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Biomimetic deposition process of an apatite coating on NiTi shape memory alloy

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Abstract

Biomimetic deposition process of an apatite coating on NiTi shape memory alloy (SMA) after it was pretreated with 30% H_2O_2 solution and subsequently 1 M NaOH solution was studied using a simulated body fluid (SBF) soaking test. Biomimetic nucleation of apatite on the chemically pretreated NiTi SMA has a short induction period down to 6 h. With longer soaking time, more apatite appeared on the NiTi substrate but our control experiments did not reveal any apatite formation on the chemically polished NiTi SMA. After immersion in SBF for 48 h, the chemically pretreated NiTi SMA was fully covered with a dense hydroxyapatite coating. The biomimetic deposition of the apatite coating was attributed to the catalytic effect of abundant Ti–OH groups and Na_2TiO_3 on the surface of the chemically pretreated NiTi SMA.

Keywords: NiTi; Shape memory alloys (SMA); Apatite coating; Biomimetic deposition

1. Introduction

Biomimetic deposition is an ideal method to produce calcium phosphate ceramic such as apatite coatings on titanium and its alloys for medical applications [1–4]. It has also been proven that the chemical pretreatment in alkali solution can improve the bonding between titanium substrate and calcium phosphate coatings fabricated by the subsequent biomimetic deposition in simulated body fluid (SBF) [5–13]. Treatment with alkali solution produces a titanate layer containing alkali ions on titanium surface, which has the ability to induce the deposition of calcium phosphate ceramics in vitro or in vivo and thus are considered bioactive [1–13]. Chen et al. [14,15] reported that bioactive NiTi shape memory alloy (SMA) could also be obtained by NaOH treatment. NiTi SMA with unique shape memory effect and superelastic properties has been frequently used as biomedical applications [16–19]. Note the fact that NiTi SMA contains a large amount of Ni, which can lead to the allergic and toxic responses [20,21]. Therefore, the biomimetic deposition of calcium phosphate coating can make NiTi implants be used in medicine more safely and widely.

Recently, Choi et al. [22], and Bogdanski et al. [23] used the biomimetic deposition method introduced by Kokubo, van Blitterswijk, de Groot and others [1–4] to fabricate an ideal calcium phosphate coating on NiTi SMA. However, their studies mainly focused on the microstructural characteristics responsible for shape memory effect and the biocompatibility of this calcium phosphate coating on NiTi SMA. Up to now, there have not been systematical investigations on the biomimetic deposition process of calcium phosphate coating on NiTi substrates in SBF. In this work, NiTi SMA was firstly oxidized in 30% H_2O_2 solution and subsequently treated in 1 M NaOH solution. Then the biomimetic deposition process of an apatite coating on the chemically pretreated NiTi substrate was investigated using a simulated body fluid (SBF) soaking test and discussed.

2. Experimental procedure

A commercially available NiTi (50.8 at.% Ni) SMA plate for medical applications with a martensite start temperature (M_s) of −12.8 °C and an austenite finish temperature (A_f) of 33.4 °C

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was cut into small rectangular blocks (10 × 10 × 1 mm^3). All samples were chemically polished to remove native surface oxides for 10 min in Kroll's reagent: a mixture of 2 ml hydrofluoric acid (HF, 40%), 4 ml nitric acid (HNO_3, 40%) and 994 ml deionized water (denoted as the chemically polished NiTi SMA). The chemically polished samples were subsequently oxidized in a boiling aqueous solution containing 30% H_2O_2 for 2 h (denoted as the H_2O_2-oxidized NiTi SMA) and ultrasonically rinsed again with deionized water for 10 min. Then the H_2O_2-oxidized NiTi SMA was treated in 1 M NaOH aqueous solution at 60 °C for 24 h (denoted as the chemically pretreated NiTi SMA). After being ultrasonically washed in acetone and rinsed again in deionized water, the chemically pretreated NiTi SMA and the chemically polished one were soaked in SBF for different times to investigate the biomimetic deposition process of an apatite coating. The SBF solution was buffered at pH 7.4 with trimethanol aminomethane-HCl. The ionic concentrations in the SBF solution are nearly equal to those in human body blood plasma and are (mM): Na^+ 142.0, K^+ 5.0, Ca^{2+} 2.5, Mg^{2+} 1.5, HCO_3^- 4.2, Cl^- 148.5, HPO_4^{2-} 1.0 and SO_4^{2-} 0.5 [24]. The SBF solution was not replenished during the soaking procedure.

The XRD patterns were taken with an X-ray diffractometer (RAD IIA, Rigaku, Japan) operated with Cu Kα under 40 kV and 25 mA, equipped with a thin-film attachment on which the glancing angle was 1°. Samples were XPS analyzed using a VG Scientific ESCALAB 5 spectrometer with monochromatic Al Kα (1486.6 eV) X-ray radiation. The operating vacuum conditions in the chamber were better than 10^{-8} mbar. High resolution XPS spectra over the Ti 2p and Ni 2p, O 1 s and Na 1 s ranges were recorded for each sample at 20 eV pass energy, and then were used for assessment of the chemical state as well as for quantification. FTIR spectra of the surfaces of the samples were recorded using FTIR spectrometry (Nicolet 800). Raman scattering spectra were recorded with a Renishaw system 2000 spectrometer, using the 514 nm line of Ar^+ for excitation. The light beam was focused to a spot of about 5 mm in size. The surface morphology of the samples was observed by a Philips XL30 FEG SEM at 20 kV accelerating voltage after the surfaces were coated with gold films.

3. Results and discussion

Fig. 1 shows SEM photographs of the surface of the chemically pretreated NiTi SMA in comparison with the chemically polished one and the H_2O_2-oxidized one. Many pores were observed on the surface of the chemically polished one (Fig. 1a) and the XPS element analysis (not shown here) indicates its surface concentration of oxygen is only about 7.9 at.%, which reveals that the native surface oxides on NiTi SMA have been removed successfully. After the chemically polished one was oxidized in H_2O_2 solution, an oxide film was formed on NiTi substrates as shown in Fig. 1b and the XRD patterns (Fig. 2a) show the poorly crystallized rutile and anatase titania phases (TiO_2) associated with the broadening peaks are present on the surface of the H_2O_2-oxidized one.

It can be found from Fig. 1c and d that the chemical pretreatment with 30% H_2O_2 solution and subsequently 1M NaOH solution resulted in the formation of a wormlike surface structure on NiTi substrate. The

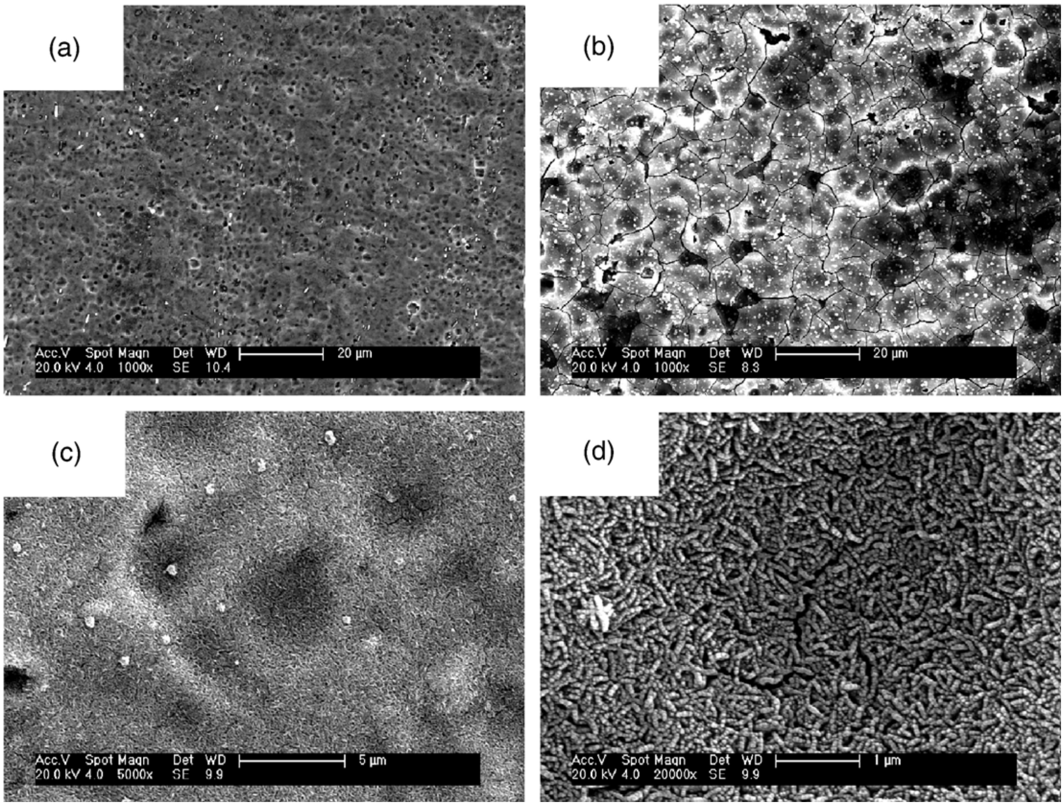

Fig. 1. SEM images of the surfaces of NiTi SMAs: (a) the chemically polished one; (b) the H_2O_2-oxidized one; (c) the chemically pretreated one; (d) high magnification of (c).

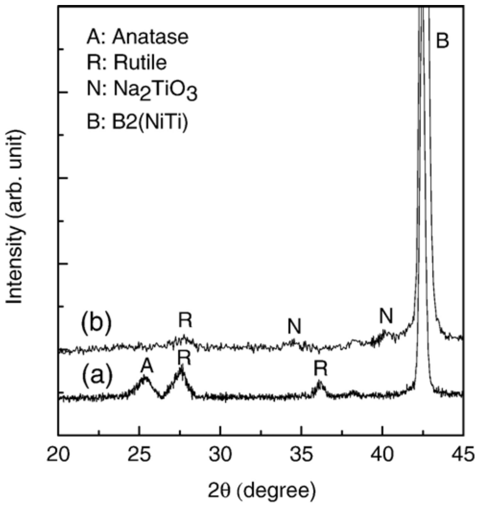

Fig. 2. XRD spectra of the surfaces of NiTi SMAs: (a) the H_2O_2-oxidized one; (b) the chemically pretreated one.

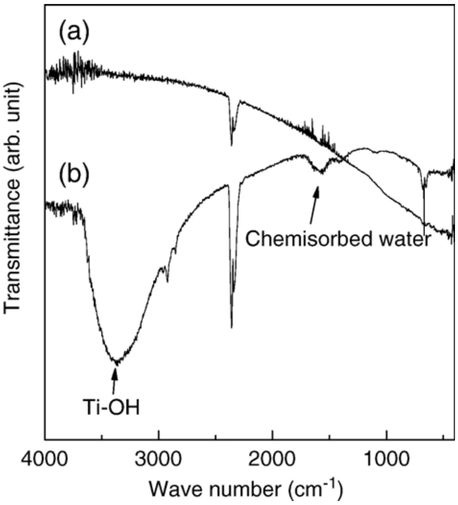

Fig. 4. FTIR spectra of the surfaces of NiTi SMAs: (a) the chemically polished one; (b) the chemically pretreated one.

XPS element analysis shows that the chemical composition of this wormlike surface layer on NiTi substrate was (at.%): Ti 32.64, Ni 5.66, O 58.52 and Na 3.18. As indicated by the XRD patterns in Fig. 2b, the wormlike surface layer on the chemically pretreated NiTi SMA is mainly comprised of sodium titanate (Na_2TiO_3) and TiO_2 phases. And its crystallinity is relatively low as indicated by the broadening XRD peaks with low intensities in Fig. 2b.

Fig. 3 shows Ti 2p and Ni 2p XPS spectra of the surface of the chemically pretreated NiTi SMA. It is seen that the Ti 2p XPS spectrum exhibits two dominant peaks, which have been identified as being Ti^{4+} (Ti–O) $2p_{3/2}$ at 459.3 eV and Ti^{4+} (Ti–O) $2p_{1/2}$ at 464.8 eV. The Ni 2p spectrum exhibits a small Ni^{3+} (Ni–O) $2p_{3/2}$ peak at 856.2 eV besides two other peaks corresponding to $Ni^{Ni–Ti}$ $2p_{3/2}$ at 853.8 eV and $Ni^{Ni–Ti}$ $2p_{1/2}$ at 870.5 eV in intermetallic NiTi state [25], which indicates a trace of Ni_2O_3 was also found although its amount is too little to be detected by XRD (Fig. 2b). Moreover, the $Ni^{Ni–Ti}$ 2p spectrum shows an evident satellite structure, which is separated from the main peaks by ~7 eV [26].

The results of the FTIR spectroscopic measurements are shown in Fig. 4. In comparison with the spectrum of the surface of the chemically polished one, the one for the chemically pretreated NiTi SMA have some additional bands, e.g. the broad OH^- stretching bands from 3700 to 2500 cm^{-1} deriving from Ti–OH groups and the band at 1625 cm^{-1} corresponding to the bending mode of chemisorbed water [27,28].

Fig. 5 shows SEM images of the apatite coating deposited on the chemically pretreated NiTi SMA in SBF after different times. After immersion in SBF for 6 h, apatite was observed to nucleate and grow on NiTi SMA. After 12 h immersion in SBF, some single and clustered ball-like particles are observed on the surface of the chemically pretreated NiTi SMA. After an immersion time of 24 h, both the number and the size of these ball-like particles increase. In contrast, no new substance could be found on the surface of the chemically polished NiTi substrate even after soaking in SBF for 24 h (not shown here). After immersion in SBF for 48 h, the chemically pretreated NiTi SMA was fully covered with a dense apatite coating.

Fig. 6 shows Raman spectra of the apatite coating deposited on the chemically pretreated NiTi SMA in SBF after 48 h. The characteristic air bands are visible at low wave numbers up to 180 cm^{-1} [29]. It is observed that the Raman spectrum of the $\nu_1(PO_4)$ band at 959 cm^{-1} is very intense and characteristic of hydroxyapatite (HA) [30]. This mode

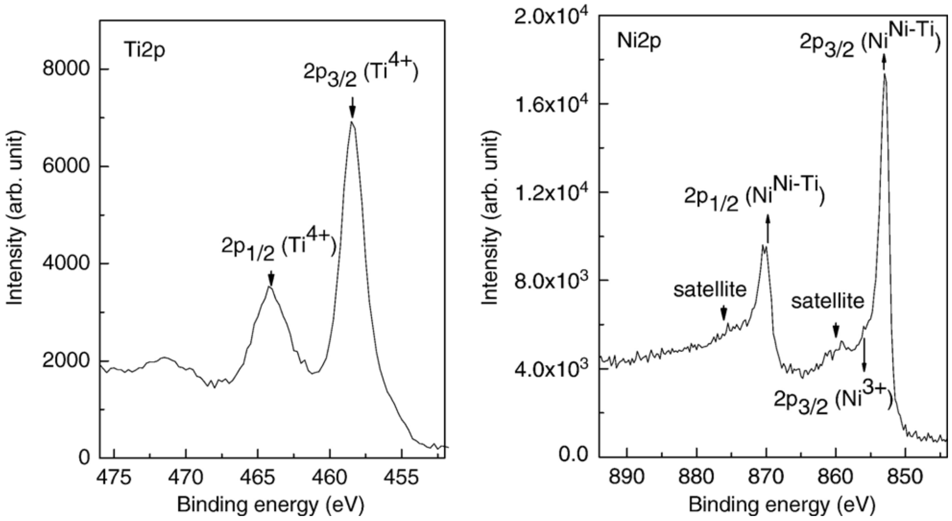

Fig. 3. Ti 2p and Ni 2p XPS spectra of the surface of the chemically pretreated NiTi SMA.

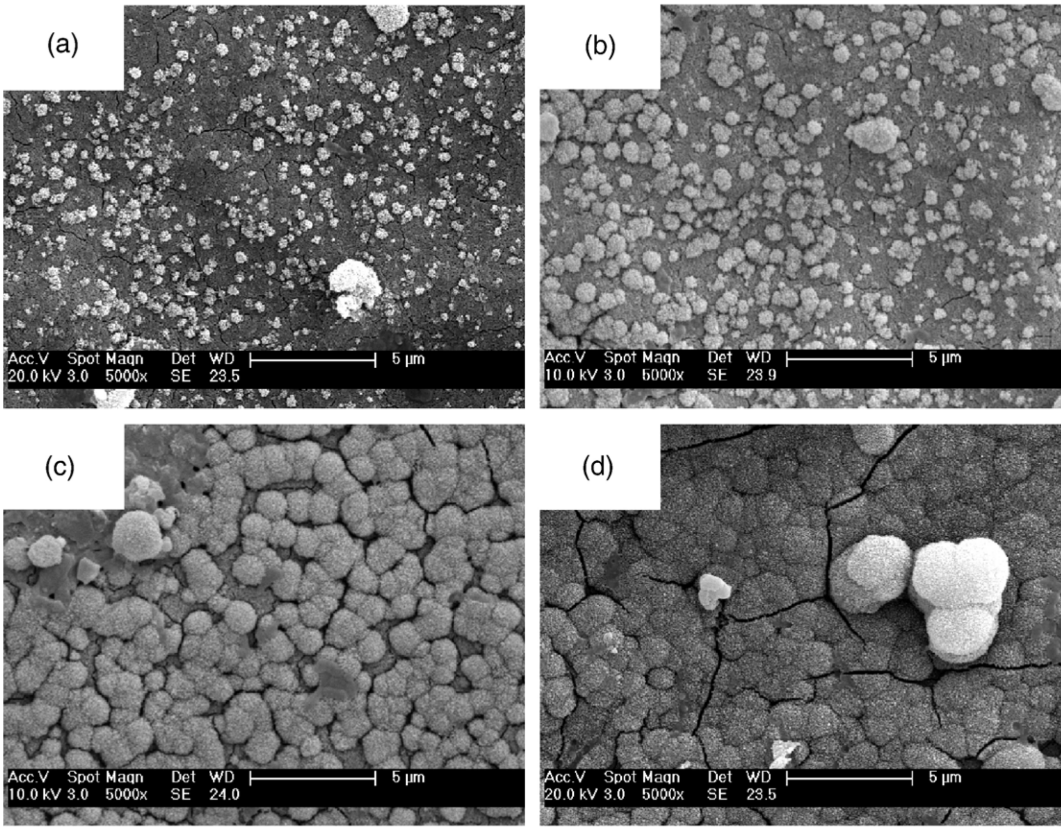

Fig. 5. SEM images of the apatite coating deposited on the chemically pretreated NiTi SMA in SBF after different times: (a) 6 h; (b) 12 h; (a) 24 h; (b) 48 h.

is associated to the totally symmetric v_1 (PO_4) A1 stretching mode of the 'free' tetrahedral phosphate ion. Other phosphate modes in HA such as 1073 cm^{-1} (v_3 (PO_4)), 590 cm^{-1} (v_4 (PO_4)), and 432 cm^{-1} (v_2 (PO_4)) can also be observed [30].

The results of the SBF soaking test conform that apatite cannot form on the surface of the chemically polished NiTi SMA even after soaking in SBF for 24 h, but on the other hand, the biomimetic nucleation of apatite on the chemically pretreated NiTi SMA has a short induction period down to 6 h. With longer soaking time, more apatite appeared on the chemically pretreated NiTi SMA. After immersion in SBF for 48 h, the chemically pretreated NiTi SMA was fully covered with a dense hydroxyapatite coating. The surface plays an important role in the response of the biological environment of the artificial biomedical device. Therefore, it is logical to believe that the decrease of the induction period for the biomimetic nucleation of apatite can be attributed to the modified surface of NiTi SMA by the chemical pretreatment with oxidizing in H_2O_2 solution and subsequent NaOH treatment.

In fact, the results from XPS, SEM and XRD reveal that a TiO_2 layer was firstly formed on the surface of NiTi substrate after oxidized in H_2O_2 solution, and then a sodium titanate/TiO_2 layer with a wormlike surface structure was formed in situ on the chemically pretreated NiTi SMA by the reaction of TiO_2 with NaOH solution. Moreover, FTIR spectra indicate the chemical pretreatment can lead to the direct creation of abundant Ti–OH groups on the surface of NiTi substrate. It is well known that the bioactivity of NaOH-treated titanium is induced by the presence of sodium titanate on its surface [5–13], which can result in the formation of Ti–OH groups via an exchange of Na^+ ions with H_3O^+ ions in SBF. In this work, the direct creation of abundant Ti–OH groups on the surface of the NiTi SMA after the chemical pretreatment can decrease the induction period of apatite formation by dispensing with the slow kinetic formation process of Ti–OH groups via the exchange of Na^+ ions from sodium titanate with H_3O^+ ions in SBF. Ti–OH groups can induce apatite nucleation and increase the ionic activity product of the apatite in the surrounding fluid by the increase of OH^- ion concentration, while the increased ionic activity product accelerates apatite nucleation. Once the apatite nuclei are formed, they spontaneously grow by consuming calcium and phosphate ions from the surrounding fluid because SBF is highly supersaturated with respect to the apatite [24].

It is obvious that the biomimetic deposition of the dense hydroxyapatite coating was attributed to the catalytic effect of abundant

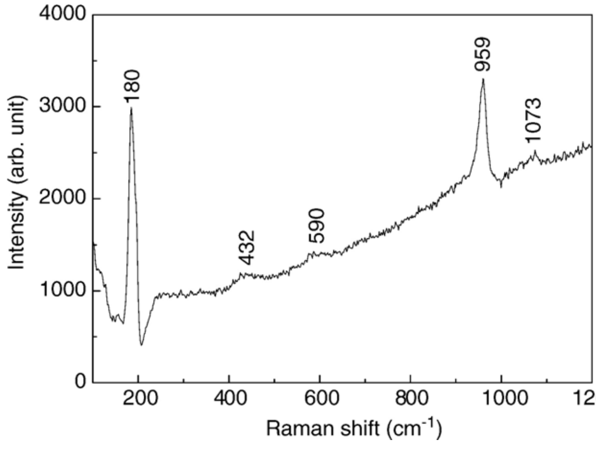

Fig. 6. Raman spectra of the apatite coating deposited on the chemically pretreated NiTi SMA in SBF after 48 h.

Ti–OH groups and Na_2TiO_3 on the surface of the chemically pretreated NiTi SMA. The characteristics of the hydroxyapatite coating fabricated by this biomimetic deposition method on NiTi substrate as well as further work are being pursued in our laboratory and will be reported in due course.

4. Conclusions

Biomimetic nucleation of apatite on NiTi shape memory alloy (SMA) after pretreated with 30% H_2O_2 solution and subsequently 1 M NaOH solution has a short induction period down to 6 h. With longer soaking time, more apatite appeared on the NiTi substrate but our control experiments didn't reveal any apatite formation on the chemically polished NiTi SMA. After immersion in SBF for 48 h, the chemically pretreated NiTi SMA was fully covered with a dense hydroxyapatite coating. The biomimetic deposition of the dense hydroxyapatite coating was catalyzed by abundant Ti–OH groups and Na_2TiO_3 on the chemically pretreated NiTi SMA with a wormlike surface structure.

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References

[1] W.Q. Yan, T. Nakamura, K. Kawanabe, S. Nishiguchi, M. Oka, T. Kokubo, Biomaterials 18 (1997) 1185.
[2] T. Kokubo, Acta Mater. 46 (1998) 2519.
[3] F. Barrěre, P. Layrolle, C.A. van Blitterswijk, K. de Groot, Bone 25 (1999) 107S.
[4] P. Habibovic, F. Barrěre, C.A. van Blitterswijk, K. de Groot, P. Layrolle, J. Am. Ceram. Soc. 85 (2002) 517.
[5] T. Kokubo, F. Miyaji, H.M. Kim, T. Nakamura, J. Am. Ceram. Soc. 79 (1996) 1127.
[6] H.M. Kim, F. Miyaji, T. Kokubo, T. Kitsugi, T. Nakamura, J. Biomed. Mater. Res. 32 (1996) 409.
[7] H.M. Kim, F. Miyaji, T. Kokubo, S. Nishiguchi, T. Nakamura, J. Biomed. Mater. Res. 45 (1999) 100.
[8] L. Jonášová, F.A. Müller, A. Helebrant, J. Strnad, P. Greil, Biomaterials 25 (2004) 1187.
[9] Y. Han, T. Fu, J. Lu, K.W. Xu, J. Biomed. Mater. Res. 54 (2001) 96.
[10] H.B. Wen, J.R. de Wijn, F.Z. Cui, K. de Groot, Biomaterials 19 (1998) 215.
[11] S.W. Ha, K.L. Eckert, E. Wintermantel, H. Gruner, M. Guecheva, H. Vonmont, J. Mater. Sci.: Mater. Med. 8 (1997) 881.
[12] M.C. de Andrade, M.R.T. Filgueiras, T. Ogasawara, J. Biomed. Mater. Res. 46 (1999) 441.
[13] C.X. Wang, X. Zhou, M. Wang, Bio-Med. Mater. Eng. 14 (2004) 5.
[14] M.F. Chen, X.J. Yang, Y. Liu, S.L. Zhu, Z.D. Cui, H.C. Man, Surf. Coat. Technol. 173 (2003) 229.
[15] M.F. Chen, X.J. Yang, R.X. Hu, Z.D. Cui, H.C. Man, Mater. Sci. Eng., C, Biomim. Mater., Sens. Syst. 24 (2004) 497.
[16] T. Duerig, A. Pelton, D. Stockel, Mater. Sci. Eng., A Struct. Mater.: Prop. Microstruct. Process. 273–275 (1999) 149.
[17] K. Otsuka, C.M. Wayman (Eds.), Shape Memory Materials, Cambridge University Press, Cambridge, 1998.
[18] I.P. Lipscomb, L.D.M. Nokes (Eds.), The Application of Shape Memory Metals in Medicine, Paston Press, Norfolk, 1996.
[19] L. Yahia (Ed.), Shape Memory Implants, Springer, Berlin, 2000.
[20] J. Ryhänen, M. Kallioinen, J. Tuukkanen, Biomaterials 20 (1999) 1309.
[21] G. Rondelli, B. Vicentini, Biomaterials 20 (1999) 785.
[22] J. Choi, D. Bogdanski, M. Köller, S.A. Esenwein, D. Müller, G. Muhr, M. Epple, Biomaterials 24 (2003) 3689.
[23] D. Bogdanski, S.A. Esenwein, O. Prymak, M. Epple, G. Muhr, M. Köller, Biomaterials 25 (2004) 4627.
[24] T. Kokubo, H. Kushitani, S. Sakka, T. Kitsugi, T. Yamamuro, J. Biomed. Mater. Res. 24 (1990) 721.
[25] S.M. Green, D.M. Grant, J.V. Wood, Mater. Sci. Eng., A Struct. Mater.: Prop. Microstruct. Process. 224 (1997) 21.
[26] S.A. Shabalovskaya, J.W. Anderegg, J. Vac. Sci. Technol., A 13 (5) (1995) 2624.
[27] S. Music, M. Gotic, M. Ivanda, S. Popovic, A. Turkovic, R. Trojko, A. Sekulic, K. Furic, Mater. Sci. Eng., B, Solid-State Mater. Adv. Technol. 47 (1997) 33.
[28] V.A. Skryshevskyy, Th. Dittrich, J. Rappich, Phys. Status Solidi, A Appl. Res. 201 (1) (2004) 157.
[29] A.P. Pino, P. Serra, J.L. Morenza, Thin Solid Films 415 (2002) 201.
[30] C.C. Silva, A.G. Pinheiro, M.A.R. Miranda, J.C. Góes, A.S.B. Sombra, Solid State Sci. 5 (2003) 553.