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Behavior of potassium titanate whisker in simulated body fluid

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ABSTRACT

Two sintering products containing potassium titanates were fabricated and cultivated in simulated body fluid for 12 days. It was found that the molar ratio of titanium/potassium of potassium titanate is a key factor to control the behavior of potassium titanate in body fluid environment. Low potassium titanates such as $K_2Ti_2O_5$ and $K_2Ti_4O_9$ transformed into calcium titanate due to its intrinsic characteristics of ion exchange. However, potassium hexatitanate was structurally stable adsorbing needle-like hydroxyapatite. The experimental results indicated that potassium hexatitanate possesses excellent biocompatibility which is better than low potassium titanates.

1. Introduction

Metallic biomaterials have attracted considerable attention in recent years due to their good mechanical properties [1–4]. Generally, metallic biomaterials such as steels, titanium alloys and magnesium alloys have good mechanical properties but shortage of biocompatibility than those biological ceramics. Except development of those low modulus alloys free of toxic elements, another strategy is to modify the surface of metallic materials to improve their biocompatibility [5–9]. Many efforts in chemical or physical modification on the surface of metals have shown great effect. For example, making a coating contained hydroxyapatite (HA), titanium-dioxide or potassium titanate (PT) on titanium alloys has been proven to be a promising methods to improve the biocompatibility of titanium alloys [10–13].

Potassium titanate, which can be rewritten as $K_2Ti_nO_{2n+1}$ (or $K_2O \cdot nTiO_2$, $n = 1, 2, 4, 6, 8$), is an important inorganic material, possessing varied structures, good mechanical properties, special functional properties and biocompatibility [14,15]. One typical PT, $K_2Ti_6O_{13}$ or potassium hexatitanate has been used as reinforcement in ceramics, polymers and metal matrix bio-composites [16–18]. When making a coating containing PT, it is difficult to obtain totally pure PTs such as $K_2Ti_6O_{13}$ or $K_2Ti_8O_{17}$ due to the presence of residual metastable phases such as $K_2Ti_2O_5$ etc. In addition, PT has different chemical behavior with different n value. It is thus necessary to study the biocompatibility of different PTs for developing new biomaterials using PTs.

2. Materials and method

Potassium titanate was prepared by sintering the mixture of raw material powder including potassium carbonate (K_2CO_3) and titanium dioxide (TiO_2). With a molar ratio of K_2CO_3 and TiO_2 (K/T) 1:3, the sintering sample P13 was prepared at 900 °C for 1 h to obtain low PT ($n \leq 6$, e.g. $K_2Ti_4O_9$). Moreover, with K/T = 1:5 (P15), high PT ($n \geq 6$, e.g. $K_2Ti_6O_{13}$) was expected to be prepared at 1000 °C for 1 h. The two sintered samples were then immersed into simulated body fluid (SBF) cultivating for 12 D to evaluate the biocompatibility and bioactivity of different PTs (S13 and S15 is the cultivated sample of P13 and P15 in this paper, respectively.). The composition of ions in applied SBF is in elsewhere [12]. The morphology evaluations of the PT samples before and after cultivation in SBF were performed on a scanning electron microscope (SEM, Philips XL30 TMP) and an optical microscope (XDS-1B, COIC, China). The microstructure of potassium hexatitanate after cultivation in SBF was examined by a transmission electron microscope (TEM, Philips Tacnai F20) with an energy dispersive spectrometer (EDS). The phase composition was investigated by an X-ray diffractometry (XRD, Philips X' pert TMD).

3. Results and discussion

Fig. 1 shows the XRD spectra of the prepared potassium titanate samples. It was found that different PTs were successfully prepared by changing K/T. For sample P15, some sharp peaks corresponding to $K_2Ti_6O_{13}$ and $K_2Ti_4O_9$ can be observed, implying that the major phase is $K_2Ti_6O_{13}$ with some amount of $K_2Ti_4O_9$ as

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residual phase. With a lower K/T, the major phases of P13 are $K_2Ti_4O_9$ and K_2TiO_3. Therefore, P15 can be regarded as high PT $K_2Ti_6O_{13}$ whisker and P13 is then regarded as low PT K_2TiO_3 or $K_2Ti_4O_9$. Fig. 1 also displays the XRD spectra of cultivated PT samples in SBF compared with the original samples, showing that the cultivation product of the two samples is quite different. For S15, the XRD spectrum contains such peaks for $CaTiO_3$, $K_2Ti_6O_{13}$ and HA as shown in Fig. 1. However, for S13, there is only $CaTiO_3$ can be found existing in its spectrum.

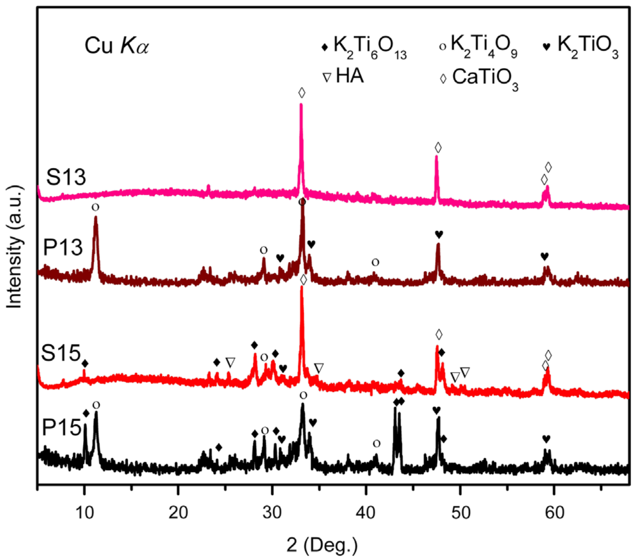

Fig. 1. XRD patterns of the potassium titanate before and after cultivating in SBF.

Fig. 2 shows the morphologies of the PT samples before and after cultivating in SBF. For P13, it shows a flake pattern for the as-prepared status as shown in Fig. 2(a). After cultivating in SBF for 12 days, it turns to a block-like pattern which the flake-like product disappeared as shown in Fig. 2(c). For P15, the sintering product is a kind of whisker (Fig. 2(b)) which also keeps the original morphology after cultivation in SBF for 12 D (Fig. 2(d)), indicating that it is very stable in SBF. Moreover, some small particles can be observed adsorbing on the whiskers as shown in the inset in Fig. 2(d).

To identify the particles adsorbing on the whiskers, TEM and EDS were used which the results are shown in Fig. 3. It was found that the particles around the whisker in Fig. 2(d) actually are some clumps formed by a kind of needle-like whisker in nano-scale rich in Ca and P as shown in Fig. 3(a). The EDS analysis results (in Fig. 3(b)) show that the atomic ratio of Ca/P of region C in Fig. 3(a) is about 1.7:1 (20.6:12.1) near the theoretical value 1.67:1 of HA. In addition, the atomic ratio of K/Ti of region C in Fig. 3(a) is about 2:7 (13.3:46.5 shown in Fig. 3(c)) which is closed to the theoretical value 2:6 of $K_2Ti_6O_{13}$. Therefore, this result shows that $K_2Ti_6O_{13}$ whisker in P15 keeps a constant chemical composition and can absorb HA nano-whisker, indicating that $K_2Ti_6O_{13}$ possesses good biocompatibility.

It is known that the precipitation of Ca/P ions implies that the cultivated material may possess good biocompatibility or bioactivity, as Ca and P are generally regarded as important ions to form HA. In the present work, Ca ions is also precipitated in S13 forming $CaTiO_3$ while not HA, which is attributed to ion exchange. The detailed process is that K^+ in low PT is replaced by Ca^{2+} from SBF, with reactions as:

$$K_2TiO_3 + Ca^{2+} \rightarrow CaTiO_3 + 2K^+ \quad (1)$$

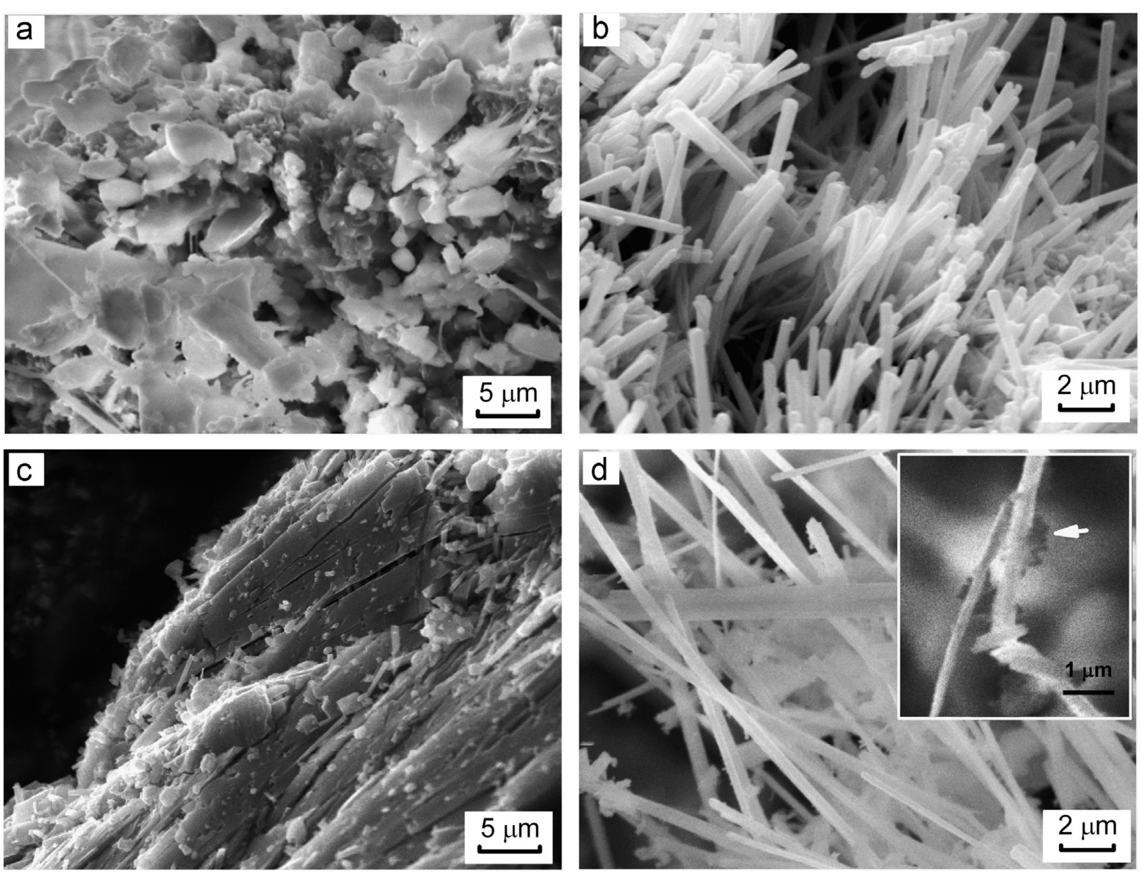

Fig. 2. Morphology of the PT samples. (a) P13, (b) P15, (c) S13 and (d) S15.