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Studies on pore morphology of titanium and its oxide by small angle neutron scattering

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Abstract. Titanium metal bodies have been prepared from the sintered powder compacts of TiO_2 by a novel molten salt electrochemical approach, known as FFC Cambridge process. The phase and compositional characterizations of both Ti and TiO_2 have been carried out by X-ray diffraction. The pore morphologies of sintered TiO_2 pellet and the metallic Ti pellet, obtained after electrochemical reduction have been studied by SANS over a scattering wave vector q range of 0.003–3.5 nm^{-1} using a double crystal diffractometer and a pin-hole collimated SANS instrument. In the case of reduced metal pellet, average pore size was found to be larger than that of the oxide pellet as the voids left behind after the oxygen atoms left the oxide matrix, could not coalesce.

Keywords. Titania; titanium; pores; neutron scattering.

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1. Introduction

Titanium and its alloys are endowed with four unique characteristics: (1) light weight (∼40% lighter than stainless steel), (2) excellent corrosion resistance even in sea water (∼4 times better than stainless steel), (3) higher specific strength (∼1800 MPa, similar to stainless steel) and (iv) good biocompatibility. The combination of these properties makes these materials most sought after for a variety of applications. The conventional method of the production of this metal involves multi-step operations and hence is cost intensive. A recent discovery in the field of molten salt electrochemistry has made it possible to reduce different oxides to their respective metals, in just one single step, thereby, rendering the process attractive from the viewpoint of economic viability so far as up-scaling of the process is concerned. In this process, the oxide is made as the cathode, which is polarized against a graphite anode in a pool of molten $CaCl_2/CaCl_2$-based electrolyte under potentiostatic condition. During polarization, oxygen present in the cathode gets ionized to O^{2-}, which subsequently gets discharged as the oxides of carbon at the anode surface. After sometime, the cathode gets transformed to the constituent metal [1,2]. The presence of open porosity in the oxide body helps in achieving reduction at a

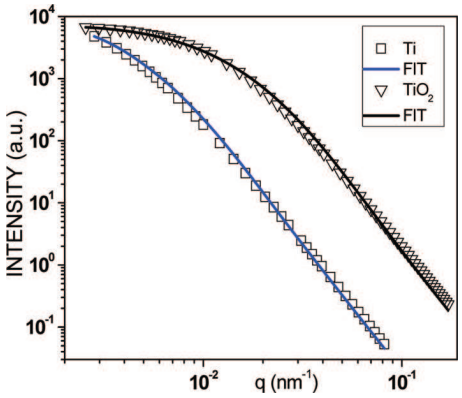

Figure 1. DCD SANS data of TiO_2 and metallic Ti specimens (with fit).

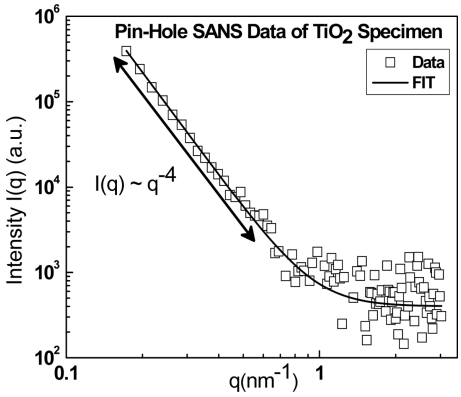

Figure 2. Pin-hole SANS data of TiO_2 specimen.

relatively faster rate. The manner in which the total pore volume is distributed with respect to pore size is more informative and important than a simple measure of porosity value (total pore volume). The metal, obtained after the reduction stage, was also found to have some amount of porosity. The percentage of the porosity in the reduced metal was observed to depend upon several process parameters during the reduction stage. Among the parameters, the porosity of the oxide precursor plays a crucial role in determining the efficacy of the overall reduction process. Too high an oxide porosity leads to disintegration of the pellet whereas a very low porosity (<10%) slows down the overall kinetics of the process of oxygen removal. In order to gain an insight into the role of porosity, it is very essential to study the size, shape and size distribution of pores in the sintered oxide pellet, prior to reduction as well as the metal body obtained after reduction. Small angle neutron scattering (SANS), which is a non-intrusive and non-destructive technique, provides valuable information so far as the characterization of the porous materials is concerned [3–5]. Current investigations are on so as to correlate the achievable metal purity with ideal pore morphology of the oxide precursor.

2. Experimental

Finely powdered (1–2 μm particle size) and high purity TiO_2 was pressed into pellets. The green pellets were sintered at 1150°C temperature for 2 h. The porosity of the sintered pellet was determined to be of 30% of the total pellet volume. XRD of the sintered pellet was first recorded prior to the reduction. Again XRD of the as-reduced metal was recorded after the reduction was over. Then, the sintered TiO_2 pellet and the reduced metallic pellet were subjected to SANS investigations. In order to obtain information about a broad size-range of inhomogeneities in the specimens, combination of measurements were performed in different regions of wave vector transfer q by using a double crystal diffractometer (DCD) and a pinhole SANS diffractometer. The accessible q range of the DCD is 0.003–0.17 nm^{-1}

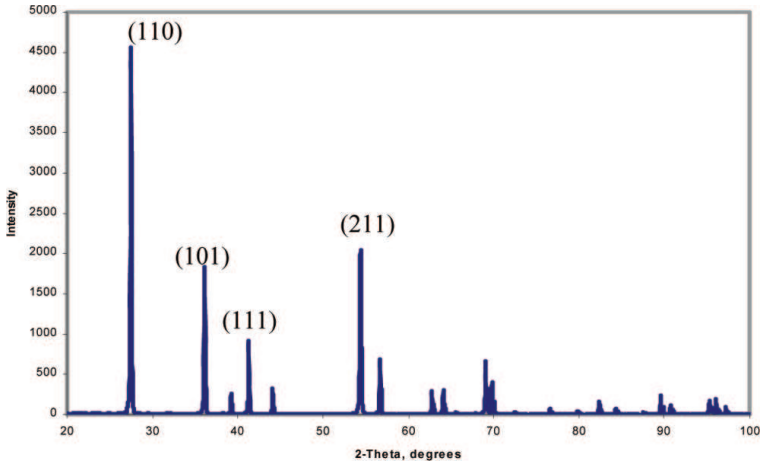

Figure 3. XRD of oxide precursor (TiO_2).

and that of the pin-hole instrument is 0.17–3.5 nm^{-1}. Both the instruments are installed at the Guide Hall of Dhruva reactor at Trombay, India [6,7]. SANS signals from both sintered TiO_2 pellet and metallic Ti pellet were observed in the wave vector q range of 0.003–0.17 nm^{-1}. Slit-height corrected [8] SANS profiles of the specimens are shown in figure 1. But scattering signal in the q range of 0.17–3.5 nm^{-1} shown in figure 2 was observed only from the TiO_2 specimen and not from the metallic specimen.

3. Results and discussion

3.1 *XRD characterization*

All the peaks in figure 3 for powder XRD profile of typical TiO_2 (sintered), matched with those found in the JCPDF profile of rutile. Figure 4 shows a typical profile of a reduced metal, obtained after the reduction stage. All the lines in the figure match with the XRD profile, obtained for a typical and high purity titanium sponge, obtained by the conventional Kroll reduction process. This XRD profile shows the absence of any other compounds/precipitates although a variety of chemicals were used during the reduction as well as subsequent cleaning (of the reduced metal) processes.

3.2 *SANS characterizations*

SANS profiles of both sintered TiO_2 pellet and metallic Ti pellet show nearly Gaussian ($\exp(-R^2q^2)$) and q^{-4} variation of intensity at very low q and intermediate (after the bent) q regimes, respectively. Scattering has been modelled assuming two phase system and near spherical pore morphology with size polydispersity in the specimens. A q^{-4} variation of scattering intensity from the specimens at higher

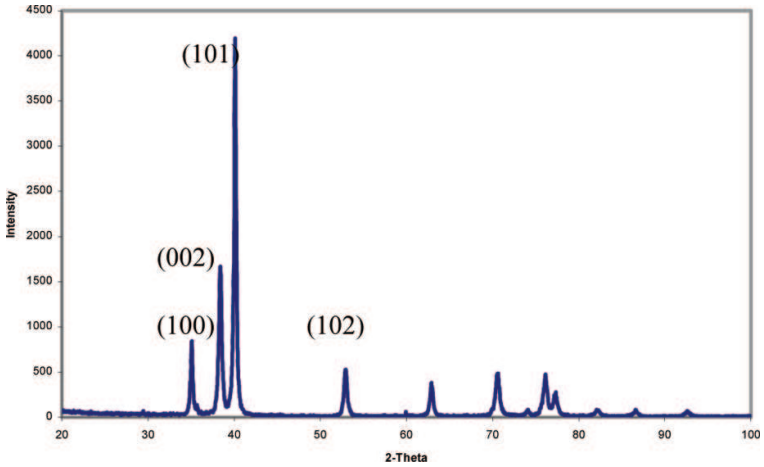

Figure 4. XRD of metallic Ti specimen.

values of q indicates smooth surface morphology of the pores. The model SANS intensity can be expressed as

$$I(q) = C \int_{R_{\min}}^{R_{\max}} P(q,R)D(R)(V(R))^2 \mathrm{d}R. \tag{1}$$

In eq. (1) $P(q)$ and $V(R)$ denote the square of the form factor and volume of the pore, respectively. The constant C is independent of scattering vector q but depends on sample and instrument parameters. $D(R)$ is the size distribution of pores in the specimens. Reasonably good fit has been obtained by applying log-normal distribution for model fitting the profiles and is given by the expression

$$D(R) = \frac{1}{\sqrt{2\pi\sigma^2 R^2}} \exp\left[-\frac{[\ln(R/R_0)]^2}{2\sigma^2}\right], \tag{2}$$

where σ is the variance and R_0 is the geometric mean of the distribution. $R_{\min}$ and $R_{\max}$ are the limits of integration which depend on window (q-range) of measurement. Estimated values of parameters of pore size distributions of the precurser TiO_2 pellet and reduced metallic Ti pellet are mentioned in table 1.

It is observed from pore size distributions in figure 5 that in the case of metallic Ti body obtained from the TiO_2 specimen after electrochemical reduction, the average pore size is larger than that of the oxide precurser. This is expected as after the oxygen atoms left the oxide matrix, the voids, left behind could not coalesce.

4. Conclusions

It was observed that porosity of the TiO_2 precursor played a very crucial role in determining the efficacy of the overall reduction process. While too high a porosity resulted in the disintegration of the pellet, during the reduction stage, a very low

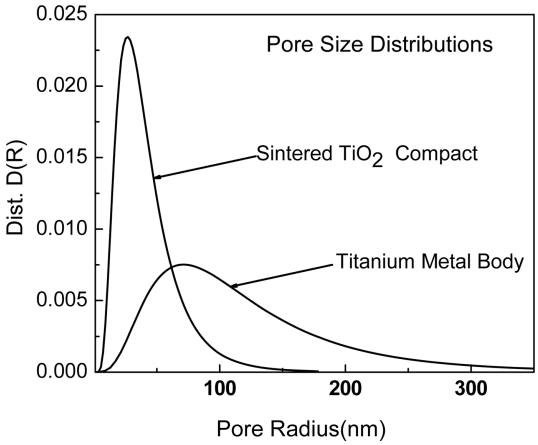

Figure 5. Pore size distributions of TiO_2 and Ti specimens.

Table 1. Estimated values of important parameters of the pore size distributions.

Specimen	R_0 (nm)	σ	$\langle R \rangle$ (nm)	$[\langle R^2 \rangle - \langle R \rangle^2]^{0.5}$ (nm)
Sintered TiO_2 pellet	36.0	0.550 ± 0.005	41.9	24.9
Metallic Ti body	107.0	0.590 ± 0.005	127.3	81.7

porosity (<10%) was observed to slow down the overall kinetics of the oxygen removal process. Also, experiments did suggest that not only the porosity of the oxide precursor, but also the pore size distribution was another crucial parameter for the success of the process. Earlier, it was presumed that the presence of a range of pore sizes gave a relatively better (reduced) metal. SANS conclusively confirmed this presumption. Current investigations are on so as to correlate the achievable metal purity with ideal pore morphology of the oxide precursor.

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