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ETA STUDIES OF THE SURFACE LAYER OF TITANIUM OXIDE POWDERS PREPARED BY VARIOUS GRINDING AND SIEVING TREATMENTS

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ABSTRACT

In order to examine the effects of both grinding and sieving treatments on the surface layer of powders, the emanation thermal analysis (ETA) technique was applied in the temperature range of 25–1400 °C for characterization of the near surface (< 50 nm thick) of 36 titanium oxide powders (rutile) with various preparation histories in terms of the grinding and sieving treatments used. Two pulverizers (planetary pulverizer and mortar grinder) and two grinding procedures (dry and wet) were used with various grinding times. The results obtained are as follows: (a) the influence of the methods of preparation of the powders appears as a variation in the ETA peaks in the first run; (b) the sieving effect appears mainly as the enlargement of the ETA peak IIa; (c) the grinding effect appears remarkably only in the initial grinding step; and (d) the ETA results are supported by the scanning electron microscopy observations.

INTRODUCTION

The thermal characterization of the surface layer of various iron oxide and aluminum oxide powders, each prepared by different grinding and sieving procedures, has been carried out previously by means of emanation thermal analysis (ETA) using ^{226}Ra as the parent isotope [1,2]. In the present study, in order to examine the effects of both grinding and sieving treatments on the surface layer of powders in further detail, the ETA technique was applied to titanium oxide powders with various pulverizing treatments.

EXPERIMENTAL

Materials

Titanium oxide (rutile) as a starting material, T1, was prepared from commercial anatase (Kanto) by calcining at 1200 °C for 5 h. The sample T1

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TABLE 1

Preparation methods and physical properties of samples: planetary micro-pulverizer; dry grinding

Sample No.	Grinding time (min)	Particle size (μm)	D_m (μm)	S_{BET} ($m^2\ g^{-1}$)	Fig. No. of SEM	Fig. No. of ETA
T1	0	Unsieved	32.5	0.2	6	1, 3
T2	0	> 32				1
T3	0	20–32				1, 4(A)
T4	0	10–20				1, 4(B)
T5	15	Unsieved	3.9	0.3	6	2(A), 3
T6	15	> 32				2(A)
T7	15	20–32				2(A), 4(A)
T8	15	10–20				2(A), 4(B)
T9	15	5–10				2(A)
T10	15	< 5				2(A), 4(C)
T11	30	Unsieved	3.9	0.4	6	2(B), 3
T12	30	> 32				2(B)
T13	30	20–32				2(B), 4(A)
T14	30	10–20				2(B), 4(B)
T15	30	5–10				2(B),
T16	30	< 5				2(B), 4(C)
T17	60	Unsieved	4.1	0.6	6	2(C), 3
T18	60	> 32			7	2(C)
T19	60	20–32			7	2(C), 4(A)
T20	60	10–20			7	2(C), 4(B)
T21	60	5–10			7	2(C)
T22	60	< 5			7	2(C), 4(C)
T23	180	Unsieved	4.9	0.5	6	2(D), 3
T24	180	> 32				2(D)
T25	180	20–32				2(D), 4(A)
T26	180	10–20				2(D), 4(B)
T27	180	5–10				2(D)
T28	180	< 5				2(D), 4(C)

is polycrystalline having median diameter (D_m) 32.5 μm, it consists of fine particles of 1–2 μm diameter (Fig. 6, T1 in series A and B). The dried TiO_2 powders thus obtained were ground for various lengths of time using a planetary micro-pulverizer (Fritsch P-7) equipped with a cylindrical vessel (12-ml volume) and four balls (12-mm diameter) which are all made of alumina. The dry-grinding procedure was used and the vessel was rotated at 2700 rpm. The preparation methods and some physical properties of the ETA samples (T1 to T28) are summarized in Table 1. In order to examine the effects of another pulverizer, a mortar grinder (Fritsch P2) equipped with alumina mortar and pestle (150-ml volume) was used under the conditions of 80 rpm and two grinding procedures (dry and wet). The

TABLE 2

Preparation methods of samples without sieving treatment: motor grinder

Sample No.	Grinding time (min)	Grinding procedure	Fig. No. of SEM	Fig. No. of ETA
T51	15	Dry	8	5(A)
T52	30	Dry	8	5(A)
T53	60	Dry	8	5(A)
T54	180	Dry	8	5(A)
T55	15	Wet	8	5(B)
T56	30	Wet	8	5(B)
T57	60	Wet	8	5(B)
T58	180	Wet	8	5(B)

preparation methods of the samples (T51 to T58) are summarized in Table 2.

Sieving

The ground TiO_2 samples were dispersed with water containing a small amount of disperse medium and sieved to various size fractions using an automatic micro-sieve apparatus (Shodex PS, Model PS-2) which enables the particles to be effectively sieved under an operation of vacuum suction and ultrasonic vibration. The samples thus prepared in the various size fractions are summarized in Tables 1 and 2.

The samples were then characterized by scanning electron photomicrographs (SEM), in part, and the results were compared with those of the emanation thermal analysis (ETA). The apparatus and procedures for the ETA studies have been described previously [1].

RESULTS AND DISCUSSION

Emanation thermal analysis

The interpretation of ETA curves has been described previously [1]. The characteristic peaks in the ETA curves observed in this work were grouped into two main stages: stage I due to E_p (diffusion via intergranular and open pores) at temperatures lower than $T_s = (0.4 - 0.5)T_m$; and stage II due to E_d (bulk diffusion via a solid matrix). T_s and T_m are the starting temperature (K) of self-diffusion of the lattice ions and the melting point (K) of the samples, respectively. T_s was calculated as 579–791 °C (around 700 °C) for the rutile form. The ETA peaks corresponding to stages I and II are

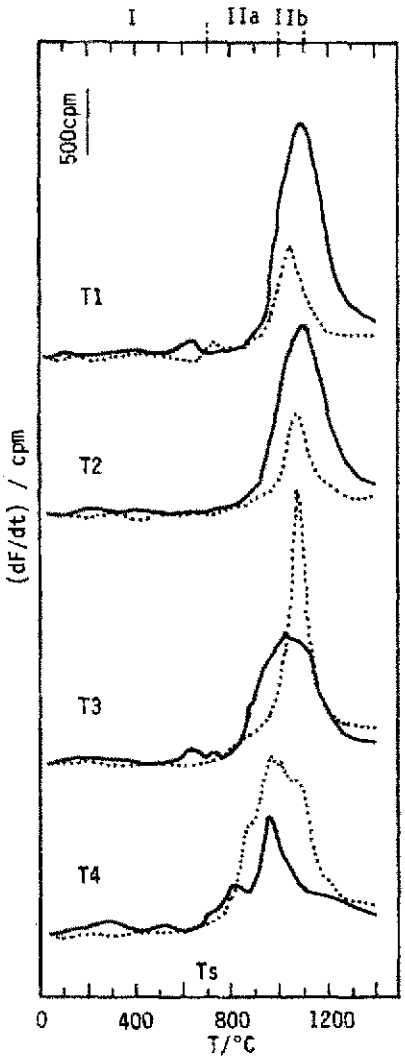

Fig. 1. ETA curves for non-ground TiO_2 powders (T1 to T4) sieved to various particle sizes (Table 1). A planetary pulverizer was used. (———) Run 1; (- - - - - -) run 2.

hereinafter referred to as peaks I and II, respectively. In many cases, peak II was split into two peaks, II_a and II_b.

Peak II_a corresponds to gas release from the defect structures such as the grain boundary (dislocation) or the amorphous part present in the surface layer (< 50 nm thick). Peak II_b corresponds to the typical peak II due to the bulk diffusion of gas. The temperature ranges of peaks I, II_a and II_b are estimated as 25–700 °C, 700–1000 °C and 1000–1100 °C, as indicated in Figs. 1 and 2 relating to ETA curves.

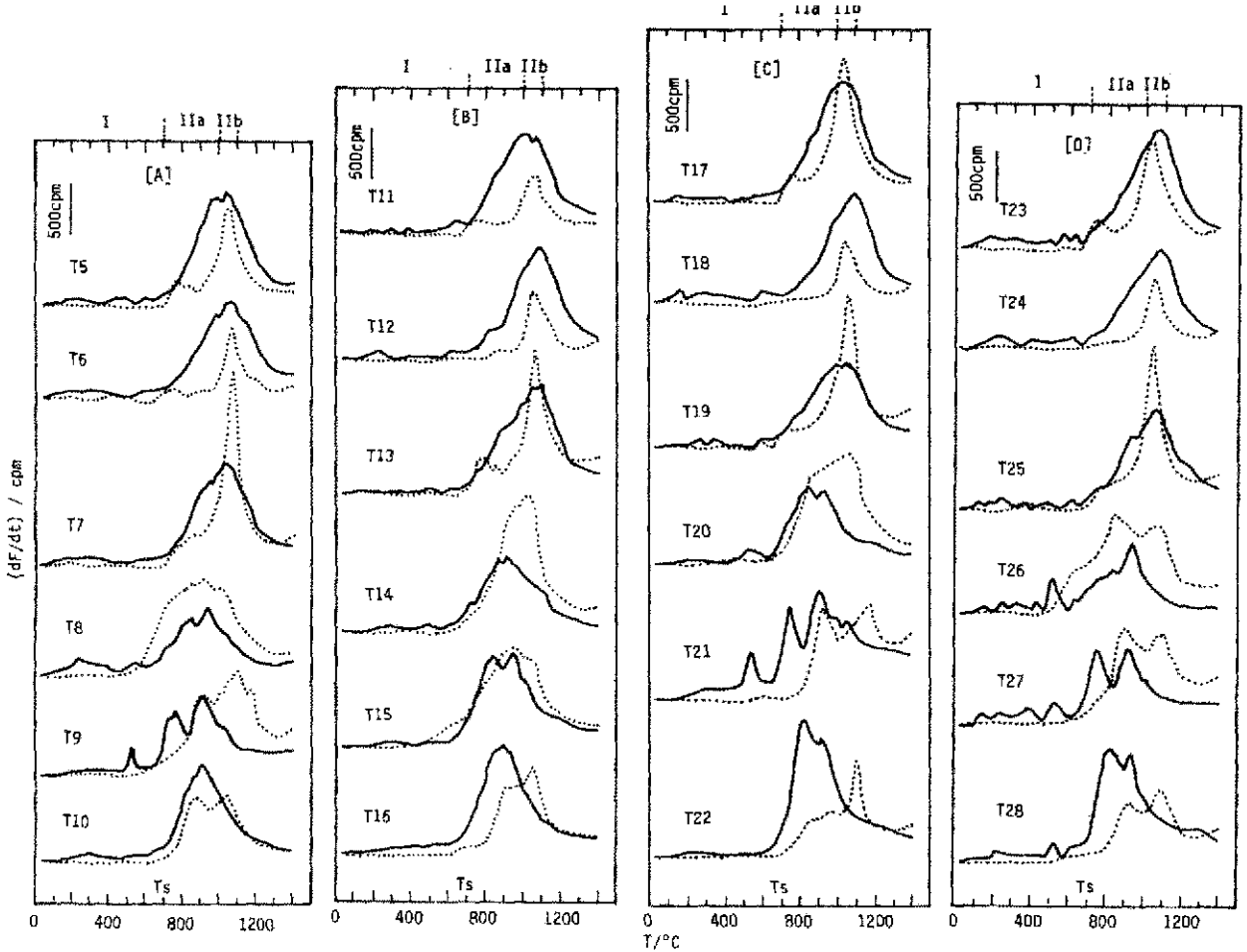

Fig. 2. ETA curves for TiO_2 powders (T5 to T28) sieved to various particle sizes (Table 1), after dry grinding for: (A) 15 min, (B) 30 min, (C) 60 min, and (D) 180 min. A planetary pulverizer was used. (——) Run 1; (- - - - -) run 2.

ETA curves

The ETA curves obtained in the first run (run 1) and the repeated run (run 2) are represented in the figures by solid and dotted lines, respectively. In general, peaks I and II (II_a, II_b) are variable in run 1, corresponding to the effects of grinding and sieving. However, in run 2 the curves become

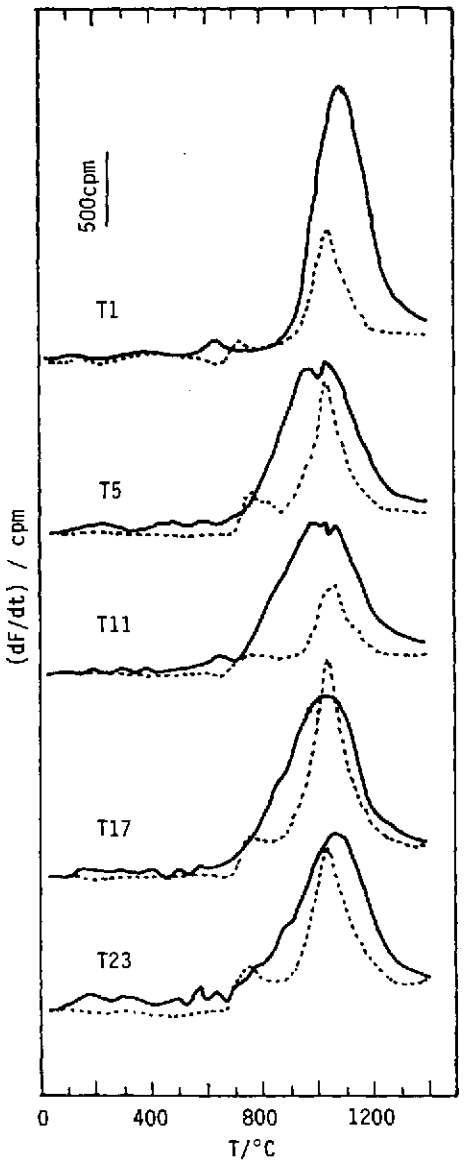

Fig. 3. ETA curves for unsieved TiO_2 powders (T1, T5, T11, T17 and T23), after dry grinding for 0–180 min (Table 1) using a planetary pulverizer. (———) Run 1; (- - - - -) run 2.

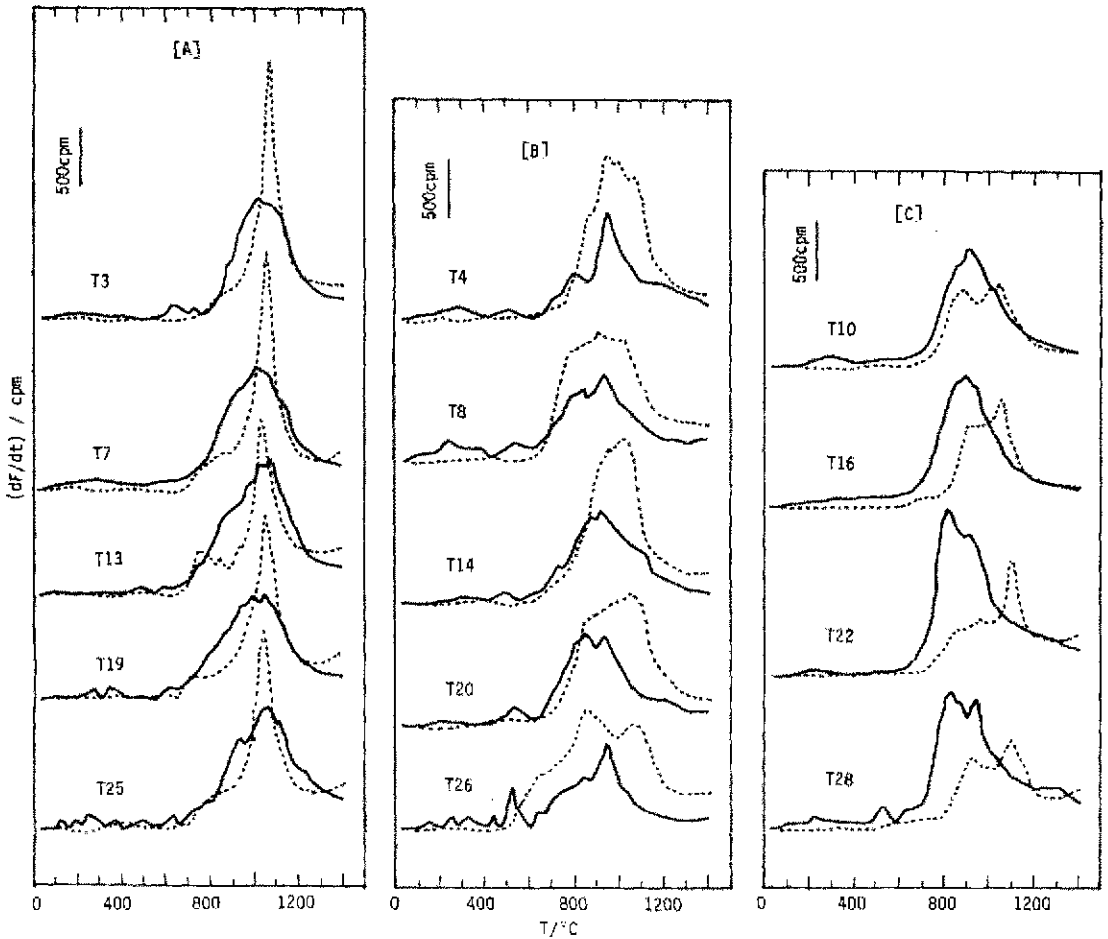

Fig. 4. ETA curves for TiO_2 powders sieved to particle sizes of (A) 20–32 μm, (B) 10–20 μm and (C) < 5 μm, after dry-grinding for 0–180 min (Table 1) using a planetary pulverizer. (———) Run 1; (- - - - - -) run 2.

typical of a rutile form with a simple peak (II_b) at 1000–1100 °C starting at about 700 °C (T_s); the peaks corresponding to stage I disappear due to annealing in the course of increasing temperature in run 1. Therefore, it is thought that the influence of the method of preparation of the powders on the surface layer appear as a variation in the ETA peaks in the first run.

Figure 1 shows the ETA curves for non-ground original TiO_2 powders (T1 to T4) which were sieved to various particle sizes (Table 1). The sieving

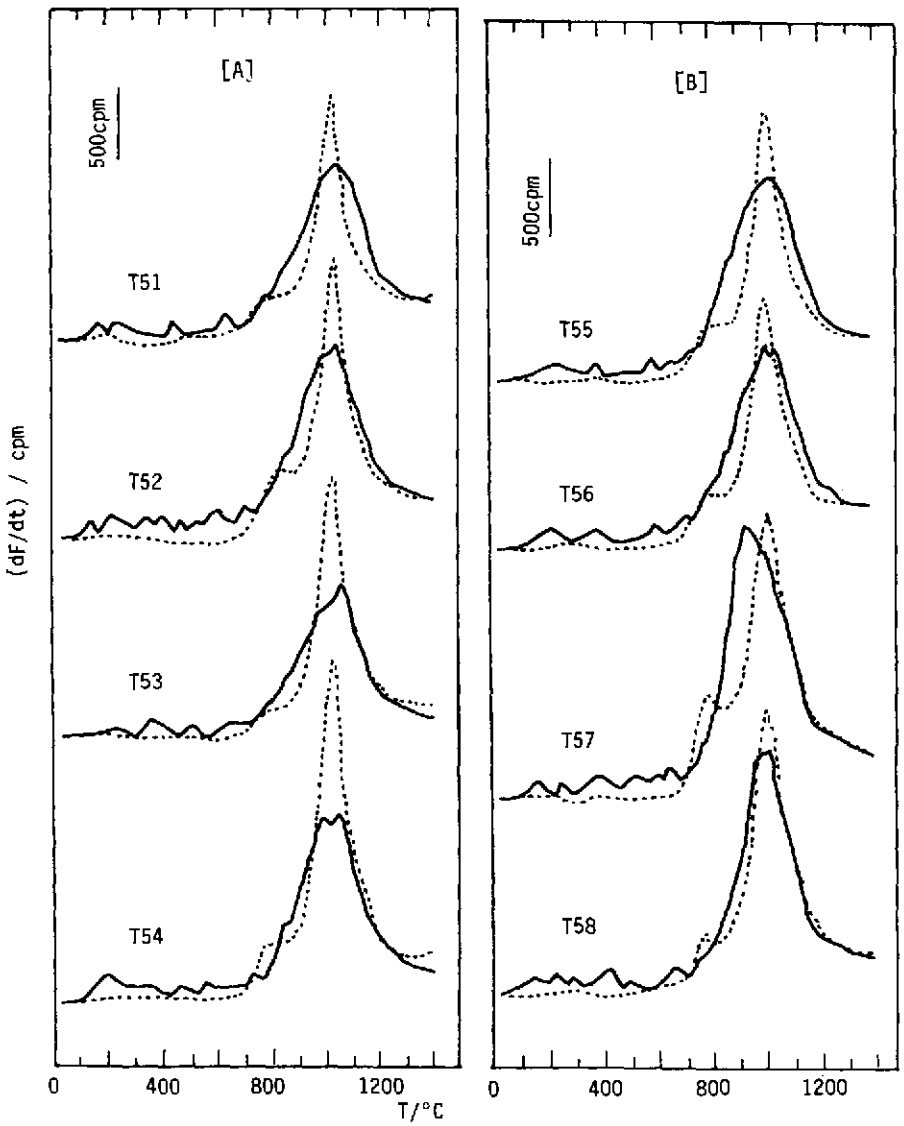

Fig. 5. ETA curves for unsieved TiO_2 powders (T51 to T58) ground for 15–180 min by two grinding procedures: (A) dry and (B) wet (Table 2). A mortar grinder was used. (———) Run 1; (- - - - -) run 2.

effect appears as a shift in peak II in run 1 to a lower temperature range, i.e. as the enlargement of peak II_a.

Figure 2 shows the ETA curves for TiO_2 powders (T5 to T28) which were sieved to various particle sizes (Table 1), after dry-grinding for 15, 30, 60 and 180 min. A planetary pulverizer was used. In run 1, a pronounced sieving effect appears as the enlargement of peak II_a for all grinding times.

Of particular interest is the anomalous behaviour shown by the powders of 5–10 μm diameter. However, there is no pronounced effect of grinding for the samples which were ground for longer than 15 min.

Figure 3 shows the ETA curves for unsieved TiO_2 powders (T1, T5, T11, T17 and T23), dry ground for various times (0–180 min) with a planetary pulverizer. Peak II of the sample T5 with 15 min grinding treatment is shifted to a lower temperature range, compared with that of the non-ground sample (T1). However, the ETA curves of the samples having longer grinding time are all similar to the curve of sample T5. This means that the grinding effect appears only in the initial 15 min grinding step.

Figure 4 shows the ETA curves for the powders sieved to particle sizes 20–32, 10–20 and < 5 μm. This figure was designed using a part of the samples employed above to show that grinding for a long time is not as effective as expected, compared with sieving.

Figure 5 shows the ETA curves for unsieved TiO_2 powders (T51 to T58) which were ground for 15–180 min under two grinding procedures: dry and wet. In this experiment a mortar grinder was used. In spite of the different grinding method, the grinding effect again appears only in the initial 15 min of grinding; see Fig. 3.

SEM photographs

The SEM photographs of the unsieved TiO_2 powders (T1, T5, T11, T17 and T23), after dry-grinding for 0–180 min using a planetary pulverizer, are shown in Fig. 6. In order to clarify the aggregation state of the powders, the photographs are shown in two different scales. The samples shown in Fig. 6 correspond to those in Fig. 3. As described in Fig. 3, the fine particles of the 15 min grinding sample (T5) are apparently different from those of the non-ground sample (T1), but other samples ground for much longer times (T11, T17 and T23) are indistinguishable from sample T5.

Figure 7 shows the SEM photographs of TiO_2 powders (T18 to T22) sieved to various particle sizes (Table 1), after grinding for 60 min, using a planetary pulverizer. In order to clarify the aggregation state of the powders, the photographs are shown in three different scales. These photographs show that the sample powders which were ground and disaggregated to various particle sizes were sieved effectively by the automatic micro-sieve apparatus. The finest sample (T22), sieved to < 5 μm, appears as if the

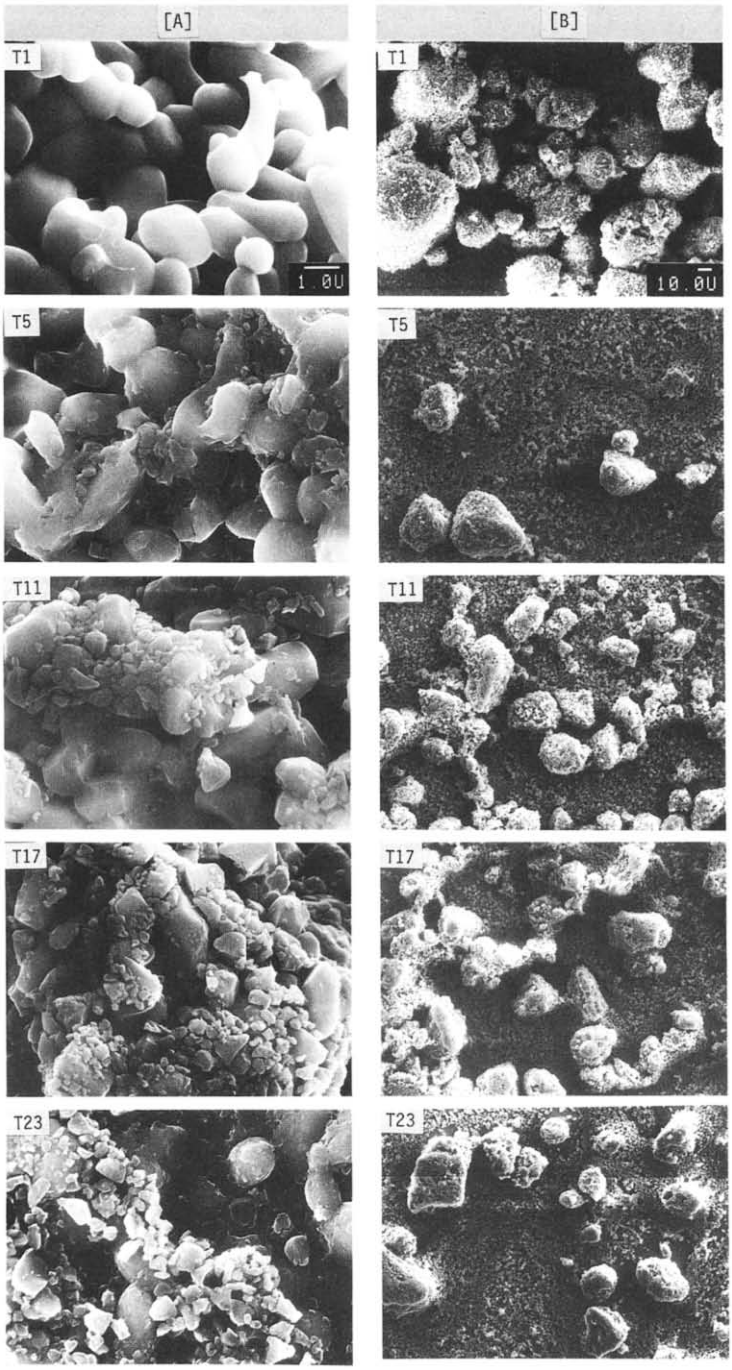

Fig. 6. Scanning electron micrographs of unsieved TiO_2 powders (T1, T5, T11, T17 and T23) after dry grinding for 0–180 min using a planetary pulverizer. Scale bars: (A) 1.0 and (B) 10.0 μm.

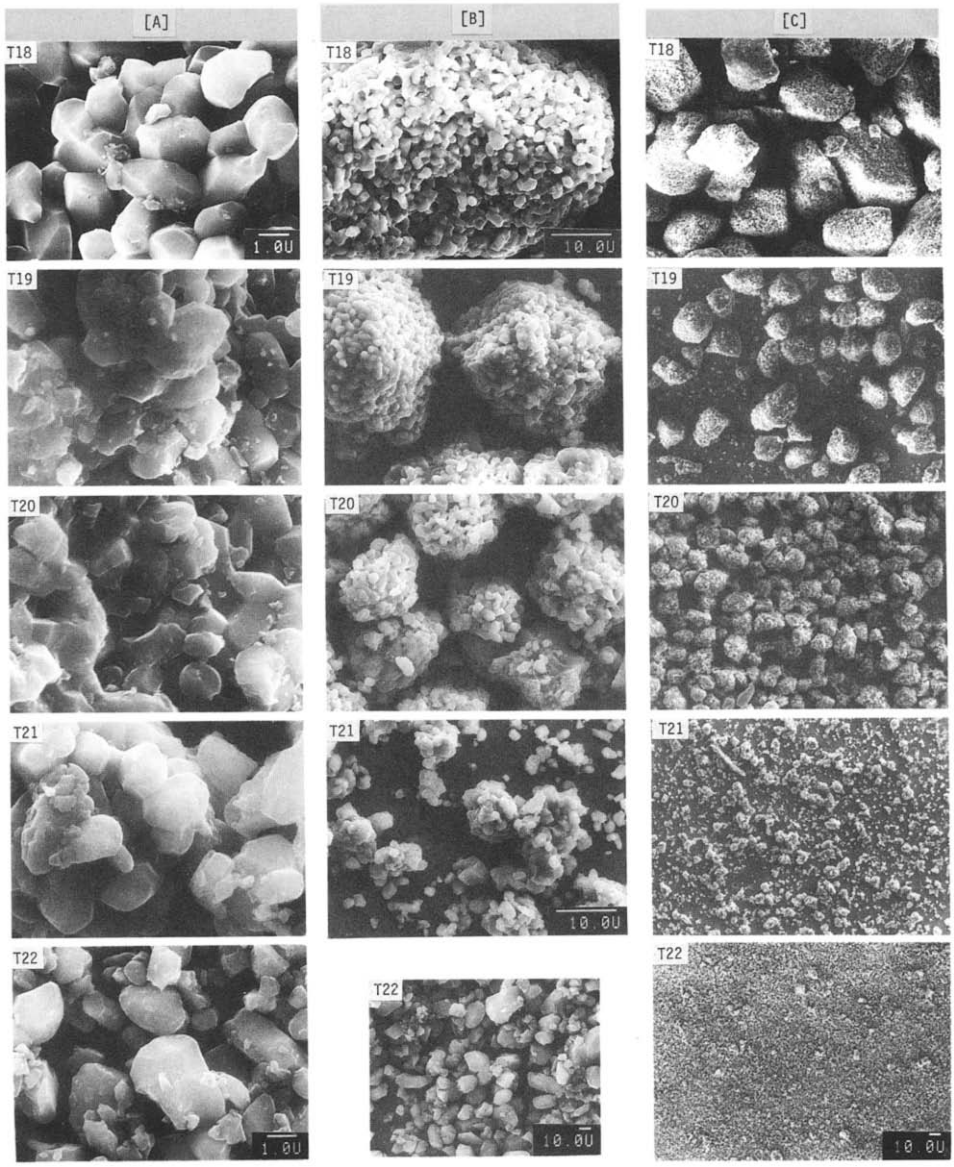

Fig. 7. Scanning electron micrographs of TiO_2 powders (T18 to T22) sieved to various particle sizes (Table 1), after grinding for 60 min using a planetary pulverizer. Scale bars: apply to the five photographs in series (A) and (C), and four micrographs (not sample T22) in series (B).

largest sample T18 was dispersed into the constituent fine particles (1–2 μm diameter) by the grinding and sieving treatments.

Figure 8 shows the SEM photographs of unsieved TiO_2 powders (T51 to T54), after dry grinding and after wet grinding for grinding times of 15–180 min (Table 2) using a mortar grinder. No appreciable effect of grinding time

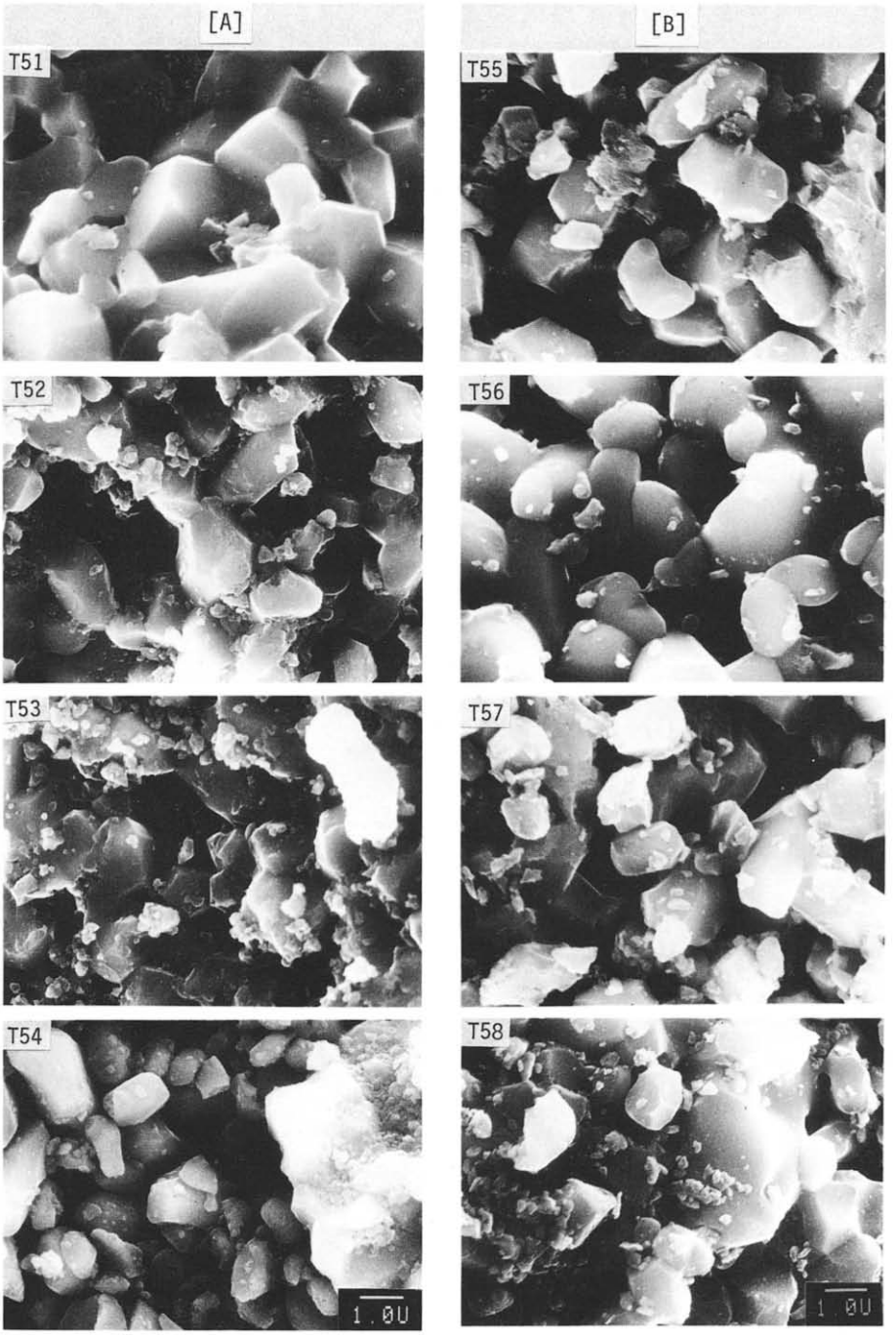

Fig. 8. Scanning electron micrographs of unsieved TiO_2 powders (T51 to T54) after (A) dry grinding and (B) wet grinding for grinding times of 15–180 min using a mortar grinder. The scale bar applies to all eight micrographs.

is observed. As in Fig. 5, the grinding effect seems to act only in the initial grinding step.

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