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Artificial bones through nanodiamonds

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One example for the medical application of nanodiamonds is their use in orthopedic implants. Detonation generated nanodiamonds (DND) are of great interest, because they are able to strengthen bone tissue, producing tougher and more flexible artificial bone implants. Carbon-based materials can be used to replace natural collagen in bone, in which the main inorganic ingredient is the calcium phosphate (CaP) phase, namely hydroxyapatite (HA). Collagen is the organic part of bone that is based on carbon and is of the same size as DND. In this work, we present the deposition of CaP through DND on TiCu alloys by their immersion in a mixture of simulated body fluid (SBF) and a suspension of DND. The layers were characterized by SEM, EDX, coherence probe microscopy and Raman spectroscopy. It was found that DND produced a stable aqueous suspension in SBF, and was able to stimulate the growth of CaP layers on the surfaces of TiCu substrates.

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1. Introduction

Nanoscale materials, currently being investigated for bone tissue engineering applications, can be placed in the following categories: ceramics, metals, and composites. Each type of material has distinct properties that can be advantageous for specific bone repairing applications. For example, HA, an inorganic compound of bone can be made synthetically. Ceramics are not mechanically tough enough to be used in bulk for large scale bone fractures; however, for a long time they have found applications as bioactive coatings, owing to their ionic bonding mechanisms that are favorable for osteoblast (bone forming cells) functions [1]. Unlike ceramic materials, metals are not present in the body as volume materials. However, because of their mechanical strength and relative inactivity with biological substances, metals (Ti, Ti_6Al_4V and CoCrMo, etc.) have been the materials of choice for large bone fractures.

Composites of the above mentioned materials can be synthesized to provide a wide range of material properties, to increase bone implant performance [2]. It was found that detonation generated nanodiamonds (DND) inclusions can stimulate the biological performance of the composite layer [7]. Because of the numerous materials currently being investigated for medical implants, this paper will present our efforts to create new nanoscale materials for bone replacement.

2. Experimental

Amorphous ribbons of $Cu_{50}Ti_{40}Al_{10}$ and $Cu_{50}Ti_{50}$ alloys, with a thickness of 0.02 to 0.03 mm and a width of 2 mm, were produced in a He atmosphere (300 mbar) by melt-spinning onto a copper quenching wheel [3]. The as-quenched ribbons (substrates) were fully amorphous as checked by X-ray diffraction and TEM. The roughness (rms), measured by CPM was of the order of order of 42 nm.

The set-up used in the experiment for HA growth from simulated body fluid (SBF) was of the open deposition type, consisting of a Plexiglas container in which the temperature of the SBF was thermostatically controlled. The samples were placed on the bottom of the container, in a horizontal position or on a holder in the vertical position. The supersaturated SBF was prepared in such a way that it resembled the composition of human blood plasma [4]. Subsequently, DND particles were added to the SBF as a suspension and to a clear solution (i.e. the solution obtained after sedimentation of the suspension).

DND powder, 4-6 nm in size, was synthesized from the free carbon of explosives with a negative oxygen balance at high pressure and high temperature, produced by the detonation. After washing, the diamond-graphite mixture obtained was purified from graphite by oxidation with potassium dichromate in sulfuric acid [5].

To study the ability of the CuTi alloys to induce CaP growth from the SBF with/without a DND suspension, three groups of samples were prepared.

The first group was prepared by soaking the samples for 4 hours in magnetically stirred SBF at 37ºC, in the vertical position.

The second group was prepared by soaking the samples for 4 hours in a magnetically stirred mixture of SBF and a suspension of DND at 37º C in the vertical position.

The third group of samples was simply soaked for 24 hours in a mixture of SBF and a clear solution of DND suspension at 37º C, in the horizontal position.

Morphological and surface chemical analysis of the TiCu alloys and the grown CaP layer were carried out using a SEM/EDX (Surface Scanning Electron Microscope, JSM-25 SIII with a GEMINI column). The topography and roughness of the TiCu ribbons were studied by CPM (Leitz Linnik interferometer) [8]. The CaP layer structure was analyzed by Raman spectroscopy (Renishaw Ramascope, λ = 488 nm, reflection mode).

3. Results and discussion

After the growth of a layer from the magnetically stirred SBF solution (first sample group), sphere-like particles with an average diameter of the order of 200 nm, grouped in clusters, were observed by SEM on the surface of both types of CuTi alloys, as shown in Fig. 1a. The corresponding Raman spectra of these particles (Fig. 1c) showed the P-O vibrational modes in PO_4^{3-} groups characteristic of the CaP phase. The two weak peaks at 419 and 550 cm^{-1} were assigned to ν_2 asymmetric and ν_4 symmetric P-O bending, respectively, and the stronger peak at 948 cm^{-1} was due to the ν_1 symmetric stretching in PO_4. The elemental composition (Fig. 1b) showed that the sphere-like particles consisted of Ca, P, O and Cl, as well as Ti, Cu and Al (in the case of $Cu_{50}Ti_{40}Al_{10}$ alloys) signals coming from the substrates.

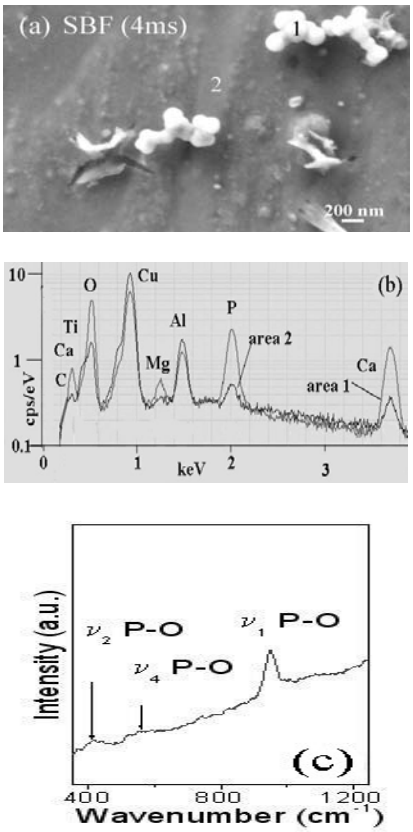

Fig. 1. Morphology structure and elemental composition of the layers grown on TiCuAl alloys in SBF, (a) SEM image, (b) Raman spectrum, (c) EDX measurements.

The mixture of the supersaturated SBF and the DND suspension (second sample group) yielded the formation of nuclei, reached of C and Ca, and about 10 nm in size (fig 2a, area 2). On these areas, sphere like particles (fig 2a, area 1) were observed. Measured Raman spectrum (Fig. 2 c) show three peaks at 1080, 1339 and 1633 cm^{1}. According to the literature, these bands

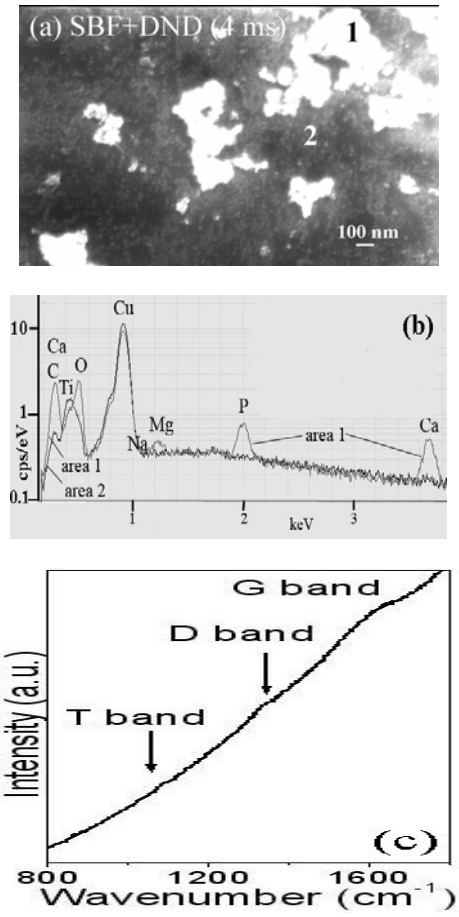

Fig . 2. Characterization of layers grown on TiCuAl alloys in a magnetic stirred mixture of SBF and a DND suspension: (a) SEM image, (b) Raman spectrum, (c) EDX measurements.

were due to spectra observed for highly oriented pyrolitic graphite [6]. The T band is usually observed in films having a high sp^3 content, the D band is linked to disordered graphite and the G band is due to crystalline graphite. The intensity ratio of the D and G bands helps one to make an estimation of the degree of disorder in graphitic compounds. The intensity of the G band increases relative to the intensity of the D band, as the graphite crystal size decreases [7]. The formation of a mixed compound of CaP and graphite cannot be excluded in this group of samples. Probably the CaP vibrational modes were hindered by the C-C vibrations in the spectrum. EDX spectra (Fig. 2b)

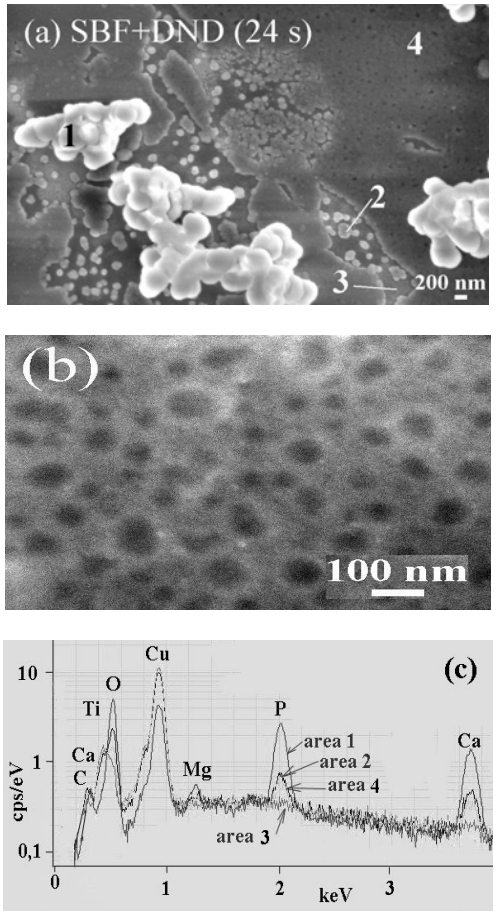

Fig. 3. Morphology structure and elemental composition of layers grown on CuTi alloys in a magnetically stirred mixture of a SBF and DND clear solution: (a) SEM image, (b) SEM image of the porous structure in area 4, (c) EDX measurements.

measured on the white particles showed that they were composed of Ca, P, O and Mg and thus revealed, together with the Raman spectrum, that they were composed of a mixture of CaP and graphite. Since the beam could reach the substrate surface, Ti and Cu were also detected. In the case of the spectrum recorded from the surface of the alloys, Ca, P, O and Mg were also present in the spectrum, but with a lower concentration. It was concluded that there was a thin CaP layer on the surface of the alloys.

Finally, an image of the surface of the alloys after their immersion for 24 hours in the mixture of SBF and a clear solution of DND particles (the third sample group) showed the formation of sphere-like particles (Fig. 3a) as well as areas with a porous structure similar to that of bone, area 4 in (Fig. 3b). The corresponding Raman spectrum (not presented here) revealed typical vibration peaks for CaP. Although this group of samples was soaked in a mixture of SBF and a clear solution of DND particles, no vibrations due to the presence of graphite in the particles, as in the second group of samples, were detected. The reason for this could be that the spot of the exciting laser beam was of the order of micrometers. As is known, the size of the DND particles in a clear solution, i.e. in a solution obtained after sedimentation of the suspension contains particles smaller than those in the suspension (i.e. about 4-6 nm). Thus, they cannot be detected from the Raman spectra. It was shown that C present in the observed four areas marked in Fig. 3a detected by EDX (Fig. 3c). The spectra were taken from the following areas: the sphere-like particles (area 1), small particles (area 2), from the background (area 3) and from the porous layer (area 4). Ca, P, Mg and O were present in all spectra, with intensities decreasing in the order: area 1-area 2-area 4-area 3-area, indicating the formation of CaP compounds with decreasing thickness. EDX spectra revealed that the Ca and P concentration depended on the C concentration in the observed layers. The highest carbon concentration was detected in the first stage of the process (area 3), where smaller Ca and P concentrations were measured. In the sphere-like particles, carbon wasn't detected. The fast deposit of DND particles in the saturated solution could be a reason for the higher C concentration in first stages of the process. The Ca/P ratio decreased with advance of the process. It was found to be 1.77 for area 3, 1.41 for area 4, 1.34 for area 2 and 0.98 for the area 1. EDX spectra of a CaP layer grown from a DND suspension and clear solution Mg and Cl were observed. An explanation could be as follows. The apatite structure on the one hand allows the inclusion of foreign atoms such as Mg, Na, K, Cl. On the other hand, the diamond structure is also an ion-exchanging material, due to it existing on the surface functional groups (for example COOH, OH, SO_3H, NO_3 and NO_2' considered as ionogenic) [7]. Thus, both apatite and DND could have stimulated the inclusion of Mg and Cl. It has also been shown that DND in aqueous solutions has possible and desirable applications in medicine [7].

4. Conclusions

The influence of TiCu alloys and DND in CaP crystal growth has been investigated. It has been shown that TiCu alloys induce CaP growth. Adding of the DND suspension and clear solution in SBF influence the grown layers morphology. Samples prepared by immersion in a mixture of SBF and DND clear solution, apart from the sphere-like particles, show also the formation of porous areas similar to those in the structure of bone. The Ca/P ratio and the C concentration in the investigated layers are decreasing with advance of the process. DND could have stimulated the CaP growth and inclusion of Mg and Cl in the composites.

Acknowledgements

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