Effect of substrate oxidation on improving the quality of hydroxyapatite coating on CoNiCrMo

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Besides its excellent corrosion resistance in the human body, the superior fatigue and ultimate tensile strength of the wrought CoNiCrMo alloy make the material suitable for the applications which require long service life without fracture or stress fatigue, such as in the case of stems of the knee and hip joint prostheses [1]. However, the recent results on tissue response to metallic implants reveal that the metallic products released from the prosthesis because of wear, corrosion and fretting may impair organs and local tissues, and moreover some alloys with a certain amount of Co can be toxic in the body [2]. A bioactive ceramic coating, especially HA coating, on metallic prostheses could be a promising approach to shortening the time for osseointegration and improving bone-bonding ability [3–12], as well as reducing the release of potentially harmful metal ions from metallic implants. Recently, a number of low temperature coating techniques, such as biomineralization in simulated body fluid [3–9], sol-gel [10–12], have been reported for synthesizing HA coatings on metallic substrates. Compared to the conventional plasma spray coating technique, low temperature coating techniques are beneficial for obtaining a highly crystalline HA layer, which could provide a longer duration for bio-degradation [13].

However, the delamination of bioactive ceramic coatings from the metallic substrates could happen during the coating processes [3]. The delamination stress was generated along the interface between coatings and substrates due to the difference of metals and ceramics in thermal coefficient and insufficient mechanical interlocking or chemical interaction between the coating and the substrate [3, 14]. So an intermediate layer between metal and HA could be helpful for improving the interfacial bonding condition [3–9]. Nowadays, alkali treatments were found effective for producing the intermediate layer for the subsequent apatite coating on Ti, Ta alloys and stainless steels [3–9]. Although, CoNiCrMo is in use as fixation parts in close bony contact, for the Co-prostheses segments, fewer investigations were reported. Furthermore, the usage of the strong alkali chemicals, applied to produce an intermediate layer to bridge the HA coating and the metallic implant, results in the extra costs incurred for handling waste solutions due to environment-protection reasons. In order to find an environmentally friendly and economical surface-pretreating method for improving the HA coating quality on the conventionally used CoNiCrMo substrate, an oxidation method was studied in the present investigation by observing the crack features of the dip-coated

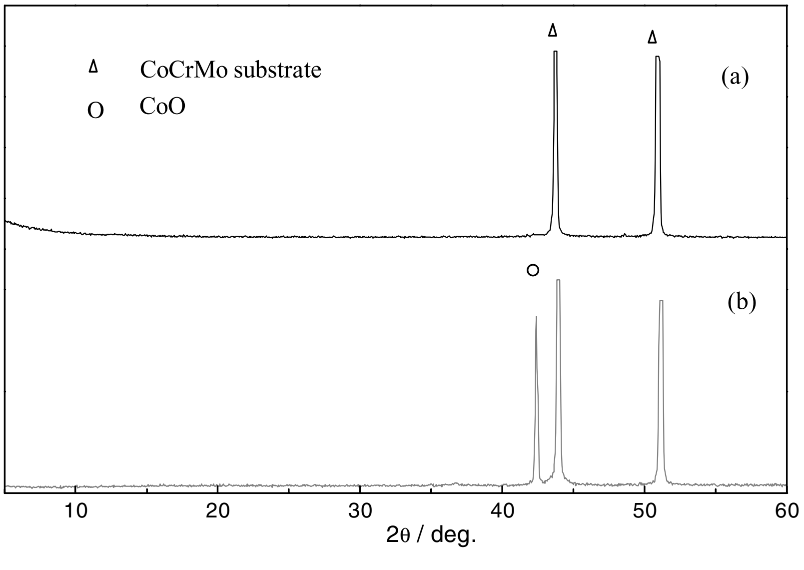

Figure 1 Grazing incidence XRD patterns of the original (a) and as-oxidized (b) substrates.

HA coatings on the substrates, with and without an oxidation pre-treatment.

The CoNiCrMo substrates were mechanically cut from the knee stem and polished to a 1 μm finish, then washed with acetone and distilled water in an ultrasonic cleaner. In order to produce an intermediate oxide layer without changing the microstructure of the CoNiCrMo stem, the oxidation temperature should be determined within the temperature range of 425–650 °C [1]. Therefore, oxidation in the present experiment was carried out at 600 °C for 1 hr at a slow heating rate of 5 °C/min, and then cooled to room temperature in the furnace. After oxidation, phase compositions in the surface layer were examined by grazing incidence X-ray diffraction (XRD) with a 2θ range of 5–60 degree. In order to verify the improving effect of oxidation, a HA dip-coating procedure was performed using $Ca(NO_3)_2{\cdot}4H_2O$ and $(NH_4)_2HPO_4$, at a Ca/P ratio of 1.67, as the precursors. Before coating, the HA suspension was aged and washed with distilled water until the pH value of waste water was neutral. The substrates, with and without oxidation, were dip-coated in HA suspension with a withdrawal rate of 4 mm/s, dried at 150 °C for 15 min and heated at 500 °C for 15 min at the heating

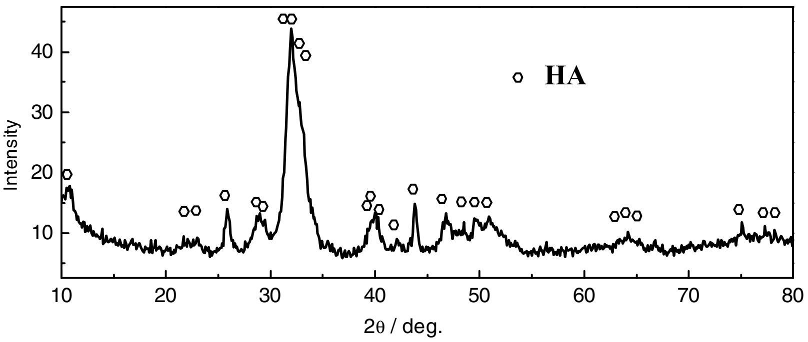

Figure 2 The grazing incidence XRD pattern of HA coating.

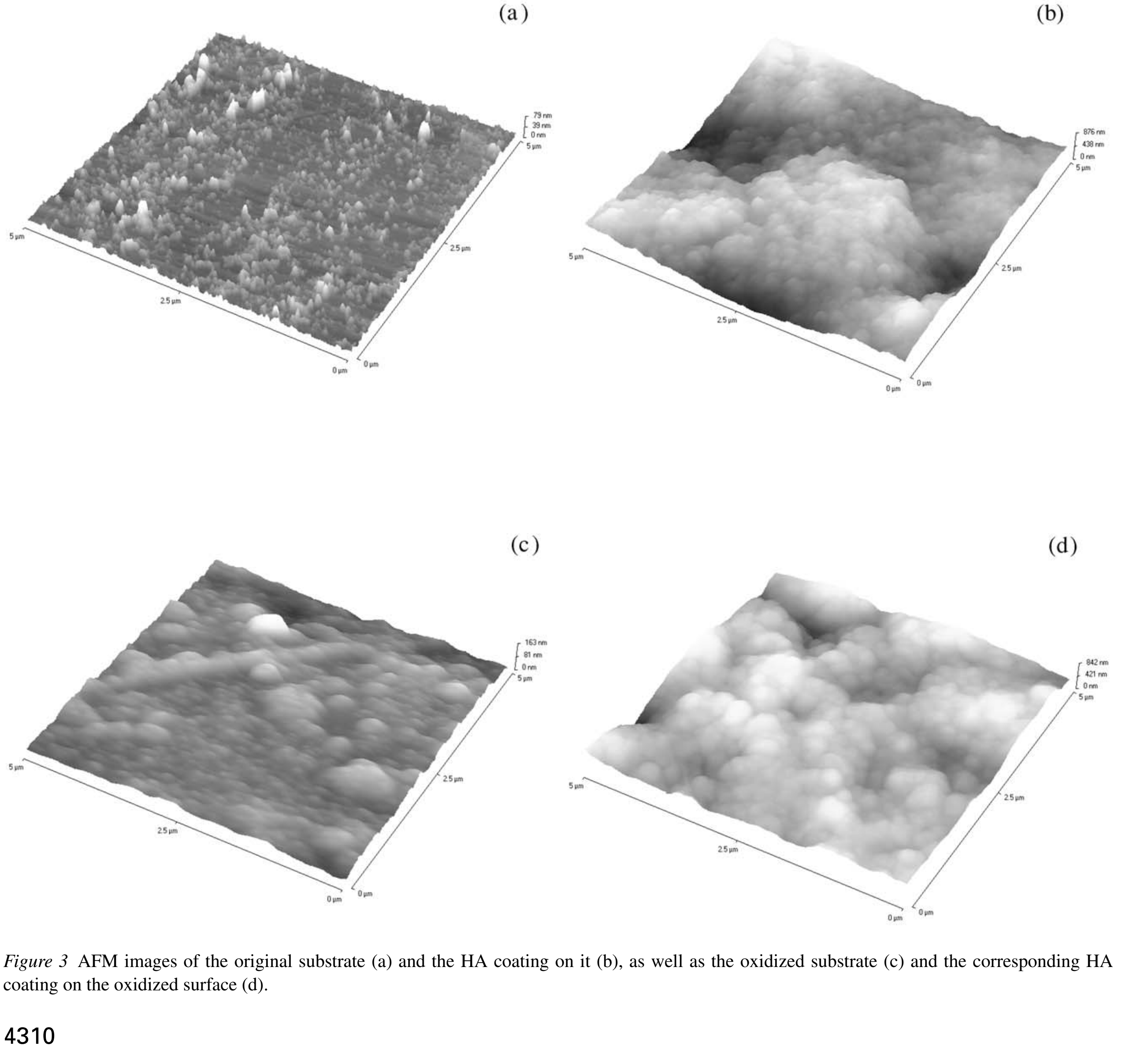

Figure 3 AFM images of the original substrate (a) and the HA coating on it (b), as well as the oxidized substrate (c) and the corresponding HA coating on the oxidized surface (d).

rate of 5 °C/min. All coating procedures were repeated 10 times in order to obtain a considerable thickness. The coating qualities were evaluated with the help of SEM by comparison of the crack features in the HA coatings on the substrates with and without pre-oxidation.

An obvious color changing was found on the CoNiCrMo substrates' surfaces after oxidation at 600 °C for 1 hr. The as-polished CoNiCrMo slice is in silver white, similar to that of the CoNiCrMo stem; whereas the oxidized surface is in bronze due to the light interference of oxide layer [15]. Fig. 1a and b are the grazing incidence XRD results of the substrate before and after oxidation at 600 °C. In Fig. 1b, a strong peak of crystalline CoO was detected on the oxidized CoNiCrMo surface, which is the resultant intermediate layer after oxidation.

The grazing incidence XRD patterns of the HA coatings on both un-oxidized and oxidized CoNiCrMo substrates are identical, as plotted in Fig. 2, which is identified as pure HA. Fig. 3a, b, c and d are the AFM images of the polished CoNiCrMo substrate, HA coating on just polished substrate, oxidized substrate, and HA coating on oxidized substrate, respectively. The surface of just polished substrate presents a morphology of separate sharp peaks with the height of 79 nm (Fig. 3a), whereas a scale-like morphology with a doubled height was observed on the oxidized surface of CoNiCrMo substrate (Fig. 3c). The HA coating on oxidized CoNiCrMo substrate is smoother than that on the un-oxidized one, according to the AFM images of both HA coatings in Fig. 3b and d.

The surface morphologies of HA coatings on the substrate, with or without oxidation, were observed using SEM, as displayed in Fig. 4. The HA coating on the untreated CoNiCrMo substrate (Fig. 4a) are full of long cracks, which could be attributed to the great difference of CTE between HA ceramic and CoNiCrMo metallic substrate, whereas the HA coating on the oxidized substrate (Fig. 4b) shows a different crack-free morphology. Additionally, the cross section of the HA coatings on un-oxidized and oxidized CoNiCrMo substrates were observed using the back-scattered electron imaging (BSI) attachment of SEM, as shown in Fig. 5a and b. According to the different atomic contrast of HA coating and CoNiCrMo substrate, the bright regions in Fig. 5a and b were determined as CoNiCrMo, as well as the gray regions which were HA coatings with the thickness of about 9 μm. Similar to the results of the surface morphology observation, long cracks along and across the HA coating were found in the coating on the un-oxidized substrate (Fig. 5a), whereas only several pores were observed in the HA coating on oxidized substrate (Fig. 5b). Both the surface morphologies and cross section features suggest that the oxidation pretreatment,

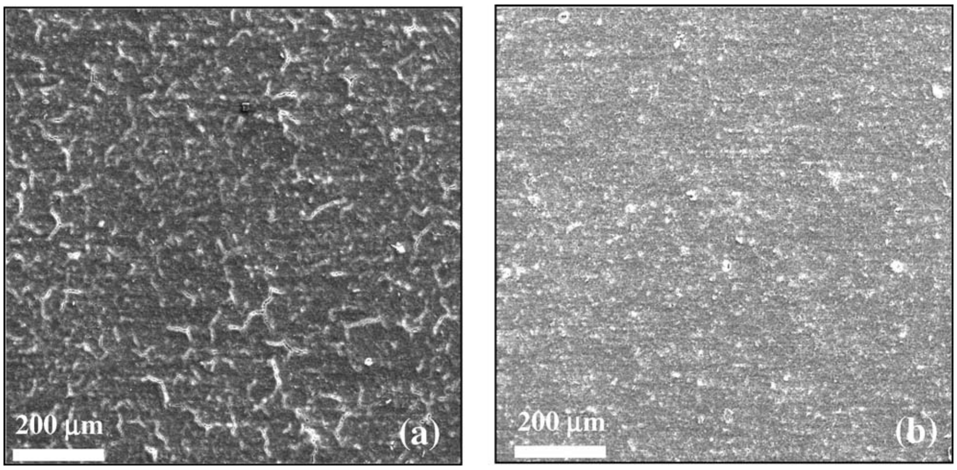

Figure 4 The SEM images of the HA coatings on the original substrate (a) and as-oxidized one (b).

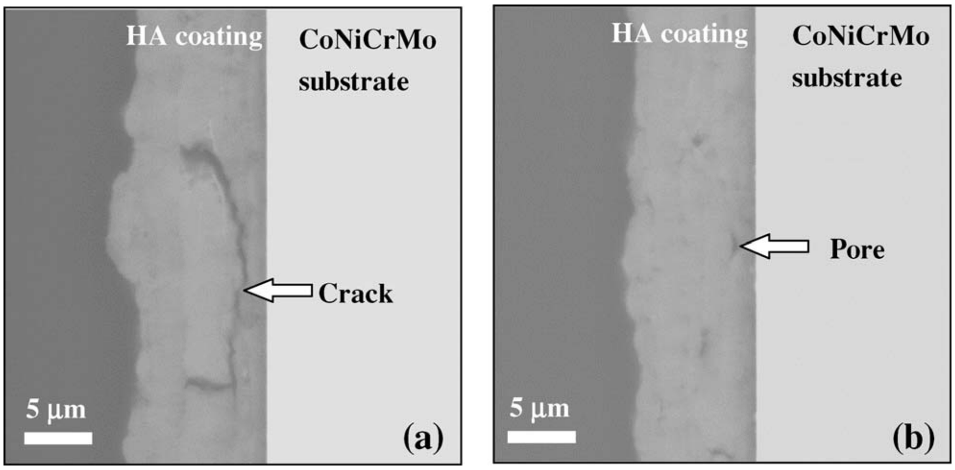

Figure 5 The back-scattered electron images of the cross section of the HA coatings on the original substrate (a) and as-oxidized one (b).

producing a crystalline CoO intermediate layer, is effective for bettering the coating quality of HA bioceramic on CoNiCrMo substrate. Compared to the previously reported alkali surface pre-treating methods [3–8, 16], direct oxidation method provides an environmentally friendly and economical approach in improving the HA coating quality via producing intermediate layer.

In brief, oxidation of CoNiCrMo substrate was found effective in reducing the cracks in HA bioceramic coating. The oxidation product CoO could be an intercompound to bridge up metallic substrate and HA ceramic coating. Direct oxidation method provides an economical and environmentally friendly approach in improving the coating quality of HA bioceramic on CoNiCrMo substrate, compared to the alkali pretreating technique.

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