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Hydroxyapatite Precursor Phases Identification by X-ray Diffraction Using Synchrotron Radiation

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Abstract. The present study presents the relevance of X-ray diffraction analysis using synchrotron light in the identification of phases with low intensity peaks. Niobium sheets were coated with monetite and then converted to hydroxyapatite in an alkali solution. Octacalcium phosphate was identified as an intermediate phase in the conversion monetite-hydroxyapatite.

Introduction

Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, HA, is the most used bioceramic for coating metallic implants for its similarity with the inorganic phase of hard tissues. In previous studies, a hydrothermal coating method on niobium substrates was developed [1, 2]. In this method, hydroxyapatite is deposited on niobium and titanium substrates by precipitation from an acidic solution containing calcium and phosphate ions. The method is a two-step process, in which a monetite coating is precipitated on the substrate and further converted to hydroxyapatite. The conversion occurs in alkaline solution, during 24 hours.

In previous studies [3], attempts have been made to investigate the presence of intermediate phases during the conversion stage. Samples corresponding to the early time points were characterized by X-ray diffraction (XRD). However, the nanostructured hydroxyapatite crystals produced by re-precipitation from the precursor monetite produce an XRD pattern with some background. In the present study, an XRD analysis with improved resolution was performed in the Brazilian Syncrotron Light Laboratory, LNLS.

Materials and Methods

Niobium sheets coated with monetite were soaked in an 0.1M NaOH solution at 60ºC. Samples were retrieved in different time points, ranging from t=0 to t=24 hours. Scanning electron microscopy and X-ray diffraction analyses were performed in order to associate morphology to structural characterisation.

The complete conversion to hydroxyapatite was obtained after 24 hours in solution. In time points between 30 minutes and 12 hours in the alkali solution, some intermediate precursor phases were identified.

X-ray diffraction analysis was performed in the XRD1 beam line in the Brazilian Synchrotron Radiation Laboratory, LNLS. The beam line operates at 9keV, using the theta–two theta method and the radiation used had λ=1.3772.

Results and Discussion

Figure 1a shows a typical XRD pattern obtained by use of Kα Cu radiation. In Figure 1b for niobium a sheet coated with monetite and Figure 1b shows the corresponding SEM morphology of the monetite coating.

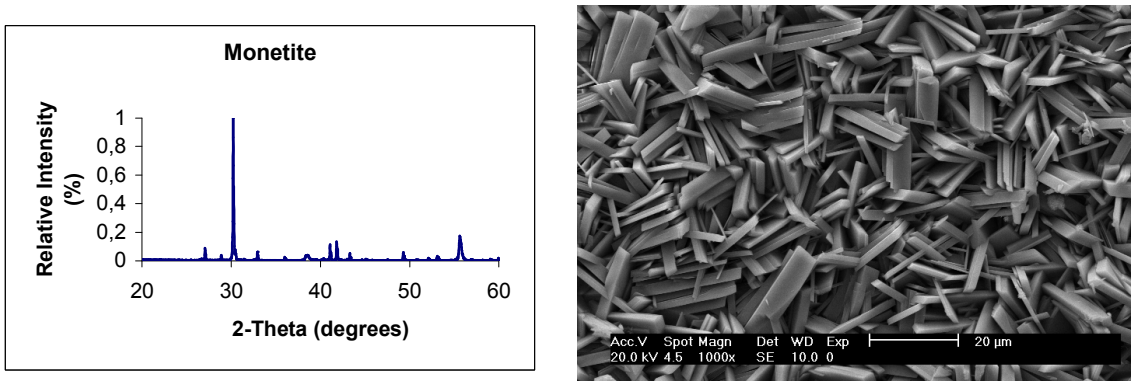


Figure 1 – XRD pattern for the monetite coating (a) and corresponding SEM analysis (b).

In Figure 2a, a typical XRD pattern using Kα Cu radiation of a hydroxyapatite coating is presented. Figure 2b presents the corresponding SEM analysis, showing the presence of nano-sized needles, that account for the background observed in the XRD pattern.

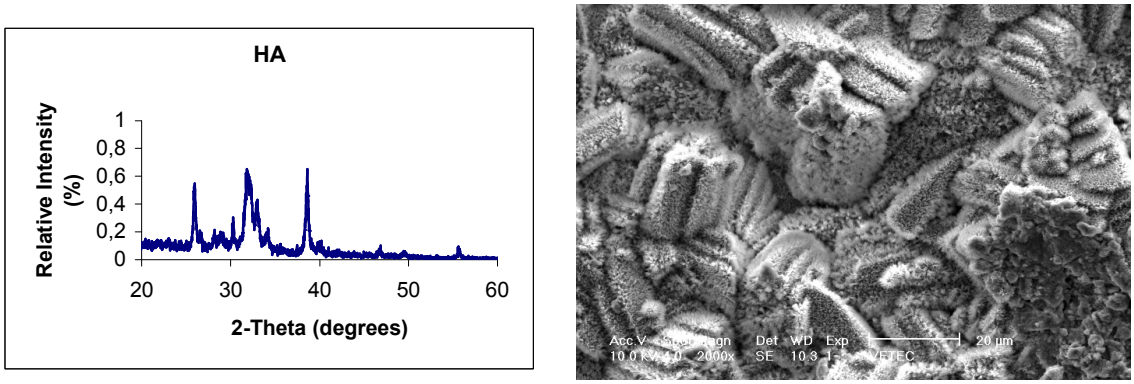
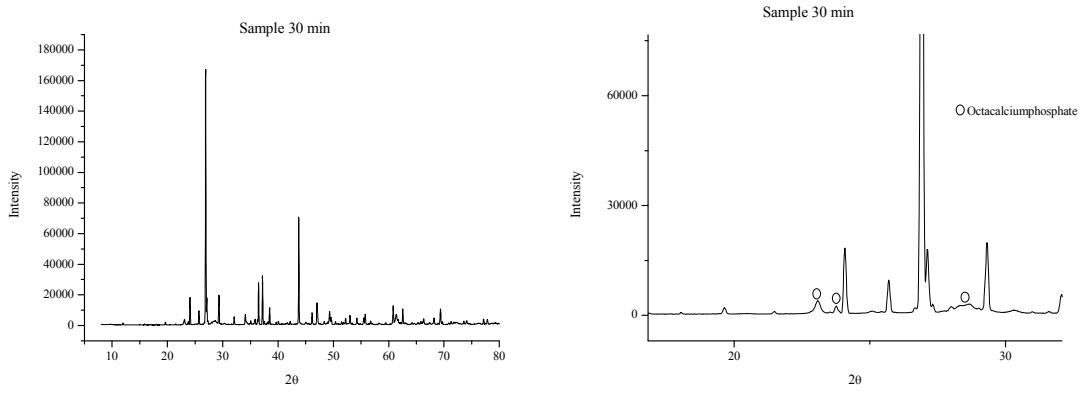


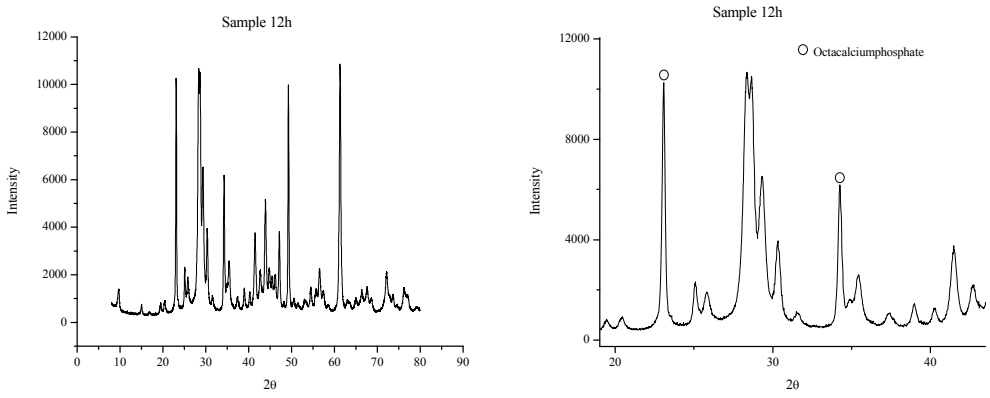
Figure 2 – XRD pattern (Cu radiation) for a HA specimen (a) and corresponding SEM picture (b).

XRD analysis using synchrotron radiation revealed the presence of octacalcium phosphate in monetite specimens incubated in the alkali solution up to 12 hours. Figure 3a shows the XRD pattern using synchrotron light for the specimen converted during 30 minutes. Figure 3b shows, in detail, the OCP peak.



(a) (b)

Figure 3 – XRD patterns using synchrotron light for a specimen converted during 30 minutes showing the presence of ocatacalcium phosphate peaks in (b).



(a) (b)

Figure 4 – XRD pattern for the sample converted at t=12h (a) and zoom in the region showing OCP main peaks.

In Figure 4, OCP peaks are still be identified, as shown in detail in Fig. 4b. This finding indicates that this phase is still present after 12 hours in the alkali solution. Figure 5 shows an SEM picture corresponding to the sample converted during 30 minutes, showing acicular phases precipitated on the precursor monetite crystals. It is worth to observe the partial dissolution of the monetite crystals, coinciding with the presence of the needles. This finding suggests the local reprecipitation of the precursor phase, from the monetite partial dissolution.

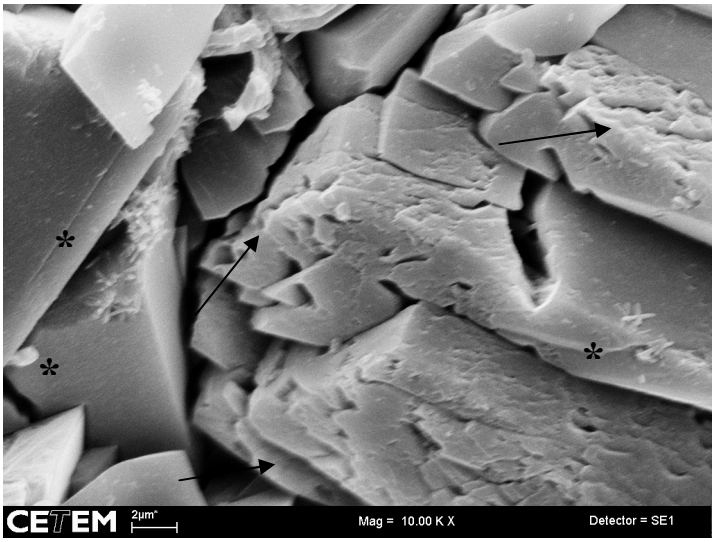


Figure 5 – SEM analysis of the specimen converted during 30 minutes, showing partial dissolution of monetite crystals (arrows) and OCP needles (asterisks).

Conclusions

This study shows the potential of synchrotron light in the identifiation of phases with low intensity.

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