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Thermochimica Acta 298 (1997) 47–54

thermochimica
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Thermal decomposition of fibrous $TiOSO_4 \cdot 2H_2O$ to TiO_2

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Received 30 October 1996; accepted 23 May 1997

Abstract

Fibres of $TiOSO_4 \cdot 2H_2O$ are used as precursor material for the preparation of TiO_2 fibres and/or particles with controlled morphology. This is achieved by heat treatment in air in the temperature range 580–1250°C for times ranging from 0.1 to 100 h. Thermogravimetric studies showed that water was expelled at temperatures below 500°C, and the conversion of $TiOSO_4$ to TiO_2 took place in the temperature range 540 to 580°C. Heat treatment at temperatures below 650°C yielded anatase, whereas rutile started to appear after extended holding times (100 h) at 650°C. Heat treatment at 950°C and higher yielded monophasic rutile samples. In the temperature region 650–950°C, both anatase and rutile appeared in the product in various relative amounts depending on the temperature and time of annealing.

The original fibre morphology was preserved in the low-temperature region where anatase was formed. In the rutile region, however, the fibres became degraded due to growth of TiO_2 particles, resulting in pearl strings of particles. The final morphology of the product depended strongly on the time and temperature of heat treatment.

The time dependence of the conversion of anatase to rutile at 750°C was monitored. The rate of conversion is rather high in the beginning of the process but substantially slower at the end. The obtained data can be fitted by the extended rate law proposed by Prout–Tomkins. © 1997 Elsevier Science B.V.

Keywords: Thermal decomposition; Fibrous; TiO_2

1. Introduction

Titanium dioxide (TiO_2) occurs in three crystalline modifications, that is, anatase, brookite, and rutile. Anatase and brookite have been reported to transform to the high-temperature modification rutile when heated to temperatures exceeding 700–900°C [1].

The anatase modification of TiO_2 is used in the so-called Grätzel solar cell, named after its inventor [2]. In this cell, submicron particles of anatase are used as electrode material. These particles are normally prepared by hydrolysis of an appropriate Ti–alkoxide solution. In this study we have shown that a fibrous TiO_2 material with the anatase structure can be prepared from $TiOSO_4 \cdot 2H_2O$ fibres. The transformation of anatase to rutile has also been studied as function of both temperature and time. The morphology of the products has been studied in scanning and transmission electron microscopes.

2. Experimental

$TiOSO_4 \cdot 2H_2O$ fibres (Tioxide Chemicals Ltd.) were used as precursor material. The fibres are white, with a diameter of 1–2 μm, and length of 30–100 μm (see Fig. 1). The X-ray powder pattern of the precursor

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PII S0040-6031(97)00206-2

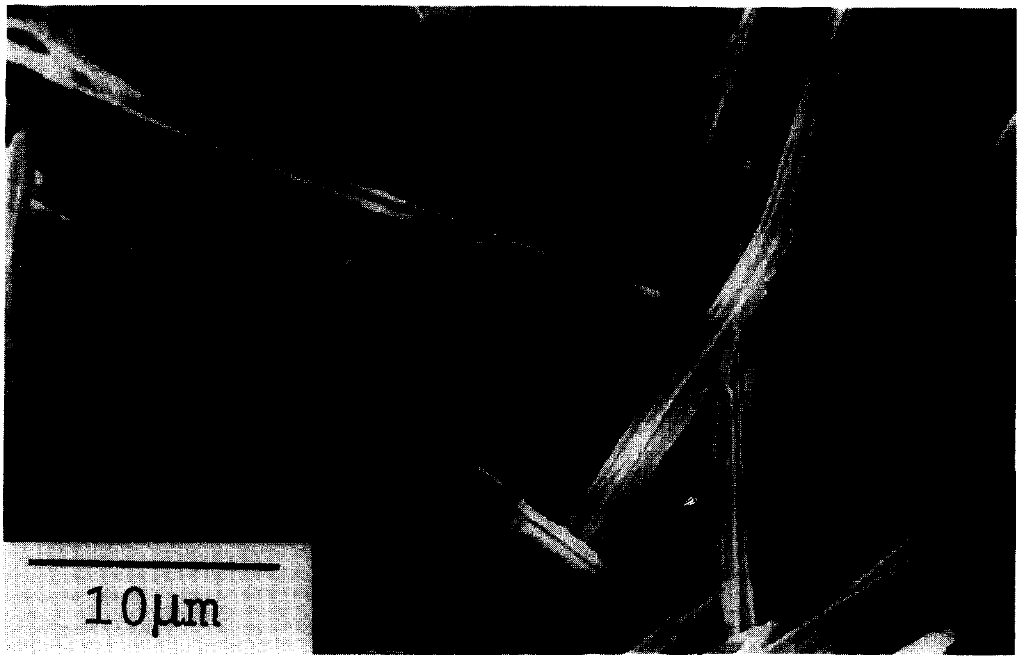


Fig. 1. Micrograph of the $TiOSO_4 \cdot 2H_2O$ fibres used as precursor material. The fibres are approximately 1 μm in diameter and 30–100 μm in length, and they show smooth surfaces.

material revealed that it is monophasic and that $TiOSO_4 \cdot 2H_2O$ has an orthorhombic unit cell with $a = 16.6509$ Å, $b = 9.3509$ Å, and $c = 3.5022$ Å, which is in close agreement with JCPDS card No. 14-503.

The thermal decomposition of $TiOSO_4 \cdot 2H_2O$ in air was followed in a thermogravimetric unit (TG, Perkin Elmer TGA7), using a heating rate of 5°C/min.

The time and temperature dependence of the conversion of anatase to rutile has been monitored. Heat treatment experiments were made in air at different temperatures ranging from 580 to 1250°C. The samples were held for 0.1, 1, 10, and 100 h at the selected temperatures. The experiments were performed in a programmable Nabertherm furnace using alumina crucibles. The heating rate was 700°C/h.

A separate study of the rate of conversion of anatase to rutile was made at 750°C. In that study, samples were heat treated for 1, 2, 4, 6, 8, 10, 20, 40, 60, 100, and 200 h.

The products were characterised by their X-ray powder diffraction patterns (XRD), obtained by a Guinier–Hägg focusing camera. $CuK_{\alpha 1}$ radiation ($\lambda = 1.5405981$ Å) was used, and finely powdered silicon ($a = 5.430880(35)$ Å) was added as an internal standard. The recorded films were evaluated in an automatic film scanner [3]. Unit cell parameters were refined with the program PIRUM [4]. The amounts of rutile and anatase in the heat-treated samples were determined from relative intensity ratios according to a method developed by Spurr and Myers [5].

The morphology and composition of the fibres and particles were investigated in a high-resolution scanning electron microscope (SEM, JEOL 880) equipped with an energy-dispersive spectrometer (LINK *ISIS*), which allows detection of boron and heavier elements. The polycrystalline nature of the fibres obtained after annealing at low temperatures was studied in a transmission electron microscope (TEM, JEOL 2000FX).

3. Results and discussion

The TG record of $TiOSO_4 \cdot 2H_2O$ is shown in Fig. 2. The weight loss below 540°C can be ascribed to the loss of water. In the temperature region 540–580°C the conversion to TiO_2 takes place. The thermal decomposition of $TiOSO_4 \cdot 2H_2O$ to TiO_2 thus occurs in two steps:

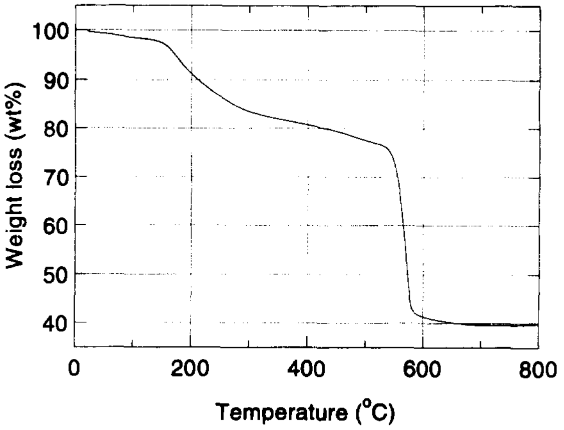


Fig. 2. TG curve of $TiOSO_4 \cdot 2H_2O$, recorded in air with a heating rate of 5°C/min. The weight loss below 540°C can be ascribed to the loss of water. In the temperature region 540–580°C $SO_2(g)$ and $O_2(g)$ are lost.

$$TiOSO_4 \cdot 2H_2O(s) \rightarrow TiOSO_4(s) + 2H_2O(g) \quad (1)$$

$$TiOSO_4(s) \rightarrow TiO_2(s) + SO_2(g) + \tfrac{1}{2}O_2(g) \quad (2)$$

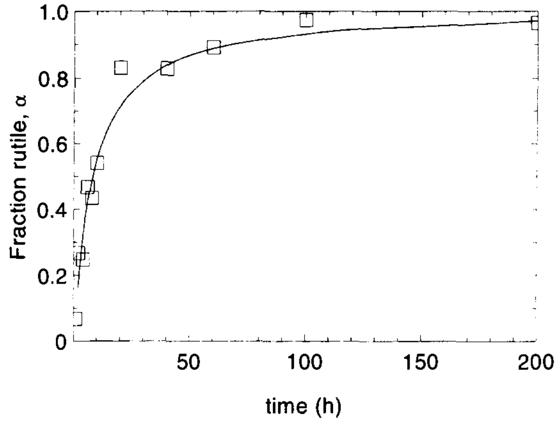


Fig. 4. Fraction rutile (α) formed in $TiOSO_4 \cdot 2H_2O$ samples heat treated at 750°C, plotted versus the time of annealing.

No remnants of sulphur were found in the annealed samples. The results of the heat treatment experiments are summarised in Fig. 3. Heat treatment at temperatures lower than 650°C yielded the anatase modification of TiO_2 for all annealing times, whereas a minor amount of rutile was present in the sample heated at 650°C for 100 h. All samples heat treated at 950°C or above contained the rutile modification. In the temperature region 650–950°C both anatase and rutile were present in the product in various relative amounts, depending on the temperature and time of annealing (see Fig. 3). The observed temperature of the anatase-to-rutile transformation (650°C) is somewhat lower than previously reported [1].

The rate of conversion of anatase to rutile at 750°C was monitored by heat treating $TiOSO_4 \cdot 2H_2O(s)$ fibres for different times and then quenching them to room temperature. The degree of conversion of anatase to rutile, α, is plotted versus time in Fig. 4. The rate of conversion was rather high in the beginning of the process but substantially slower at the end. As shown in Fig. 5, the obtained data can be fairly

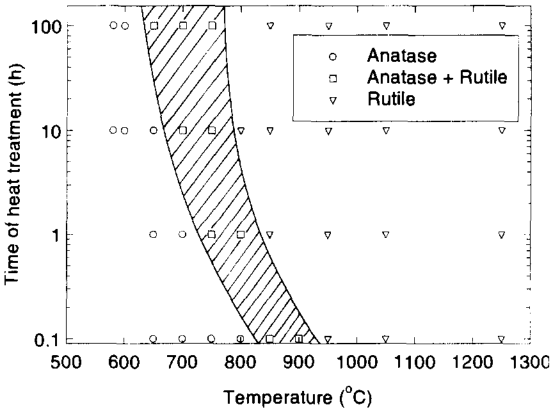


Fig. 3. Summary of the phase analysis of the $TiOSO_4 \cdot 2H_2O$ samples heat treated in the temperature interval 580–1250°C for different times.

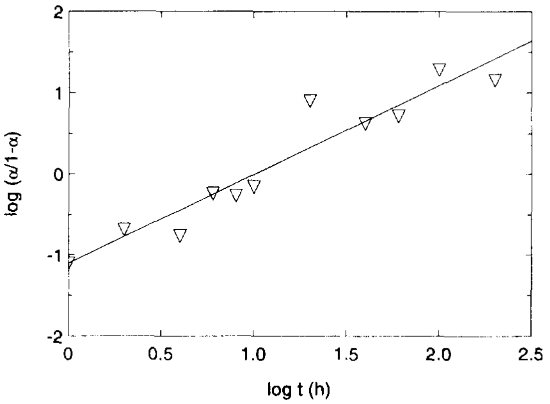
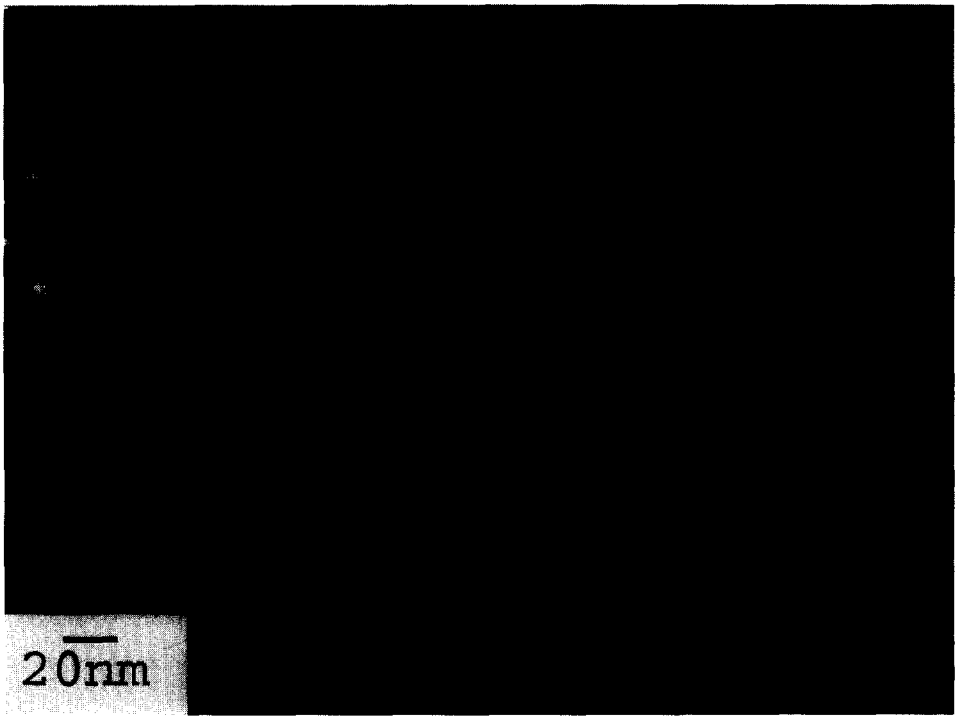


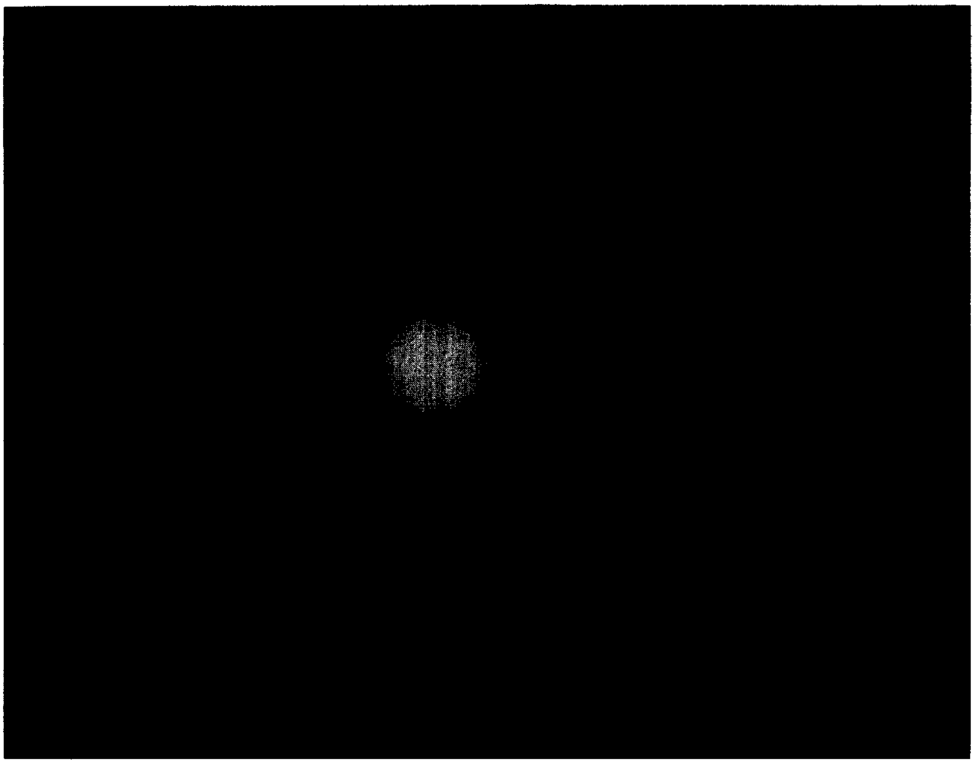
Fig. 5. A plot according to Prout–Tomkins of $\log(\alpha/1-\alpha)$ versus the logarithm of time for $TiOSO_4 \cdot 2H_2O$ samples heat treated at 750°C.

(a)



(b)

Fig. 6. $TiOSO_4 \cdot 2H_2O$ fibres heat treated at 650°C for 10h; (a) A SEM micrograph showing that the original fibre morphology is preserved after the heat treatment; (b) A TEM image showing the polycrystalline nature of the fibres. The size of the individual particles is about 20 nm; (c) The obtained circular electron diffraction pattern could be ascribed to anatase, and it verifies the presence of randomly oriented TiO_2 particles.



(c)

Fig. 6. (Continued)

(a)

Fig. 7. SEM micrographs of fibres heat treated for 10 h at (a) 850°C, (b) 950°C, (c) 1050°C and (d) 1250°C.

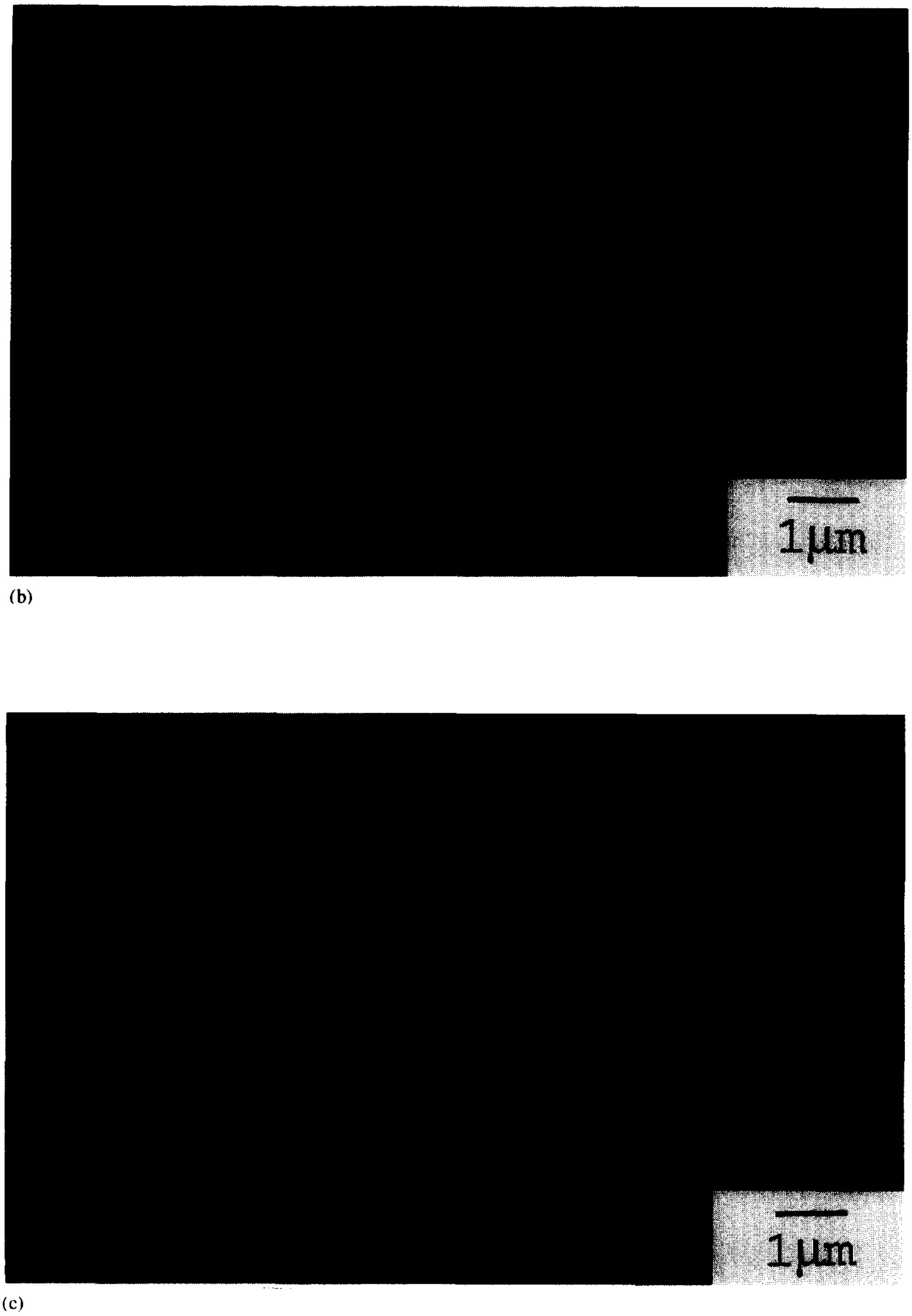
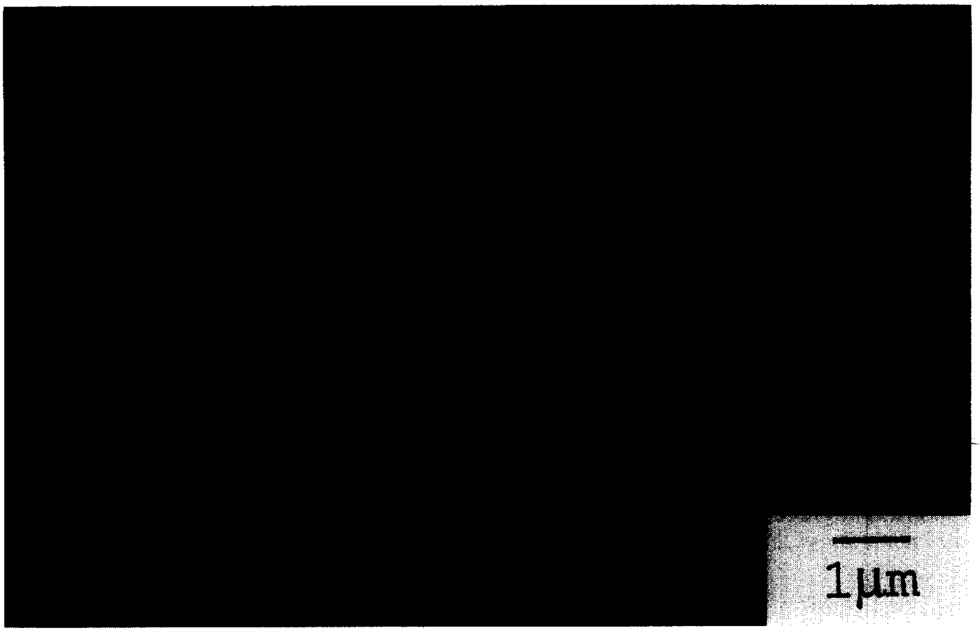


Fig. 7. (Continued)



(d)

Fig. 7. (Continued)

well fitted by an extended version of the rate law proposed by Prout–Tomkins [6], reading:

$$\log\left(\frac{\alpha}{1-\alpha}\right) = k \cdot \log(t) + C \qquad (3)$$

The mechanism leading to this equation is considered to be the appearance of branching nuclei with interference between the nuclei during growth, and it is derived on the basis of a variation in the rate of branching with time. The formation of nuclei appears to be unimportant. The TEM studies described below seem to support such an interpretation.

The original fibre morphology is preserved when anatase is formed (see Fig. 6(a)). The anatase particle size is very small (≈20 nm), and crystals with random orientations nucleated both at the surface and throughout the bulk of the fibres (see Fig. 6(b) and Fig. 6(c)).

Heat treatment in the rutile temperature region resulted in much coarser TiO_2 particles. After oxidation at 850°C for 10 h, the primary fibrous morphology still remained, but the formed rutile particles had coarsened to such an extent that the fibre surfaces were no longer smooth (see Fig. 7(a)). At 950°C, individual rutile particles could easily be identified (see Fig. 7(b)). After oxidation at 1050°C, the fibres were transformed to strings of TiO_2 pearls (Fig. 7(c)). The pearl-like TiO_2 particles had a diameter of less than 1 µm. After oxidation at 1250°C, the pearls tended to coalesce, forming larger particles with diameters of 1–4 µm (Fig. 7(d)).

The coarsening of the particles is most pronounced in the temperature region where rutile is formed, that is, above 950°C. The observation that the anatase particles are of submicron size and do not coarsen on prolonged annealing is most probably due to the fact that at these comparatively low annealing temperatures the reaction(s) responsible for the coarsening process are kinetically hindered.

4. Summary

From thermogravimetric data we know that full conversion of $TiOSO_4{\cdot}2H_2O$ to TiO_2 has occurred at 580°C. Annealing $TiOSO_4{\cdot}2H_2O$ between 580–650°C yielded TiO_2 with the anatase structure, while rutile started to appear at 650°C after extended times of heat treatment (100 h). All samples heat treated at 950°C or above contained the rutile modification. In the temperature region 650–950°C both anatase and rutile were present in the product. The original fibre morphology was preserved after oxidation in the anatase temperature region. The TiO_2 particles did not coarsen markedly in this region. At higher temperatures, larger rutile particles were formed, and the fibres became degraded. It can furthermore be noted that the brookite modification of TiO_2 never formed.

The time dependence of the conversion of anatase to rutile at 750°C was monitored, and the data obtained could be fitted by an extended Prout–Tomkins rate law.

Acknowledgements

We are grateful to Dr. Gunnar Svensson for his assistance in connection with the TEM studies. This study has been financially supported by the Swedish Board for Technical Development.

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