

High Resolution Microscopy of Nanocrystalline Hydroxyapatite Coatings

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Introduction

Coating biocompatible metals with bioactive ceramics is a well-known pathway to combine properties of bioactive ceramics with toughness of metallic biomaterials. Niobium is a biocompatible metal, like titanium and tantalum. In the present study, nano-sized apatite coatings were produced on niobium substrates. The coating process consists of hydrothermally coating niobium with monetite, CaHPO_4 , followed by alkali conversion to hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. In previous studies, these nano-sized apatite coatings were produced in niobium substrates by alkali conversion of monetite [1]. It was also observed that the coatings presented a good adhesion to the substrates. In the present study, high-resolution electron microscopy using synchrotron light was used to assess both the coating morphology and the coating-metal interface. Nano-sized hydroxyapatite morphology was assessed by field emission gun scanning electron microscopy (FEG-SEM). The coating interface was assessed by high-resolution transmission electron microscopy (HR-TEM). High-resolution transmission electron microscopy revealed the existence of an amorphous region in the interface. Energy dispersive X-ray microanalysis with nanometric resolution revealed the presence of calcium and phosphorous in this amorphous interfacial region.

Materials and Methods

In this study, niobium sheets ($10 \times 10 \times 2 \text{ mm}^3$) were hydrothermally coated with monetite and further converted to hydroxyapatite by an alkali treatment with NaOH. The starting solution has the composition: 0.3M H_3PO_4 , 0.5M $\text{Ca}(\text{OH})_2$, 1M $\text{CH}_3\text{CHCO}_2\text{HOH}$. The monetite coating was produced by the immersion of the specimens in the solution at 80°C during 1 hour. The sheets were then removed, washed in ultra-pure water and dried in an oven at 60°C overnight. Hydroxyapatite coatings were produced by alkali conversion in a solution of NaOH with $\text{pH}=12.5$ during 24 hours at 60°C . Specimens were then removed from the alkali solution, washed in ultra-pure water and dried in an oven at 100°C during 1 hour. Field emission gun scanning electron microscopy (FEG-SEM) analysis was used to assess the morphology of the nano-sized coatings. SEM analysis was performed in a scanning electron microscope (FEG-SEM Jeol JSM 6330F). HR-TEM was used to investigate the interface between metal and ceramic. Thin foils of the interface niobium-monetite and niobium-hydroxyapatite were prepared for following the protocol suggested in the . Electron Microscopy Laboratory, Brazilian Synchrotron Light Laboratory, LME-LNLS. Cross-section specimens were prepared in dimple grinder and ion milling and observed in a Jeol JEM 3010-URP HR-TEM. Energy dispersive X-ray analyses with nanometric resolution were performed in the interfaces. All microscopy preparation and analyses were performed in the Electronic Microscopy Laboratory, Brazilian Synchrotron Light Laboratory, LME-LNLS.

Results and discussion

FEG-SEM observation of the hydroxyapatite coatings showed the presence of nano-sized needles composing coarser needles. This feature could not be resolved in conventional SEM. Figure 1 shows a FEG-SEM image of the coating. The high specific area generated by this topography may be associated to the high bioactivity of this coating.

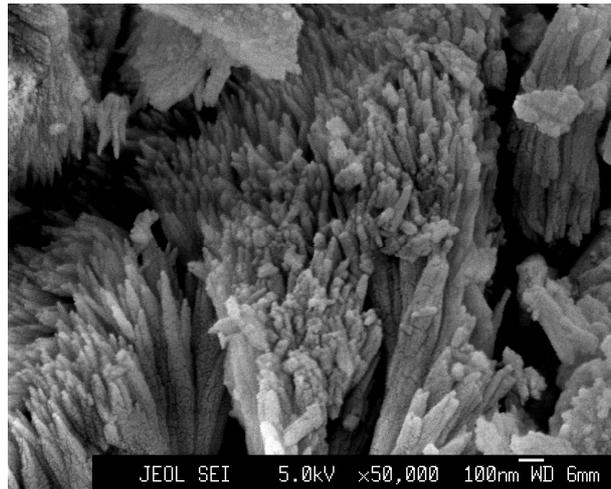


Figure 1 – FEG-SEM image of nano-sized hydroxyapatite needles on niobium substrate.

TEM observation on monetite-niobium and hydroxyapatite-niobium interfaces showed coating detachment at some points as shown in Figure 2. Energy dispersive X-ray analyses with nanometric resolution revealed that these detachments occurred with a metal-rich layer. This fact is indicative of a good adhesion between the coating and the substrate.

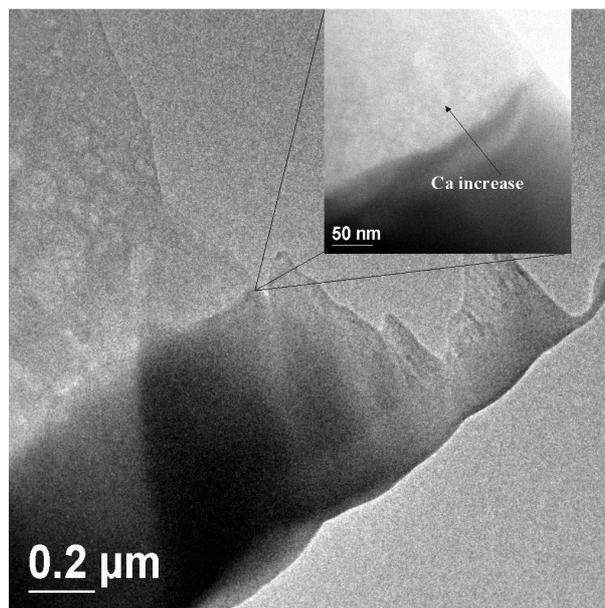


Figure 2 – HR-TEM image of a detached portion of the monetite coating.

HR-TEM observation on the interface revealed the presence of an amorphous layer between the ceramic and the metal, as shown in Figure 3. Amorphous interfaces bonding hydroxyapatite coatings to metallic substrates are shown in the literature [2; 3] in well-adhered ceramic coatings. Energy dispersive X-ray analyses with nanometric resolution revealed calcium and phosphorous gradients from the metal-rich portion of the interfaces towards the ceramic coatings, Figure 4.

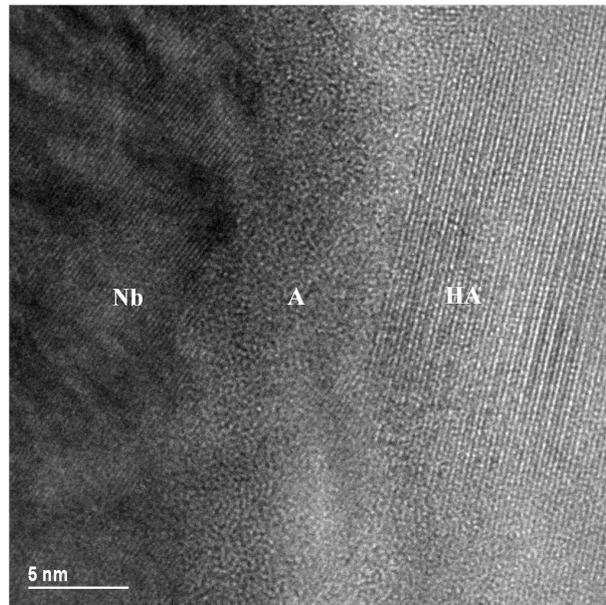


Figure 3 – Hydroxyapatite-niobium interface showing the presence of an amorphous layer (A) between niobium (Nb) and hydroxyapatite coating (HA).

The observed amorphous layer between the metal and the substrate indicates the presence of an intermediate layer bonding the ceramic coating to the metallic substrate. This finding can explain the good adhesion observed for the produced coatings. The presence of calcium and phosphorous gradients confirms the presence of intermediate an layer.

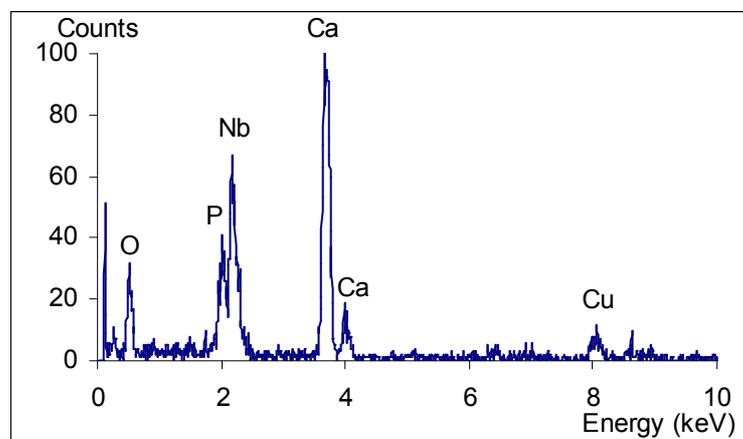


Figure 4 – EDS spectrum showing the presence of calcium, phosphorous and niobium in the amorphous interface.

Conclusion

An amorphous layer rich in calcium and phosphorous was observed in the interface between the substrate and the ceramic coatings. This layer may account for the chemical bond between the coating and the substrate.

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