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Pyrite (FeS_2) is one of the most abundant sulphur minerals on earth and plays an important role in many natural processes, e.g. acid mine drainage and heterogeneous catalysis. Its surface adsorption properties to organic molecules in hydrothermal setting where shown by Lindgren et al. [1] and are important in the iron-sulphur world scenario published by Wächtershäuser et al. [2].

Non-specular crystal truncation rods (CTR) of the pyrite surface under ambient conditions, that provide information about the periodic order of the vertical and lateral surface and the water-pyrite interface structure, were collected with grazing incidence X-ray diffraction (GIXRD) at the ESRF, Grenoble, France. The surface/interface structures of the (100) face in dry and aqueous ambient conditions were investigated using integrated and corrected intensities in a least square fit.

Different models for the surface cell dimensions and the site occupation factors (sofs) were tested. The (100) face in dry conditions shows a defect structure resulting from S and Fe vacancies with sofs of 0.1-0.3 for the topmost atom layer, decreasing with increasing depth. The surface cell is bulk structure terminated with only small relaxations in the topmost surface layers.

For the (100) face covered with a water film a pyrite/water interface model was ascertained by refining models with different start parameters: site occupation factors, positions and occupation factors of O-atoms mimicking water molecules. The pyrite surface is also bulk terminated with a defect structure resulting from S- and Fe-vacancies. It shows only small relaxations of <0.1Å for the bottom and 0.5Å for topmost surface layers without reconstruction.

In good agreement with results from molecular dynamic [3] and ab initio [4] simulations three layers of H2O molecules are adsorbed to the surface. Additionally, water molecules occupy the Fe-vacanies of the topmost Fe-layer and a transitional zone up to 8Å, above the topmost Fe-layer, between adsorbed and bulk water can be found. The first H_2O-layer is located 1.9(1)Å above the topmost Fe-layer and is bound to the iron atoms. The second layer interacts with the topmost sulphur layer and is located 3.0(3)Å above the topmost Fe-layer. The third layer interacts with the second H_2O-layer and the transitional zone and can be found at a distance of 5.4(4)Å to the topmost Fe-layer. There is an electrostatic interaction in x-direction, whereas the interaction in y-direction is more dynamic, because of the surface anisotropy of the (100)-face of pyrite.

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MS21.P12

X-ray characterization of sol-gel TiO_2 thin films

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TiO_2 thin films deposited on a Ti-6Al-4V alloy by means of the sol–gel dip-coating technique were characterized using X-ray synchrotron radiation. The crystalline structure and thickness of the films were obtained and related to the parameters of the sol-gel process.

The process involves immersing the substrate (Ti-6Al-4V) in a colloidal dispersion (sol), withdrawing the substrate at constant low velocity, drying of the coating and heat treatment. For the dispersion preparations, titanium butoxide, isopropanol, ethyl acetoacetate, HCl and distilled H_2O were used. Several withdrawing velocities and number of layer were used, these ranged from 1 to 3 cm/min and from 1 to 3, respectively. Two values of titanium butoxide/isopropanol molar ratio were used in the dispersions: 1/20 and 1/10. Dispersions with aging times ranged from 1 to 10 days were used. The samples received a heat treatment for 1 h at a fixed temperature of 500 C to each layer of coating and heated to 10 C/min and cooling inside the furnace. The morphology of the coatings was observed by optical microscopy and SEM. The crystalline structure was determined by X-ray diffraction with a glancing incidence angle of 1º and the thickness was determined by the X-ray reflectometry technique. These experiments were carried out at the D12A-XRD1 beamline of the LNLS (Campinas, Brazil).

The coatings were homogeneous, compact and smooth to the optical microscope, and of different colors according to their thickness. With increase of the withdrawing velocity, the number of layers, the titanium butoxide/isopropanol ratio or the aging time of the dispersions, the thicknesses of the coatings increased, all in a range from 25 nm to 142 nm. Cracks were observed on films with thicknesses thicker than 100 nm. By X-ray diffraction of the monolayer and multilayer coatings was determined the presence of anatase and rutile.

The results show a relation between thickness and structure. In the thinnest films no crystal structure was detected, while for films with intermediate thickness rutile phase was detected, and for the thickest films both rutile and anatase phases were detected. The brookite structure was not detected in any film.

Keywords: sol-gel, film, synchrotron

MS21.P13

Characterization of TiO_2 nano-films obtained by anodic oxidation of Ti-6Al-4V

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Anodic oxidation of Titanium and Titanium alloys produce a TiO_2 coating with better mechanical properties and corrosion resistance than the substrate. In addition, this TiO_2 coating is a film with biocompatible properties [1], [2].

In the present report, we determined and analyzed the effects of different acid electrolytes on the color, thickness, morphology and crystalline structure of the coating. The electrolytes used were sulfuric acid (H_2SO_4) 0.1M to 4M and phosphoric acid (H_3PO_4) 1M, and the substrates were plates of Ti-6Al-4V alloy; the oxidation voltages used ranged from 10V to 100V.

The thicknesses of the films were determined by X-ray reflectometry with synchrotron radiation (D12A-XRD1 beamline of the Brazilian Synchrotron Light Laboratory, LNLS). The morphology of the films was observed using optical and scanning electron microscopy and the crystalline phases of the oxides formed were determined by the glancing incidence angle X-ray diffraction technique with a glancing angle of 1º.

The oxide films produced different interference colors depending

on the type of electrolyte and the voltage for oxidation applied. For both electrolytes, the film thickness increased with the voltage applied.

The concentration of the electrolyte produced minor shifts in color, negligible enough to establish a relation between color and thickness of the film for each electrolyte as a way to have a quick method to determine thickness.

The films produced at low voltages were homogeneous, with low roughness and amorphous. At higher voltages, sparks discharges were observed and porous films, with a degree of crystallinity, were produced. The voltage for spark discharge depended on the electrolyte.

Using H_2SO_4 1M as electrolyte, the films produced were compact, homogeneous and no crystalline phases of TiO_2 were detected up to 60V. From 70V to 80V, the films were porous and crystalline with the anatase phase formed, and above 80V, the rutile phase was formed. As the concentration of electrolyte increased, the conductivity increased and the homogeneous/amorphous to porous/crystalline transition was produced at lower voltages.

In the case of the H_3PO_4 1M electrolyte, there were no spark discharges or crystalline phases up to a voltage of 100V, which was the highest voltage used.

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MS21.P14

Evaluation of polychromators for angle-wavelength dispersive X-ray reflectometry

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We are developing a method for time-resolved measurements of the specular X-ray reflectivity [1], [2], [3]. In this method, a convergent X-ray beam with a one-to-one correspondence between angle and X-ray energy impinges onto the sample (Figure). The incident beam has a range of specular angles θ and wavelengths λ. The reflected X-rays are detected with a two-dimensional detector. The reflectivity curve in the range $q_{min}=4\pi\sin\theta_{min}/\lambda_{max}$ to $q_{max}=4\pi\sin\theta_{max}/\lambda_{min}$ can be measured in a single detector exposure, with no need to scan the sample, incident beam, or detector.

A key element of the reflectometer is the polychromator that produces the convergent X-ray beam. It consists of a Si crystal curved in two dimensions so that the Bragg angle and the angle to the horizontal plane change continuously with the position on the crystal. The curvature is adjusted to focus the incident white X-rays onto the sample.

In this report, different methods for bending the Si crystal to the desired shape are compared. They were evaluated using visible laser light. Size and shape of the reflected laser beam were recorded with a CCD camera at different distances from the focus. Finite-element simulations of the bending were done as well.

In the first method for bending the Si crystal, the crystal is fixed at two opposite edges. The crystal is bent by moving the edges independently. This method has the advantage that the curvature of the crystal can be adjusted during the experiment, but it is difficult to produce small focus sizes. In the second method, a Si crystal is pressed

to a copper support that was machined to the desired shape. Alignment is comparatively simple and small focus sizes are easier to achieve.
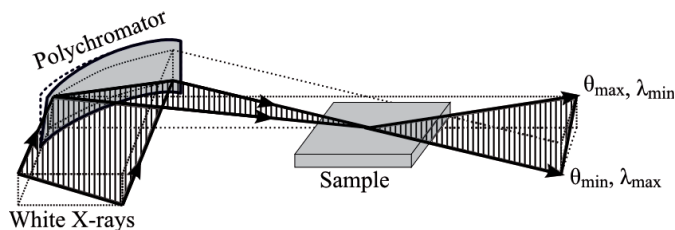
Setup for the X-ray reflectometry measurements.

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The five twin laws of gypsum. A theoretical analysis on interfaces of the growth contact twin

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All the twin laws of gypsum belong to the [010] zone, which is not an important one from the morphological point of view, as it ensues from the fact that the [010] direction does not correspond to a periodic bond chain (PBC), in the sense of Hartman-Perdok.

Our research starts from the experimental observation that the five twin laws of gypsum can be divided in two groups: to the first one belong the 100 and $\bar{1}$01 laws, both characterized by a high occurrence frequency, while to the second and less important group belong the 20$\bar{1}$, 001 and the 101 twin laws. Concerning both the natural and the solution grown crystals, the $\bar{1}$01 penetration twins have by far the highest occurrence frequency, while the $\bar{1}$01 contact twins were never observed; the 100 penetration twins are more frequently observed that the 100 contact twins, for every supersaturation value.

We considered the contact twins only and attempted at calculating the twin energy for each twin law, starting from suitable unrelaxed profiles of each twin interface and evaluating the convergence of the twin energy values once the interface was allowed to relax. Hence, we were able to model both the amount and the extent of the perturbations occurring at atomic level, for each twinned interface, and compare with the relaxed and untwinned one.

The most probable contact twin law results to be 100, the corresponding twin energy being 13 erg cm^{-2}. The twin energy of $\bar{1}$01 and 001 laws is higher by an order of magnitude, being 145 and 255 erg cm^{-2}, respectively. For the remaining laws the twin energy value is even more higher and the convergence is hard to obtain.

This should change our mind on the interpretation on the genetic mechanism of gypsum twins:
- the only "true" contact twin is 100, all other twins being related to penetration mechanism;
- the morphological confusion between 100 and $\bar{1}$01 laws can be experimentally avoided by the control of the optical extinction, according to the Cody's hypothesis;