Selective Leaching and Surface Properties of Cu–Al–Ni Shape Memory Alloys

Shih-Hang Chang^{*1}, Chin Kuo^{*2} and Jin-Lin Han

Department of Chemical and Materials Engineering, National I-Lan University, I-Lan 260, Taiwan

This study investigated the selective leaching, chemical compositions, and electrochemical properties of Cu–XAl–4Ni (X = 12.5, 13.0, and 13.5) shape memory alloys (SMAs). The selective leaching results showed that the Cu–XAl–4Ni SMAs released approximately 200 ppb of Cu ions, 200 ppb of Al ions, and 600 ppb of Ni ions after immersion in Ringer's solution for 90 days. The low concentrations of Cu and Al ions stem from the oxidation of Cu and Al atoms near the surface of the Cu–XAl–4Ni SMAs to form Cu₂O and Al₂O₃ films. The selective leaching properties of the Cu–XAl–4Ni SMAs were inferior to that of the TiNi SMA, which possessed a highly passive TiO₂ film on the surface, but were much better than those of the TiNiCu and TiNiFe SMAs, whose TiO₂ films were deteriorated by the formation of NiO, Cu₂O, and Fe₂O₃ oxides. Cu–XAl–4Ni SMAs are potential candidates to serve as biomaterials, owing to their acceptable surface and selective leaching properties, high martensitic transformation temperatures, low cost, good machinability, and excellent electric and thermal conductivities.

[doi:10.2320/matertrans.M2017287]

(Received September 21, 2017; Accepted February 15, 2018; Published April 25, 2018)

Keywords: Cu–Al–Ni shape memory alloys, biomaterials, selective leaching, X-ray photoelectron spectroscopy

1. Introduction

Nickel–titanium shape memory alloys (TiNi SMAs) have been widely investigated owing to their unique shape memory effect, superelasticity, and good damping capacity.¹⁾ TiNi SMAs typically exhibit low cytotoxicity and low genotoxicity,^{2–4)} and therefore are suitable for biomedical applications such as laparoscopic surgery, intracoronary stents, ligament replacement, endodontic instruments, and osteosynthesis devices.^{5–8)} However, long-term interactions between TiNi SMAs and living tissues may cause the release of nickel ions,⁹⁾ which may induce undesirable allergy or cancer.^{10,11)} The selective leaching characteristics of TiNi-based SMAs have been widely investigated.^{12–19)} Chu *et al.*^{12–14)} reported that the surface properties of TiNi SMAs oxidized using boiling H₂O₂ solution and a UV/H₂O₂ photocatalytic system could notably suppress Ni ion release and improve the biocompatibility of the alloys. Gil *et al.*^{15–17)} studied the Ni release behaviors of TiNi orthodontic archwires and reported that the titanium oxide on their surface significantly improves the corrosion resistance and decreases the Ni ion release of the alloys. Chang *et al.*^{18,19)} reported that TiNiCu and TiNiFe SMAs exhibited higher selective leaching rates of Ni ions compared to that of TiNi SMA.

Compared with TiNi SMAs, Cu–Al–Ni SMAs also exhibit a good shape memory effect, superelasticity and damping capacity, but possess the advantages of lower cost, better workability, superior thermal and electrical conductivities, and more easily obtainable desirable martensitic transformation temperatures by adjustment of the chemical composition of the alloys.^{20–27)} Nevertheless, only a few studies have investigated the feasibility of biomedical applications of Cu–Al–Ni SMAs. Čolić *et al.*^{28–30)} reported via an *in vitro* investigation that rapidly solidified Cu–Al–Ni SMA ribbons possessed good corrosion resistance, cytotoxicity, and biocompatibility. Chang *et al.*³¹⁾ investigated the toxicity of Cu–Al–Ni SMAs for *Escherichia coli* using a probit dose-response model and augmented

simplex design. According to their study, high concentrations of Al and Ni ions inhibited the growth of *Escherichia coli*; however, the toxicity of Cu ion was found to be chronic, rather than acute. Moreover, the surface properties and the selective leaching behaviors of Cu–Al–Ni SMAs have not been studied in detail. Therefore, the aim of this study is to investigate the surface properties and concentrations of the Cu, Al, and Ni ions released from Cu–XAl–4Ni (X = 12.5, 13.0, and 13.5) SMAs immersed in Ringer's solution. Ringer's solution was used in this study because it is an isotonic solution similar to bodily fluid, which is widely used in *in vitro* experiments. Cu–XAl–4Ni (X = 12.5, 13.0, and 13.5) SMAs were selected for this study because they typically exhibit a more significant $\beta_1 \leftrightarrow \beta'_1$ martensitic transformation at a higher temperature than the $\beta_1 \leftrightarrow \gamma'_1$ martensitic transformation of Cu–XAl–4Ni SMAs with X > 14.0.²⁴⁾ Moreover, γ_2 phase typically precipitated on the surface of Cu–XAl–4Ni SMAs with X > 14.0, which may deteriorate the surface property of the alloys.^{23,24,32)}

2. Experimental Procedures

The Cu–XAl–4Ni (X = 12.5, 13.0, and 13.5) SMAs were prepared from pure raw materials of copper (purity 99.9 wt.%), aluminum (purity 99.99 wt.%), and nickel (purity 99.9 wt.%). The raw materials were melted at 1100°C in evacuated quartz followed by quenching in ice water. The quenched ingots were annealed at 900°C for 30 min and then cooled in the furnace to room temperature. The crystallographic features of the Cu–XAl–4Ni SMAs were determined using a Rigaku IV X-ray diffraction (XRD) instrument with Cu K α radiation ($\lambda = 0.154$ nm). Microstructural observations of the Cu–XAl–4Ni SMAs were performed using a Tescan 5136MM scanning electron microscope (SEM). The surface of each specimen was mechanically polished by sand papers followed by etching with a solution composed of 2.5 g FeCl₃·6H₂O and 10 ml HCl in 48 ml methanol for approximately 4 min. The martensitic transformation behaviors of the Cu–XAl–4Ni SMAs were determined using a TA Q10 differential scanning calorimeter (DSC) under a constant cooling/heating rate of

^{*1}Corresponding author, E-mail: shchang@niu.edu.tw

^{*2}Graduate Student, National I-Lan University

Table 1 The chemical composition of the Ringer's solution.

Constituent	g/l
NaCl	8.6
KCl	0.3
CaCl ₂ ·2H ₂ O	0.33
H ₂ O	Balance

10°C/min. The cathodic and anodic polarization Tafel curves of the Cu–XAl–4Ni SMAs were analyzed using a Jiehan ECW-5600 electrochemical workstation, in which a platinum plate was used as the counter electrode, a saturated calomel electrode was used as the reference electrode, and Ringer's solution was used as the test solution, to calculate the average corrosion potential (E_{corr}) and average corrosion current density (i_{corr}) values of each specimen. The chemical composition of the Ringer's solution is listed in Table 1. The surface chemical compositions of the Cu–XAl–4Ni SMAs were determined using Thermo Scientific (VGS) K-Alpha X-ray photoelectron spectroscopy (XPS) with a monochromatic Al K α radiation source of 1468.6 eV. The survey spectrum of each specimen was measured over a range of 0 to 1200 eV in 1 eV steps. High-resolution Cu, Al, and Ni 2p spectra for each specimen were determined in 0.05 eV steps. The selective leaching properties of the Cu–XAl–4Ni SMAs were evaluated by immersing the Cu–XAl–4Ni SMAs in test flasks containing 500 mL of Ringer's solution. Each test flask was maintained at 37°C in an orbital shaker incubator for 90 days. The concentrations of the Cu, Al, and Ni ions released from the Cu–XAl–4Ni SMAs were determined using an Agilent 7500ce inductively coupled plasma mass spectrometer (ICP-MS).

3. Results

3.1 XRD and SEM results

Figure 1(a) presents the XRD results of the Cu–13.5Al–4Ni SMA. Figure 1(a) reveals that the Cu–13.5Al–4Ni SMA exhibited (110), (112), (022), (122), (202), (0018), (128), (208), and (1210) diffraction peaks of β'_1 martensite phase at approximately $2\theta = 26.2^\circ$, 26.8° , 33.7° , 39.6° , 40.9° , 42.6° , 44.4° , 44.9° , and 45.8° , respectively.³³⁾ According to Fig. 1(a), the Cu–13.5Al–4Ni SMA was typical β'_1 martensite with an 18R structure at room temperature. The β'_1 (18R) martensite phase has an ordered 9R structure with stacking faults. The β'_1 martensite phase is labeled as 18R because the unit cell of this structure in orthorhombic coordinates consist of 18 layers. Monoclinic distortion takes place in some cases and the 18R structure is slightly distorted from an orthorhombic cell to a monoclinic and modified as M18R.³⁴⁾ Therefore, both three-index and four-index axes are used in Fig. 1(a). Figure 1(b) shows a SEM microstructure image of the Cu–13.5Al–4Ni SMA. As shown in Fig. 1(b), the surface of the Cu–13.5Al–4Ni SMA exhibited obvious self-accommodating zigzag groups of martensite variants. This feature also demonstrates that the Cu–13.5Al–4Ni SMA

Fig. 1 (a) XRD pattern and (b) SEM image of the Cu–13.5Al–4Ni SMA.

Fig. 2 DSC curves of the Cu–12.5Al–4Ni, Cu–13.0Al–4Ni, and Cu–13.5Al–4Ni SMAs.

was in a β'_1 (18R) martensite phase at room temperature.^{24,29)} The XRD and SEM results of the Cu–13.0Al–4Ni and Cu–12.5Al–4Ni SMAs are not presented here, because they are very similar to those of the Cu–13.5Al–4Ni SMA.

3.2 DSC results

Figure 2 shows the DSC curves for the Cu–12.5Al–4Ni, Cu–13.0Al–4Ni, and Cu–13.5Al–4Ni SMAs. Figure 2 reveals that the Cu–13.0Al–4Ni and Cu–13.5Al–4Ni both exhibit $\beta_1(\text{DO}_3) \rightarrow \beta'_1(18\text{R})$ and $\beta'_1(18\text{R}) \rightarrow \beta_1(\text{DO}_3)$ martensitic transformations in cooling and heating,

respectively. The martensitic starting (M_s) temperatures for the Cu–13.0Al–4Ni and Cu–13.5Al–4Ni SMAs were determined as 180.9°C and 153.7°C, respectively. Figure 2 also shows that the transformation enthalpies (ΔH) for the Cu–13.0Al–4Ni and Cu–13.5Al–4Ni SMAs were both determined as approximately 10 J/g. However, the Cu–12.5Al–4Ni SMA did not show any martensitic transformation peak in Fig. 2. This is because the martensitic transformation temperatures of the Cu–12.5Al–4Ni SMA was beyond the upper temperature limit of the DSC instrument (250°C). According to the DSC results, we could ensure that the Cu–12.5Al–4Ni, Cu–13.0Al–4Ni, and Cu–13.5Al–4Ni SMAs were all in the same β'_1 (18R) martensite phase when they were subjected to the electrochemical, XPS, and selective leaching measurements.

3.3 Electrochemical properties

Figures 3(a) to 3(c) plot the cathodic and anodic polarization Tafel curves of the Cu–12.5Al–4Ni, Cu–13.0Al–4Ni, and Cu–13.5Al–4Ni SMAs, respectively. The potential was measured versus saturated calomel electrode (vs. SCE), in which the electrode potential of SCE is +0.244 V vs. standard hydrogen electrode (SHE) at 25°C. According to Tafel curves, the E_{corr} values for the Cu–12.5Al–4Ni, Cu–13.0Al–4Ni, and Cu–13.5Al–4Ni SMAs were calculated as -0.193 ± 0.007 , -0.205 ± 0.006 , and -0.204 ± 0.004 V, respectively. Moreover, the i_{corr} values for the Cu–12.5Al–4Ni, Cu–13.0Al–4Ni, and Cu–13.5Al–4Ni SMAs were calculated as $(9.31 \pm 0.489) \times 10^{-6}$, $(8.54 \pm 0.468) \times 10^{-6}$, and $(12.2 \pm 0.796) \times 10^{-6}$ A/cm², respectively. Compared with our previous studies,^{18,19} the E_{corr} values for the Cu–XAl–4Ni SMAs (approximately –0.2 V) are slightly higher than those of the Ti₅₀Ni₅₀ (approximately –0.496 V), Ti₅₀Ni_{50–x}Cu_x (from –0.330 to –0.416 V), and Ti₅₀Ni_{50–x}Fe_x (from –0.379 to –0.433 V) SMAs. However, the i_{corr} values for the Cu–XAl–4Ni SMAs (approximately 10×10^{-6} A/cm²) are also higher than those of the Ti₅₀Ni₅₀ (approximately 7.57×10^{-7} A/cm²), Ti₅₀Ni_{50–x}Cu_x (from 2.43×10^{-7} to 4.13×10^{-7} A/cm²), and Ti₅₀Ni_{50–x}Fe_x (from 3.27×10^{-7} to 5.52×10^{-6} A/cm²) SMAs. This indicates that the corrosion rates of the Cu–XAl–4Ni SMAs in Ringer's solution are relatively higher than those of the TiNi-based SMAs. This feature may correspond to the fact that the Cu–XAl–4Ni SMAs were in the β'_1 (18R) martensite phase, which exhibited a rough surface due to the surface relief phenomenon (Fig. 1(b)), when subjected to the electrochemical measurement. On the contrary, the Ti₅₀Ni₅₀, Ti₅₀Ni_{50–x}Cu_x, and Ti₅₀Ni_{50–x}Fe_x SMAs were in the B2 parent phase with a smooth surface.

3.4 X-ray photoelectron spectroscopy

Figures 4(a) to 4(d) show the XPS survey, Cu 2p, Al 2p, and Ni 2p spectra, respectively, of the surfaces of the Cu–13.5Al–4Ni SMA. Only the XPS results of the Cu–13.5Al–4Ni SMA are shown here because those of the Cu–12.5Al–4Ni and Cu–13.0Al–4Ni SMAs are almost identical to them. According to Fig. 4(a), the Cu–13.5Al–4Ni SMA showed significant characteristic peaks associated with Cu, Al, O, and contamination C in the XPS survey spectrum. Figure 5(b) shows that the Cu 2p characteristic peaks of the Cu–13.5Al–

(a) Cu–12.5Al–4Ni SMA

(b) Cu–13.0Al–4Ni SMA

(c) Cu–13.5Al–4Ni SMA

Fig. 3 Cathodic and anodic polarization Tafel curves for the (a) Cu–12.5Al–4Ni, (b) Cu–13.0Al–4Ni, and (c) Cu–13.5Al–4Ni SMAs.

4Ni SMA can be deconvoluted into a Cu₂O 2p_{3/2} peak at 932.7 eV and a Cu₂O 2p_{1/2} peak at 952.5 eV. Figure 5(c) shows that the Al 2p characteristic peaks of the Cu–13.5Al–4Ni SMA can be deconvoluted into an Al₂O₃ 2p_{3/2} peak at 77.3 eV and an Al₂O₃ 2p peak at 75.0 eV. Unexpectedly, as shown in Fig. 5(d), no Ni characteristic peak was obtained. According to Fig. 5, we can conclude that the surfaces of the Cu–13.5Al–4Ni SMA were dominantly composed of Cu₂O and Al₂O₃ oxide layers. The NiO oxide layer, which was normally observed on the surface of TiNi-based SMAs,^{18,19} was not observed on the surface of the Cu–XAl–4Ni SMAs.

Fig. 4 XPS (a) survey spectrum, (b) Cu 2p spectrum, (c) Al 2p spectrum, and (d) Ni 2p spectrum of the surfaces of the Cu-13.5Al-4Ni SMA.

3.5 Selective leaching behaviors

Figures 5(a) to 5(c) show the concentrations of Cu, Al, and Ni ions, respectively, which were selectively leached from the Cu-XAl-4Ni ($X = 12.5, 13.0$, and 13.5) SMAs immersed in Ringer's solution, as a function of immersion time. Figure 5(a) shows that the concentrations of Cu ions selectively leached from the specimens are approximately 200 ppb after 90 days. The selective leaching behaviors of the Cu-XAl-4Ni SMAs do not show significant difference. Figure 5(b) shows that the concentrations of Al ions selectively leached from the specimens are below 200 ppb after 90 days. Figure 5(c) shows that the concentrations of Ni ions selectively leached from the Cu-XAl-4Ni SMAs gradually increased with the immersion time and approach greater than 600 ppb after 90 days. As shown in Fig. 5, the selective leaching behaviors of the Cu, Al, and Ni ions for the Cu-12.5Al-4Ni, Cu-13.0Al-4Ni, and Cu-13.5Al-4Ni SMAs did not show significant differences. Moreover, Fig. 5 also reveals that the selective leaching rate of Ni ions from the Cu-XAl-4Ni SMAs is much higher than those of Cu and Al ions, even though the weight percentage of Ni atoms is only approximately 4 wt.%, which is much lower than those of Cu and Al atoms in the Cu-XAl-4Ni SMAs. Compared with our previous studies,^{18,19)} the concentrations of the Ni ions selectively leached from the Cu-XAl-4Ni SMAs

(approximately 600 ppb after 90 days) are much higher than that of the Ti₅₀Ni₅₀ SMA (approximately 25 ppb after 30 days), but are much lower than those of the Ti₅₀Ni_{50-x}Cu_x (approximately 2500 ppb after 30 days) and Ti₅₀Ni_{50-x}Fe_x (above 1500 ppb after 80 days) SMAs. Moreover, the concentrations of the Cu ions selectively leached from the Cu-XAl-4Ni SMAs (approximately 200 ppb after 90 days) are also much lower than that of the Ti₅₀Ni₄₅Cu₅ SMA (above 800 ppb after 30 days), even though the weight percentage of Cu atoms is above 80% for the Cu-XAl-4Ni SMAs.

4. Discussion

According to the selective leaching measurement results shown in Fig. 5, there are approximately 200 ppb of Cu ions, 200 ppb of Al ions, and 600 ppb of Ni ions released from the Cu-XAl-4Ni SMAs after immersion in Ringer's solution for 90 days. The concentrations of Ni ions after selective leaching from the Cu-XAl-4Ni SMAs are much higher than those of Cu and Al ions, indicating that the Ni ions are more easily leached from the surface of the Cu-XAl-4Ni SMAs than the Cu and Al ions, even though the weight percentage of Ni atoms was only 4 wt.% for each specimen. This feature corresponds to the fact that the Cu and Al atoms near the surface were oxidized to become Cu₂O and Al₂O₃ films on

Fig. 5 Concentrations of the (a) Cu, (b) Al, and (c) Ni ions selectively leached from the Cu–12.5Al–4Ni, Cu–13.0Al–4Ni, and Cu–13.5Al–4Ni SMAs.

the surface of the Cu–XAl–4Ni SMAs, as demonstrated by the XPS results shown in Fig. 5, which inhibited the selective leaching of the Cu and Al atoms.

Compared with the selective leaching results of the Ti₅₀Ni₅₀ SMA reported previously,¹⁸⁾ the concentrations of the released Cu, Al, and Ni ions from the Cu–XAl–4Ni SMAs are much higher than those of the Ti and Ni ions released from the Ti₅₀Ni₅₀ SMA, which were both below 25 ppb after 30 days. The extremely low concentrations of Ti and Ni ions selectively leached from the Ti₅₀Ni₅₀ SMAs is attributed to the good corrosion resistance and protection of

the highly passive TiO₂ film formed on the surface. However, the main shortcoming of the Ti₅₀Ni₅₀ SMAs is that their martensitic transformation temperatures are typically low and difficult to control, which severely limits their practical biomedical applications. Substituting Cu or Fe for Ni in the Ti₅₀Ni₅₀ SMA could effectively increase the martensitic transformation temperature and the mechanical properties of the Ti₅₀Ni₅₀ SMAs. Unfortunately, the concentrations of Ni ions selectively leached from the Ti₅₀Ni_{50–x}Cu_x SMAs (approximately 2500 ppb after 30 days) and the Ti₅₀Ni_{50–x}Fe_x SMAs (above 1500 ppb after 80 days) were simultaneously significantly increased.^{18,19)} This is because the uniformity and protection of the highly passive TiO₂ films were deteriorated by the formation of NiO, Cu₂O, and Fe₂O₃ oxides on the surface of the Ti₅₀Ni_{50–x}Cu_x and Ti₅₀Ni_{50–x}Fe_x SMAs.

From the results of this study, the selective leaching property of the Cu–XAl–4Ni SMAs are not as good as that of the Ti₅₀Ni₅₀ SMA, but are still far superior to those of the Ti₅₀Ni_{50–x}Cu_x and Ti₅₀Ni_{50–x}Fe_x SMAs. Moreover, the Cu–XAl–4Ni SMAs also possess the advantages of low cost, good workability, exceptional electrical and thermal conductivities, and easily obtainable wide range of martensitic transformation temperatures by precise adjustment of the chemical compositions of the Cu–XAl–4Ni SMAs. Owing to these benefits, the Cu–XAl–4Ni SMAs are potential candidates for biomaterial applications. Nevertheless, considering the mediocre corrosion resistance of the Cu–XAl–4Ni SMAs, appropriate surface modifications would be required for them to be considered for use as long-term implants in human bodies. For example, surface modifications using bioactive coating materials, including hexamethyldisilazane, calcium phosphate, bioactive glass, chitosan, or some kinds of polymers which are also non-toxicity and exhibit good biocompatibility and antifungal activity.

5. Conclusions

This study investigated the selective leaching and surface properties of the Cu–XAl–4Ni (X = 12.5, 13.0, and 13.5) SMAs. The SEM, XRD, and DSC results all demonstrated that the Cu–XAl–4Ni SMAs were in a β'_1 (18R) martensite phase during the selective leaching tests. The electrochemical tests revealed that the E_{corr} and i_{corr} values for Cu–XAl–4Ni SMAs are approximately -0.2 V and 10×10^{-6} A/cm², respectively. The XPS results showed that the surface of Cu–XAl–4Ni SMAs was primarily comprised of Cu₂O and Al₂O₃ films. The ICP-MS results indicated that the concentrations of Ni ions selectively leached from Cu–XAl–4Ni SMAs were higher than those of Cu and Al ions. The surface and selective leaching properties of the Cu–XAl–4Ni SMAs were inferior to those of the Ti₅₀Ni₅₀ SMA, but were much better than those of the Ti₅₀Ni_{50–x}Cu_x and Ti₅₀Ni_{50–x}Fe_x SMAs. The Cu–XAl–4Ni SMAs remain potential candidates for biomedical applications because of their irreplaceable higher martensitic transformation temperatures, lower cost, higher electrical and thermal conductivities, and better machinability compared to the TiNi-based SMAs.

Acknowledgements

The authors gratefully acknowledge the financial support provided by the Ministry of Science and Technology (MOST), Taiwan, under Grant No. MOST 104-2221-E-197-004-MY3.

REFERENCES

- 1) K. Otsuka and X. Ren: *Prog. Mater. Sci.* **50** (2005) 511–678.
- 2) M. Assad, N. Lemieux, C.H. Rivard and L.H. Yahia: *Biomed. Mater. Eng.* **9** (1999) 1–12.
- 3) M. Es-Souni, M. Es-Souni and H. Fischer-Brandies: *Anal. Bioanal. Chem.* **381** (2005) 557–567.
- 4) M. Assad, A. Chernyshov, M.A. Leroux and C.H. Rivard: *Biomed. Mater. Eng.* **12** (2002) 225–237.
- 5) P. Filip, J. Lausmaa, J. Musialek and K. Mazanec: *Biomaterials* **22** (2001) 2131–2138.
- 6) Y. Oshida, R.C.L. Sachdeva and S. Miyazaki: *Biomed. Mater. Eng.* **2** (1992) 51–69.
- 7) J.Y. Xiong, Y.C. Li, X.J. Wang, P.D. Hodgson and C.E. Wen: *J. Mech. Behav. Biomed. Mater.* **1** (2008) 269–273.
- 8) S.A. Shabalovskaya: *Biomed. Mater. Eng.* **6** (1996) 267–289.
- 9) F.El. Feninat, G. Laroche, M. Fiset and D. Mantovani: *Adv. Eng. Mater.* **4** (2002) 91–104.
- 10) H. Takahashi, M. Kinbara, N. Sato, K. Sasaki, S. Sugawara and Y. Endo: *Int. Immunopharmacol.* **11** (2011) 1534–1540.
- 11) V. D'Antò, A. Eckhardt, K.A. Hiller, G. Spagnuolo, R. Valletta, L. Ambrosio, G. Schmalz and H. Schweikl: *Biomaterials* **30** (2009) 1492–1501.
- 12) C.L. Chu, C.Y. Chung and P.K. Chu: *Mater. Sci. Eng. A* **417** (2006) 104–109.
- 13) R.M. Wang, C.L. Chu, T. Hu, Y.S. Dong, C. Guo, X.B. Sheng, P.H. Lin, C.Y. Chung and P.K. Chu: *Appl. Surf. Sci.* **253** (2007) 8507–8512.
- 14) C.L. Chu, C. Guo, X.B. Sheng, Y.S. Dong, P.H. Lin, K.W.K. Yeung and P.K. Chu: *Acta Biomater.* **5** (2009) 2238–2245.
- 15) E. Espinar, J.M. Llamas, A. Michiardi, M.P. Ginebra and F.J. Gil: *J. Mater. Sci. Mater. Med.* **22** (2011) 1119–1125.
- 16) C. Abalos, A. Paül, A. Endoza, E. Solano and F.J. Gil: *J. Mater. Sci. Mater. Med.* **22** (2011) 2813–2821.
- 17) F.J. Gil, E. Espinar, J.M. Llamas, J.M. Manero and M.P. Ginebra: *J. Mech. Behav. Biomed. Mater.* **6** (2012) 113–119.
- 18) S.H. Chang and W.C. Chiu: *Appl. Surf. Sci.* **324** (2015) 106–113.
- 19) S.H. Chang, J.S. Liou and B.Y. Huang: *Mater. Tehnol.* **51** (2017) 251–257.
- 20) H. Scherngell and A.C. Kneissl: *Acta Mater.* **50** (2002) 327–341.
- 21) S.H. Chang: *Mater. Lett.* **64** (2010) 93–95.
- 22) G. Lojen, M. Gojić and I. Anžel: *J. Alloys Compd.* **580** (2013) 497–505.
- 23) N. Suresh and U. Ramamurty: *J. Alloys Compd.* **449** (2008) 113–118.
- 24) S.H. Chang: *Mater. Chem. Phys.* **125** (2011) 358–363.
- 25) H. Kato, R. Stalmans and J. Van Humbeeck: *Mater. Trans.* **39** (1998) 378–386.
- 26) C. Picornell, J. Pons and E. Cesari: *Mater. Trans.* **45** (2004) 1679–1683.
- 27) Y. Nakata, Y. Iizuka and T. Ono: *Mater. Trans.* **57** (2016) 257–262.
- 28) M. Čolić, R. Rudolf, D. Stamenković, I. Anžel, D. Vučević, M. Jenko, V. Lazić and G. Lojen: *Acta Biomater.* **6** (2010) 308–317.
- 29) M. Čolić, S. Tomić, R. Rudolf, I. Anžel and G. Lojen: *J. Biomater. Appl.* **25** (2010) 269–286.
- 30) R. Rudolf, K. Mehrabi, A.C. Kneissl, M. Bruncko, I. Anžel, S. Tomić, T. Džopalic and M. Čolić: *Int. J. Immunol. Stud.* **1** (2010) 214–228.
- 31) S.H. Chang, B.Y. Chen and J.X. Lin: *J. Appl. Biomater. Funct. Mater.* **14** (2016) e59–e64.
- 32) N. Zárubová, A. Gemperle and V. Novak: *Mater. Sci. Eng. A* **222** (1997) 166–174.
- 33) R. Zengin and M. Ceylan: *Mater. Lett.* **58** (2004) 55–59.
- 34) U. Sari and İ. Aksoy: *J. Alloys Compd.* **417** (2006) 138–142.