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doi:10.1017/S1431927616007789

Microsc. Microanal. 22 (Suppl 3), 2016
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Electron Microscopy Observations Over the Processes Yielding to Obtaining TiO_2 from Natural Ilmenite Mineral

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Chlorination is an industrial process that has a better environmental performance when compared to processes such as the sulphate process for processing ilmenite mining for yielding titanium dioxide. This procedure allows obtaining TiO_2 polymorphs as function of the process variables subject to control. In the presence of a reducing agent, chlorination of ilmenite produced $TiCl_4$ as precursor of Ti and TiO_2 [1]. However, without the presence of a reducing agent, the selective chlorination of impurities is promoted, resulting in a solid product enriched in TiO_2 [2].

The aim of this study was to characterize the products of chlorination, with and without the presence of reducing agent, to identify the nature of polymorphs obtained through these two pathways similar processing, and to establish the influence of operational parameters such as temperature , chlorine gas flow and time in the process kinetics. Both, the starting material, a sandy beach, and the obtained products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X- ray spectroscopy (EDS), X-ray fluorescence (FRX), and transmission electron microscopy (TEM).

As observed in the micrograph of Fig. 1a, the as-received material was constituted essentially of coarse particles labeled as 1, corresponding to ilmenite particles, iron and titanium being major component as confirmed with the EDS analysis shown in Fig. 1b. Fig 1c show a EDS spectrum acquired from a impurity particle rich in barium, marked 2 in Fig 1a. Figure 2 refers to the product of chlorination without reducing agent, which gives a solid powder rich in TiO_2 rutile crystals, as confirmed in the EDS spectrum of the powder shown in Fig.2a. At this stage much of the iron has been eliminated as volatiles chlorides and this was confirmed by EDS (Fig. 2b) and XRD (Fig 2c) analysis. Figures 2d to 2f, show a typical robust TiO_2 rutile particle in bright and dark field TEM images respectively, together with the corresponding diffraction pattern.

In a similar fashion, chlorination with reducing agent allows to obtaining TiO_2 anatase that has been characterized in the set of micrographs of Fig. 3, where Figs. 3a to 3c show a typical TiO_2 anatase polycrystalline aggregate of nanoparticles in bright and dark field images together with its diffraction pattern, resulting from a high nucleation rate of clusters . A HRTEM image shown in Fig 3d, which corresponds to the marked box in Fig 3b, corroborates that this processing route leads to obtaining as final product TiO_2 nanoparticles. Fig. 3e confirms that this product is TiO_2 anatase [3].

References:

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[2]. L.M. Cáceres, I.G. Solorzano, E. Brocchi, CIAM Symposium**,** Proceedings Brazilian Society for Microscopy and Microanalysis, 2015**.**
[3] The authors are grateful to LaBNano /CBPF for the access of TEM and XRD, the financial support of CAPES, CNPq and FAPERJ (Brazil), and the technical assistance Dr N. Midory.

https://doi.org/10.1017/S1431927616007789 Published online by Cambridge University Press

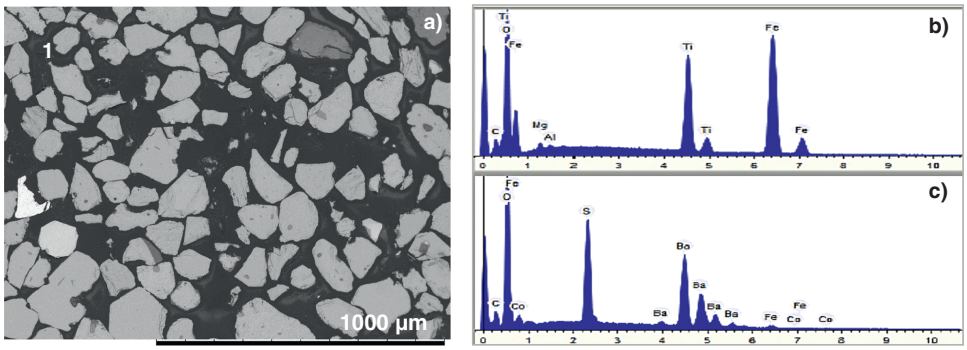

Figure 1. a) SEM of as received mineral. b) EDS from particle labeled 1 (ilmenite) in a. c) EDS from particle labeled 2 in a. Ba-rich

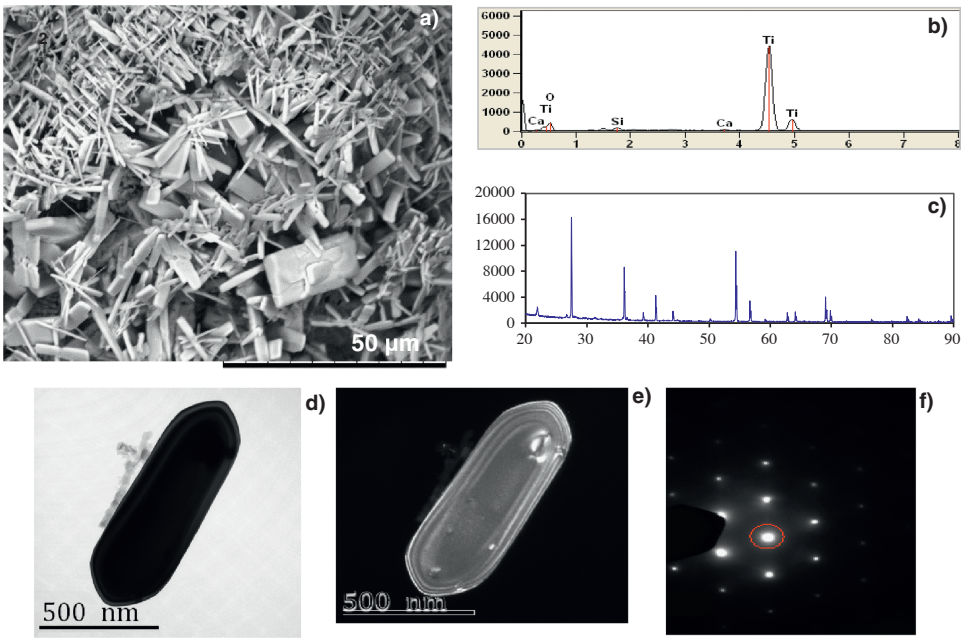

Figure 2. a) SEM b). EDS. c) XRD of crystals TiO_2 rutile-rich. d), e), f) TEM Bright field⁄dark field pair, corresponding electron diffraction pattern of pure rutile TiO_2 particles.

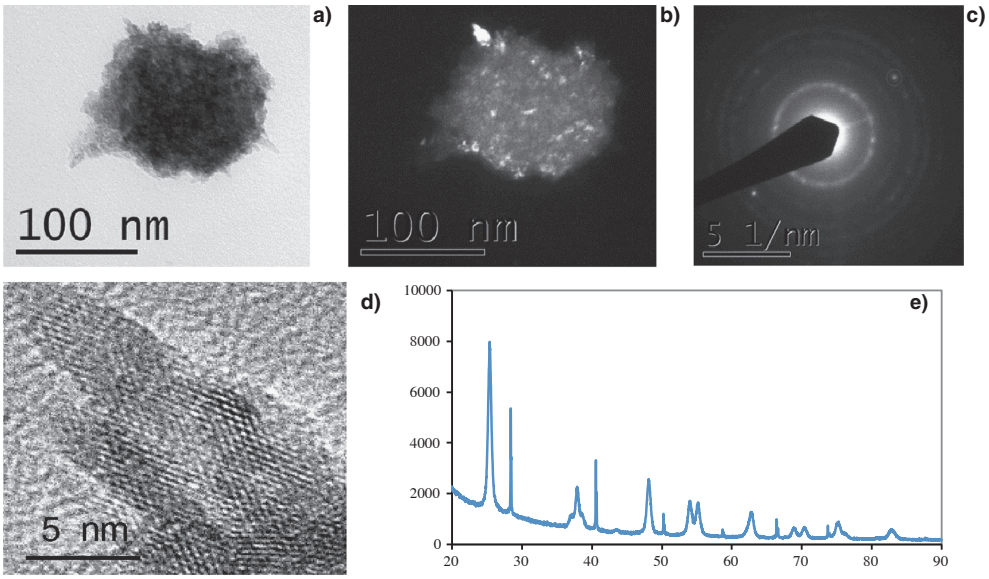

Figure 3. a), b), c), TEM Bright field⁄dark field pair, corresponding electron diffraction pattern of TiO_2 Anatase particles. d) HRTEM of nanocrystals of TiO_2 Anatase-rich. e) XRD of crystals TiO_2 Anatase-rich

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