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# Particle Growth in Oxalate Process II; Control of Barium Titanyl Oxalate Particle Size

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On the basis of growth mechanism proposed by recent work, particle size of barium titanyl oxalate was controlled by aging in water. From aging at 25°C for 3 hours, uniform particles of 0.3 μm were obtained. During aging, abnormal particle growth was observed, which were thought to be caused by impurities in water. With increase of aging time and temperature, particle grows more, and differential growth was promoted. In aging for long time, grown particles were cracked.

***Key words :*** BT-oxalates, Aging

## I. Introduction

Recent work proposed that barium titanyl [BT-oxalate], strontium titanyl and calcium zirconyl oxalate grow in aging fluids by the solution and reprecipitation mechanism. But, BT-oxalate show nonuniform abnormal particle growth caused by nonuniform distribution of particles in fluid.[1]

In this experiment, BT-oxalate was prepared and aged at various temperature for several time on the basis of growth mechanism proposed above. Particle size of BT-oxalate and barium titanate was controlled.

## II. Experimental Procedure

### *1. Preparation of BT-Oxalates*

$TiCl_4$ (SHOWA Chmicals Inc., Japan, 99%), $BaCl_2 \cdot 2H_2O$ (JUNSEI Chemical Co. Ltd., Japan, 99%) and $H_2(C_2O_4)_2 \cdot 2H_2O$ (SHINYO Pure Chemicals Co. Ltd., Japan, 99.5%) were chosen as starting materials. To prevent hydrolysis of $TiCl_4$, $TiCl_4$ was dropped into agitated distilled water, in nitrogen atmosphere at 2°C. Some of this $TiCl_4$ solution was fired at 600°C for 3 hours to examine precise titanium content in the solution. $BaCl_2 \cdot 2H_2O$ was solved in this solution to the ratio, $Ba^{2+}$:$Ti^{4+}$=1:1. Concentration of mixed barium and titanium solution was fixed at 0.5 M. $H_2(C_2O_4)_2 \cdot 2H_2O$ was solved in methanol to excess 50% stoichiometry. Concentration of oxalic acid solution was fixed at 1.0 M. Mixed metal ion solution was added into oxalic acid solution by two-flow-spraying. In spraying, nitrogen was used as a carrier gas. Precipitated BT-oxalates were aged in third-distilled-water (Resistivity was 0.2 MΩ $cm^{-1}$ at minimum). Aging time was from 0 to 12 hours and temperature from 10 to 60°C. Aged BT-oxalates were filtered and dried at 80°C for 12 hours. Dried BT-oxalates were decomposed at 700°C for 2 hours.

### *2. Evaluation*

Centrifugal particle size analyzer (SHIMADZU, SA-CP 3) was used for particle size distribution of each oxalate. Shapes and sizes of each oxalate was examined by scanning electron microscope (JEOL, JSM-5400). Thermal behavior was examined by TG/DTA and XRD was used to examine formation of barium titanate.

## III. Results and Discussion

Figure 1 is particle size distribution comparing various BT-oxalates. Compared to BT-oxalate which is not aged, those aged in water shows much fractions in larger size region. Especially, that aged in first-distilled-water, has very large particles. It had been proposed that very high growth rate in first distilled water cause abnormal particle growth.[1] In order to control particle size, low growth rate or normal growth is required. So, third-dis-

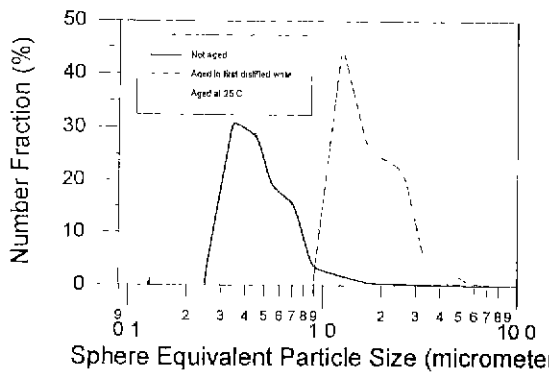


**Fig. 1.** Particle size distribution comparing various BT-oxalates.

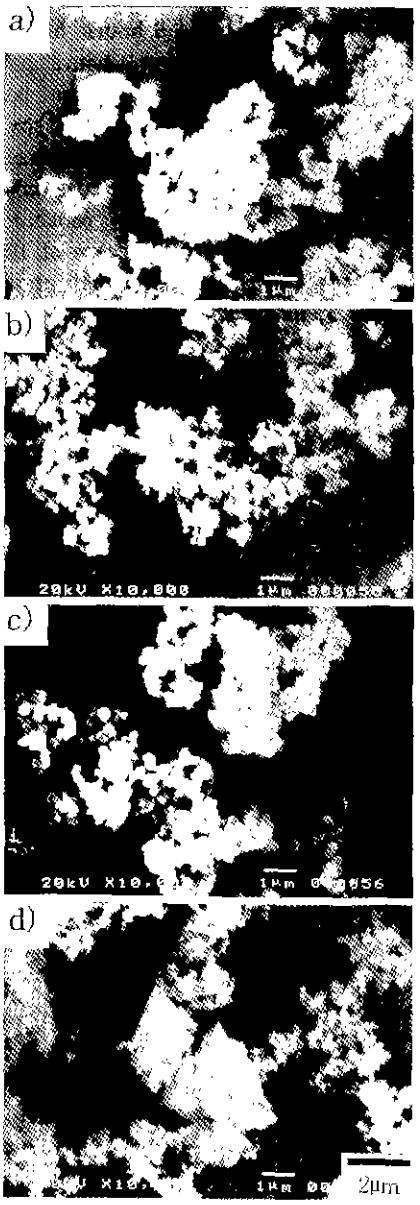


**Fig. 2.** SEM photographs of BT-oxalates with variation of aging time in water at 10°C. a) 3 hours, b) 6 hours, c) 9 hours, d) 12 hours.

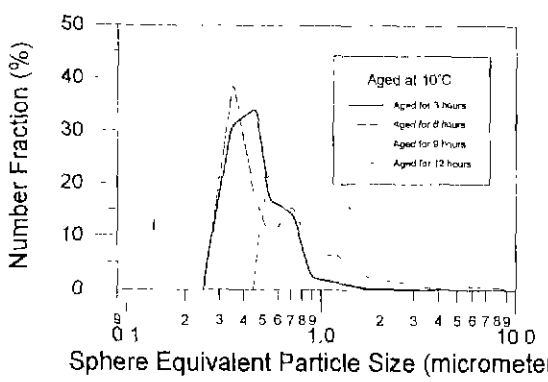


**Fig. 3.** Particle size distribution of BT-oxalates aged at 10°C.

tilled-water was used in the following experiments.

BT-oxalates were aged at 10°C (figure 2). BT-oxalates show normal growth up to 9 hours and they have 0.4 μm of mean diameter in case of 9 hour aging. But, abnormal particles appeared in case of 12 hours. It is thought that certain particles behaved as nuclei of abnormal growth during aging for long time. Meanwhile, particles grew slightly on the whole and interparticle agglomeration occurred.

Figure 3 shows particle size distributions of BT-ox-

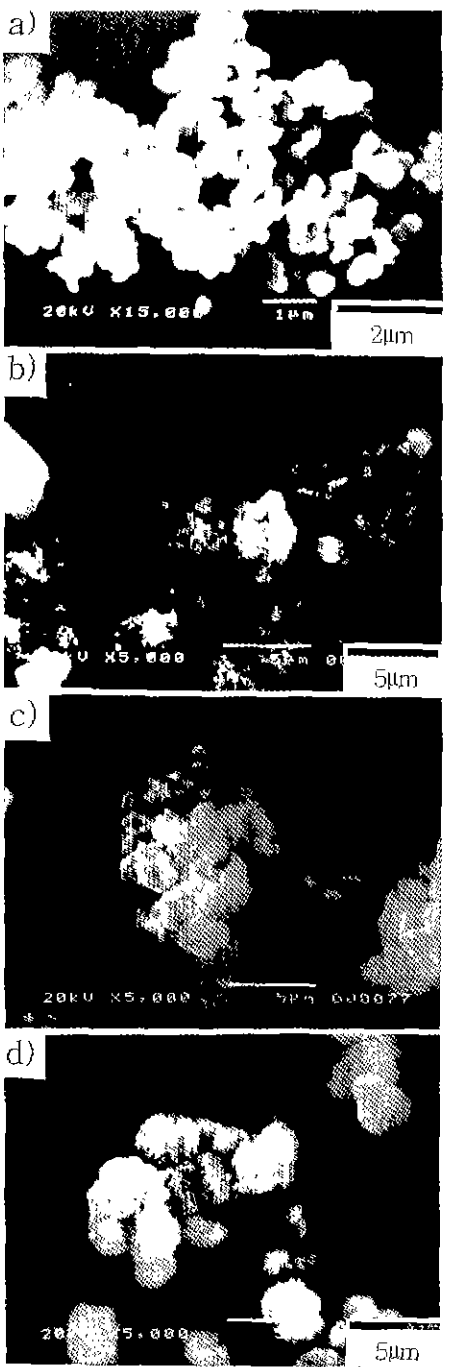


**Fig. 4.** SEM photographs of BT-oxalates with variation of aging time in water at 25°C. a) 3 hours, b) 6 hours, c) 9 hours, and d) 12 hours.

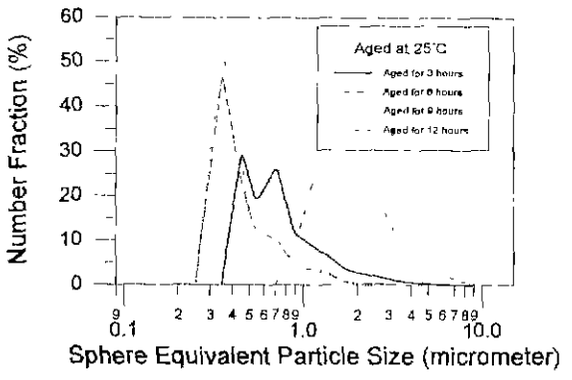


**Fig. 5.** Particle size distribution of BT-oxalates aged at 25°C.

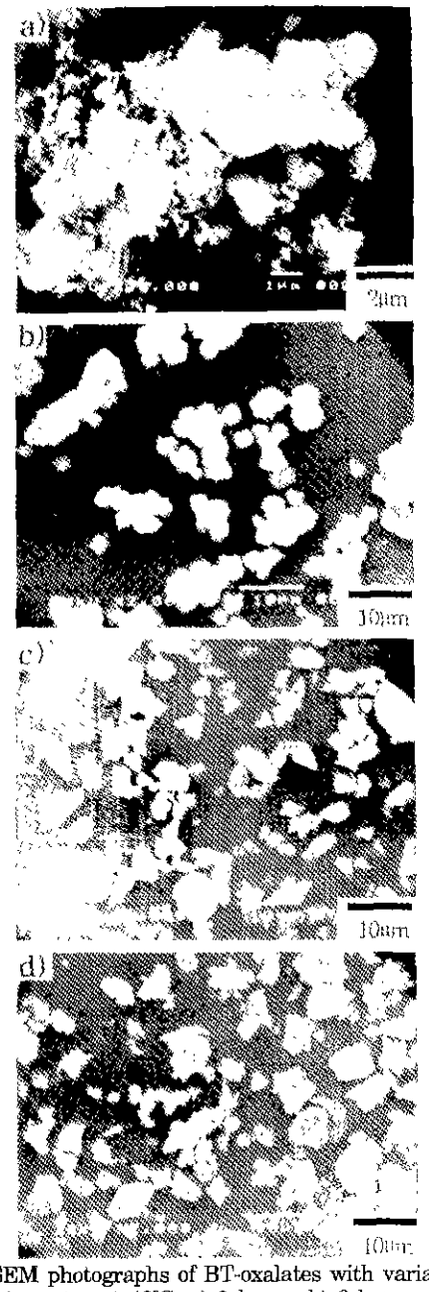


**Fig. 6.** SEM photographs of BT-oxalates with variation of aging time in water at 40°C. a) 3 hours, b) 6 hours, c) 9 hours, and d) 12 hours

alates aged at 10°C. From 3 to 6 hours, fraction of large particles increased, but, in case of 9 hours, particle sizes appeared to reduce. In figure 2, abnormal particles appeared at 12 hours, but these abnormal particles are thought to have already appeared at 9 hours. This is so because size reduction in spite of increasing aging time implies that certain particles grow continuously with solution of small particles. But, in case of 12 hours, so many particles grow to size large enough and hence particle size distribution appears to move to the larger size region completely.

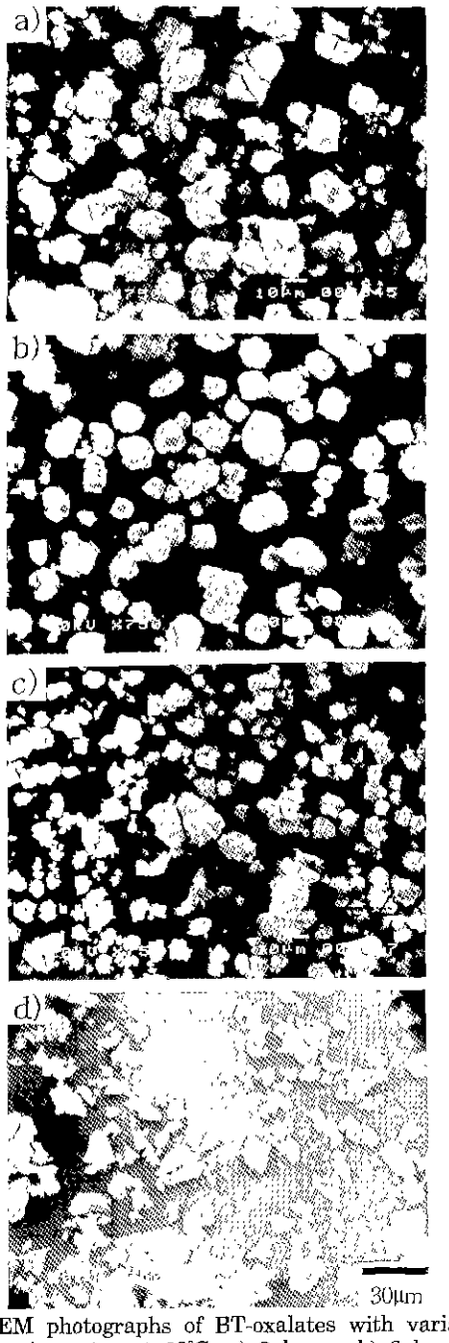


**Fig. 7.** SEM photographs of BT-oxalates with variation of aging time in water at 60°C. a) 3 hours, b) 6 hours, c) 9 hours, and d) 12 hours

Figure 4 is SEM photographs of BT-oxalates aged at 25°C. In case of 3 hours, uniform spherical particles were observed and abnormal particles appeared in case of 6 hours, as similar trend to that aged at 10°C for 9 hours. For 9 hours, most particles have large size through abnormal growth, and particle size distribution appeared to be nonuniform. Stripes in c), d) are thought to be caused by oriented reprecipitation, for solution was stirred during aging.

Figure 5 is particle size distributions of BT-oxalates aged at 25°C. It is similar to figure 3, but particle size reduction appeared in earlier time. From this, it can be inferred that growth rate increases with increase of aging temperature. With increase of temperature, energy of the system increases and nuclei of abnormal growth can be formed more easily.

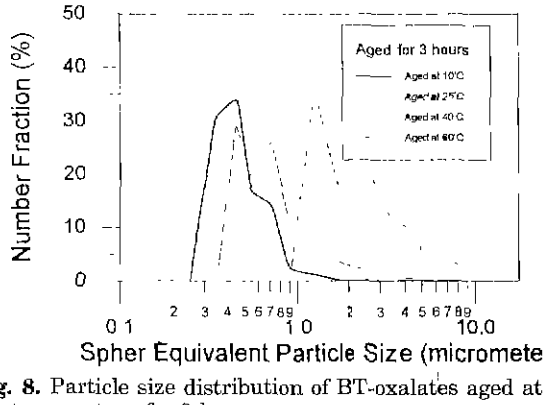


**Fig. 8.** Particle size distribution of BT-oxalates aged at various temperature for 3 hours.

Figure 6 shows SEM photographs of BT-oxalates aged at 40°C. In case of 3 hours, nonuniform distribution already appeared. In c), d), spherical shape of particles disappeared since certain interface that has lower energy would broaden to equilibrium interface state. Particle size distributions of these BT-oxalates approved the result of SEM photographs.

Figure 7 shows BT-oxalates aged at 60°C. Even in a), particles of 20 μm were observed, and in d), particles appeared to be crushed with stirring. Particle size distribution showed wide distribution to smaller size region in d).

Figure 8 is particle size distributions of BT-oxalates aged at various temperature for 3 hours. With increase of temperature, mean diameter increases. But, in case of 40°C, where abnormal growth starts, there are many small particles solving into fluids. In other words,

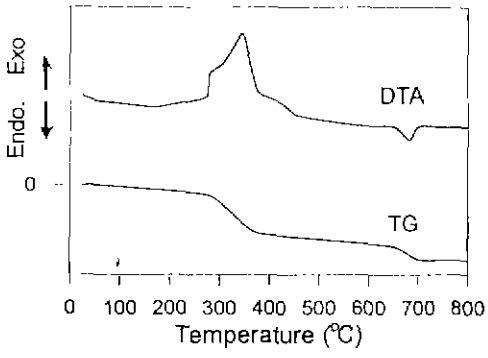


**Fig. 9.** TG/DTA pattern of BT-oxalates.

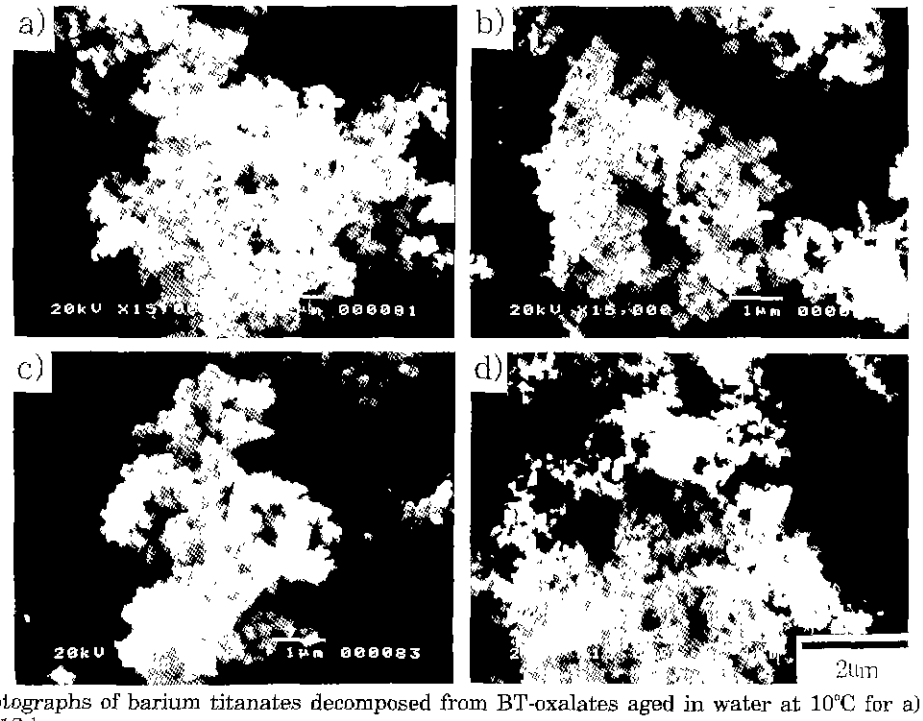


**Fig. 10.** SEM photographs of barium titanates decomposed from BT-oxalates aged in water at 10°C for a) 3 hours, b) 6 hours, c) 9 hours, and d) 12 hours.

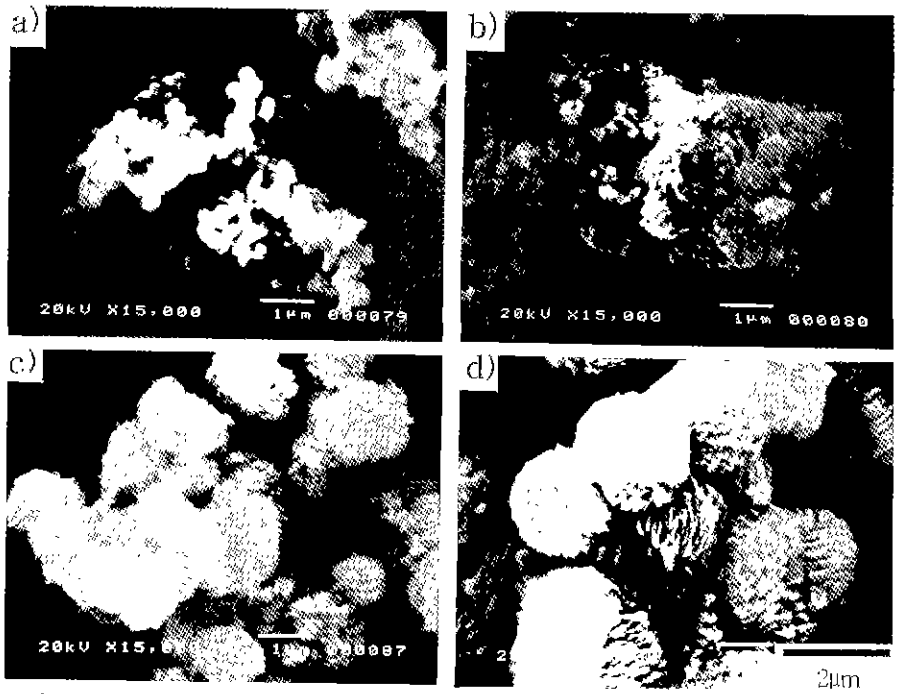


**Fig. 11.** SEM photographs of barium titanates decomposed from BT-oxalates aged in water at 25°C for a) 3 hours, b) 6 hours, c) 9 hours, and d) 12 hours.

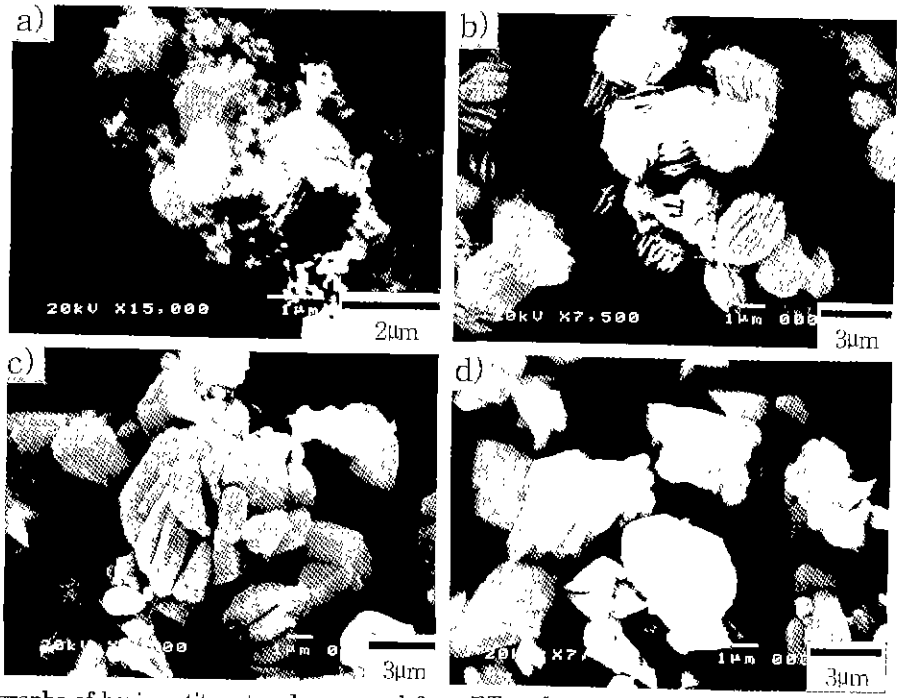


**Fig. 12.** SEM photographs of barium titanates decomposed from BT-oxalates aged in water at 40°C for a) 3 hours, b) 6 hours, c) 9 hours, and d) 12 hours.

growth rate increases with increases of temperature, and there exist small particles becoming rather small where abnormal growth starts.

Figure 9 shows pattern of TG/DTA. Exothermic peak about 300°C is by the decomposition of oxalate while endothermic peak about 700°C is not approved. Above 700°C, BT-oxalates converted to barium titanates completely which was verified by XRD. From this, prepared

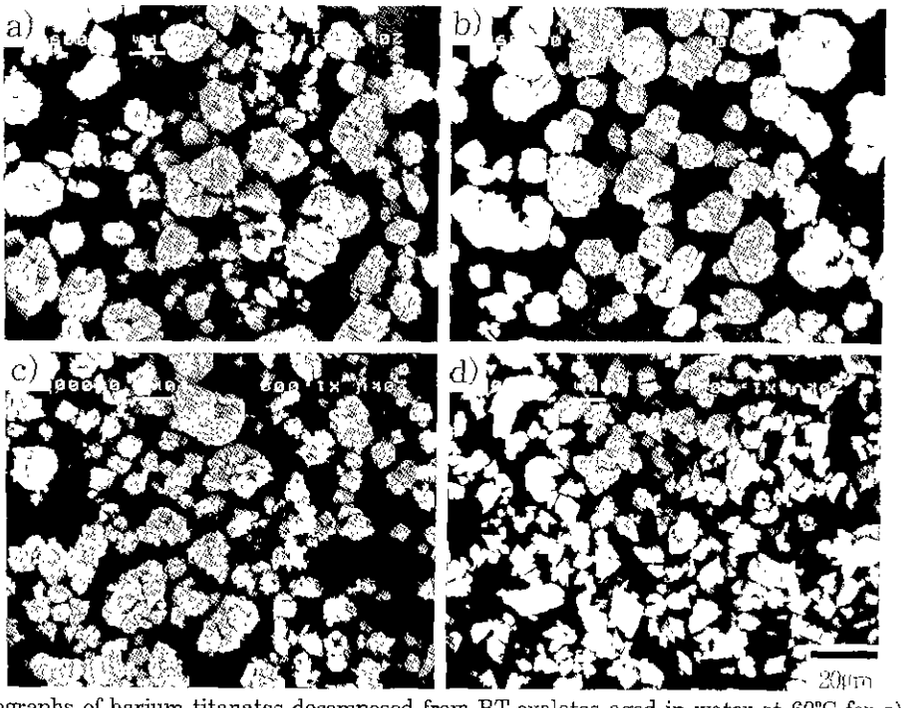


**Fig. 13.** SEM photographs of barium titanates decomposed from BT-oxalates aged in water at 60°C for a) 3 hours, b) 6 hours, c) 9 hours, and d) 12 hours.

BT-oxalates above are decomposed at 700°C for 2 hours.

Figure 10 shows SEM photographs of barium titanates decomposed from BT-oxalates aged at 10°C. It appears similar to Fig. 2, but with decomposition, particle size reduces a little. Necking between primary particles and large particles in BT-oxalates are maintained after decomposition. So, the assumption that control of dispersion and particle size in precipitates determines barium titanate powders could be approved.

Figures 11, 12, and 13 show BT decomposed from BT-oxalates aged at 25,40 and 60°C, respecively. The results again demonstrate that the size and shape of BT-oxalates are retaind at BT decomposed at a relatively low temperature of 700°C.

## IV. Conclusion

In oxalate process, state of precipitate powders determine state of ceramic powders decomposed.

Size of BT-oxalate can be controlled by aging in water with variation of time and temperature. Aging at 25°C for 3 hours, uniform powders of 0.3 μm can be obtained.

In aging of BT-oxalates in water, abnormal particle growth occurred, and it is thought to be caused by impurities in water.

As aging time and temperature increases, particle grows and abnormal growth is promoted. Crushing occurred during aging for long time.

## References

1. Particle Growth in Oxalate Process I.