met. Soc. China Vol. 18 (2008), p. s140.
[10] H. E. kim, J.H. Jo, S.B. Kim, U.S. Patent application 20,100,305,684 (2010)
[11] B. Denkena, L. de Leon and A. Lucas, In: Proc. ofWorld Congress on Medical Physics and Biomedical Engineering, Vol. 25 (2010), p. 977.
[12] D. Poerschke: The Effects of forging on the microstructure and tensile properties of magnesium alloys AZ31 and ZK60, Case Western Reserve University, Cleveland, OH, USA (2009)
[13] Y.W. Chang, N.J. Kim and C.S. Lee: Adv. Mater. Res. Vol. 26-28 (2007), p. 437.
[14] E. Zhang and L. Yang: J. Mater. Sci. Eng. A Vol. 497 (2008), p. 111.
[15] S. Jalota, S.B. Bhaduri and A.C. Tas: Mater. Sci. Eng. C Vol. 28 (2008), p. 129.
[16] X. Gu, Y. Zheng, S. Zhong, T. Xi, J. Wang and W. Wang: J. Biomater. Vol. 31(2010), p. 1093.
[17] Y. Song, D. Shan, R. Chen, F. Zhang and EH. Han. J. Mater. Sci. Eng. C Vol. 29 (2009), p. 1039.
[18] R.K. Singh Raman. Metall. Mater. Trans. A Vol. 35 (2004), p. 2525.