

Particle Growth in Oxalate Process I

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Barium titanyl oxalates, strontium titanyl oxalates and calcium zirconyl oxalates were prepared with variation of solution concentration and method of adding mixed metal ion solution into oxalic acid. Then they were aged in distilled water, ethanol or methanol, respectively. Barium titanyl oxalates and calcium zirconyl oxalates were grown in water and strontium titanyl oxalates were grown in both water and methanol. They were supposed to be grown through the solution and reprecipitation mechanism. Nonuniform dispersion of particles in liquid phase is thought to cause abnormal particle growth

Key words : BT-oxalates, ST-oxalates, CZ-oxalates, Aging, Solution and reprecipitation

I. Introduction

The advantages of the nonconventional processes over conventional routes for ceramic powders are: high purity, chemical homogeneity, small and uniform particle size, and controllability of particle shape. Solution techniques have been widely adopted in the preparation of multicomponent oxide systems. This derives from the ease of mixing at the molecular level using soluble salts or chemicals for sources of metal ions. Ceramic powders or the ceramic preforms are directly synthesized from the solution and thus show excellent chemical uniformity and controlled particle size and shape.¹⁻³⁾

Oxalate process is a kind of coprecipitation method and has been widely investigated in the solution technique field. In this process, a mixed solution containing metallic cations is added into oxalic acid solution where metal oxalate precipitates. The oxalate process is simple and its product yield is very high.^{4,7)} But, there is few studies about the control of particle size and interparticle agglomeration. Barium titanate is one of the most widely studied system. Gallagher et. al.²⁾ prepared some barium and strontium titanates and studied their electric properties. F. Schrey⁸⁾ reported about an effect of pH on barium-strontium titanate preparation by oxalate process.

As shown in figure 1, particle size and shape of barium titanates decomposed from the barium titanyl oxalates [BT-oxalates] retains the size and shape of BT-oxalate. Thus, it is necessary to control synthesis of BT-oxalate in order to control particle size and shape of decomposed BT. Although BT, doped (Ba, Sr)TiO₃ for PTC materials and so forth are produced commercially using oxalate process for a long time, process variables or mechanism for controlling particle size and shape are not well documented and are kept as company expertise.

In this experiments, the growth of BT-oxalate during aging has been studied in various aging media with varying metal ion concentration and oxalic acid equivalent volume. From the experimental observation, the growth mechanism has been inferred.

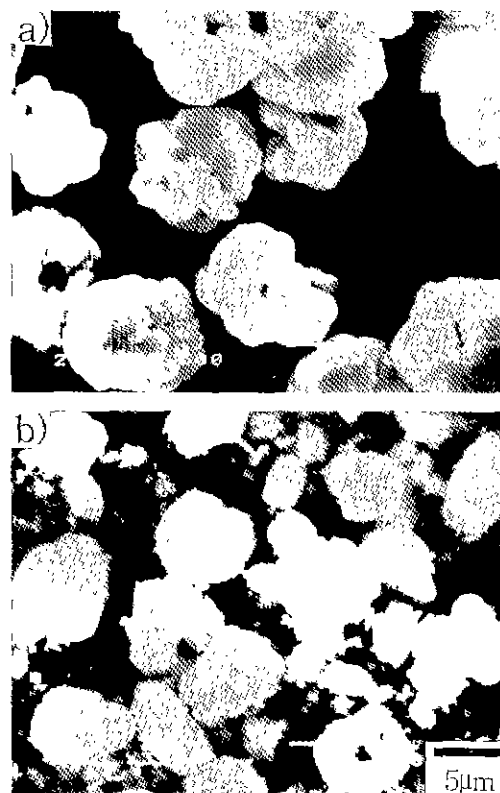


Fig. 1. SEM photographs of a) BT-oxalates, and b) barium titanate decomposed at 600°C for 3 hours.

II. Experimental Procedure

1. BT-Oxalates

TiCl_4 (SHOWA Chemicals Inc., Japan, 99%), $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (JUNSEI Chemical Co. Ltd., Japan, 99%) and $\text{H}_2(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ (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 at 2°C in nitrogen atmosphere. Some of this TiCl_4 solution was fired at 600°C for 3 hours to examine precise titanium content in the solution. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ was solved in this solution to the ratio, $\text{Ba}^{2+}:\text{Ti}^{4+}=1:1$. Concentration of mixed barium and titanium solution was fixed at 0.5 M. $\text{H}_2(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ was solved in methanol to excess 50% stoichiometry to a concentration of metal ions. Concentration of oxalic acid solution was varied from 0.5 to 2.0 M. Basic concentration for reference was 0.5 M for mixed barium titanium solution and 1 M for oxalic acid solution. Mixed metal ion solution was added into oxalic acid solution by burette-dropping or two-flow-spraying. In spraying, nitrogen was used as a carrier gas. Precipitated BT-oxalates were aged in distilled water, methanol or ethanol respectively at room temperature (25°C). Aging time was varied from 0 to 24 hours. Aged BT-oxalates were dried at 80°C for 12 hours.

2. ST- and CZ-Oxalates

TiCl_4 , $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (SIGMA Chemical Corp., 99%), $\text{ZrCl}_4 \cdot 8\text{H}_2\text{O}$ (Fluka, 98%), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Avondale Lab. Ltd., England, 99%) and $\text{H}_2(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ were chosen as starting materials. TiCl_4 solution, prepared by the same procedure as that of preparation of BT-oxalates, was used in the preparation of ST-oxalates. Calcium and zirconium chlorides were made to aqueous solutions, and some of these solutions were fired at 600°C for 3 hours, to examine precise metal ion content of each solution. Concentrations of both mixed strontium titanium solution and mixed calcium zirconium solution were fixed at 0.5 M. Concentration of oxalic acid solution was also fixed at 0.5 M, but excess 50% stoichiometry to a concentration of metal ions was maintained. Mixed metal ion solutions were added into oxalic acid by two-flow-spraying with nitrogen gas as a carrier gas. Each oxalate precipitated was aged in distilled water, methanol, ethanol or acetone at room temperature (25°C). The oxalates were also aged without adding any fluid just after spraying. Aging time was varied from 0 to 4 hours. Aged oxalates were dried at 80°C for 12 hours. Figure 2 shows schematics of experimental procedure.

3. 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).

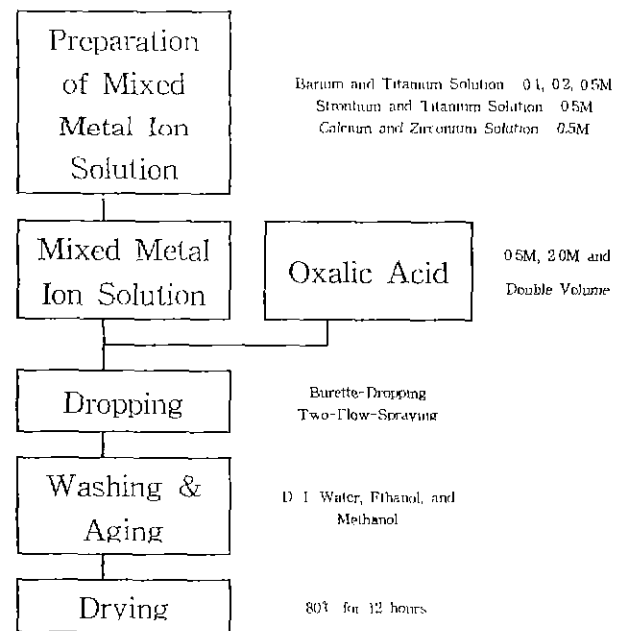


Fig. 2. Experimental procedure of preparing metal-oxalate.

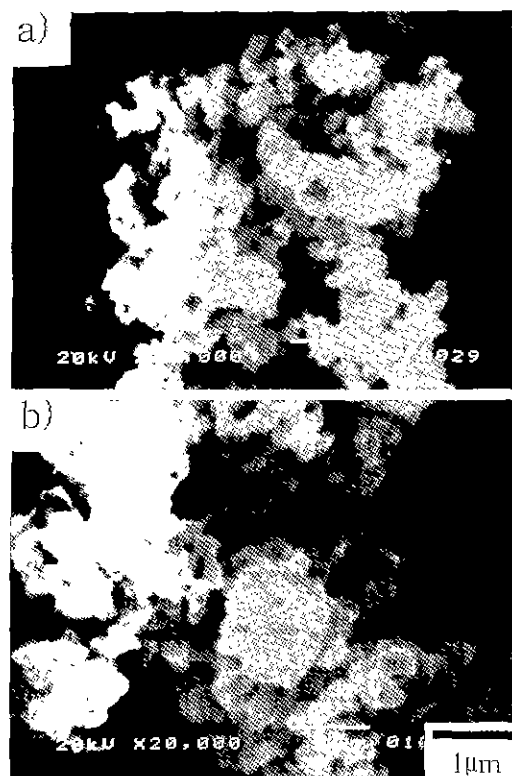


Fig. 3. SEM photographs of BT-oxalates by a) burette-dropping and b) two-flow-spraying.

III. Results and Discussion

1. BT-Oxalates

Figure 3 a) and b) are the SEM photographs of BT-ox-



Fig. 4. SEM photographs of BT-oxalates with variation of oxalic acid solution condition. a) 0.5 M, b) 2.0 M, and c) 1.0 M with twice as normal volume. All of them have been aged in water for 12 hours.

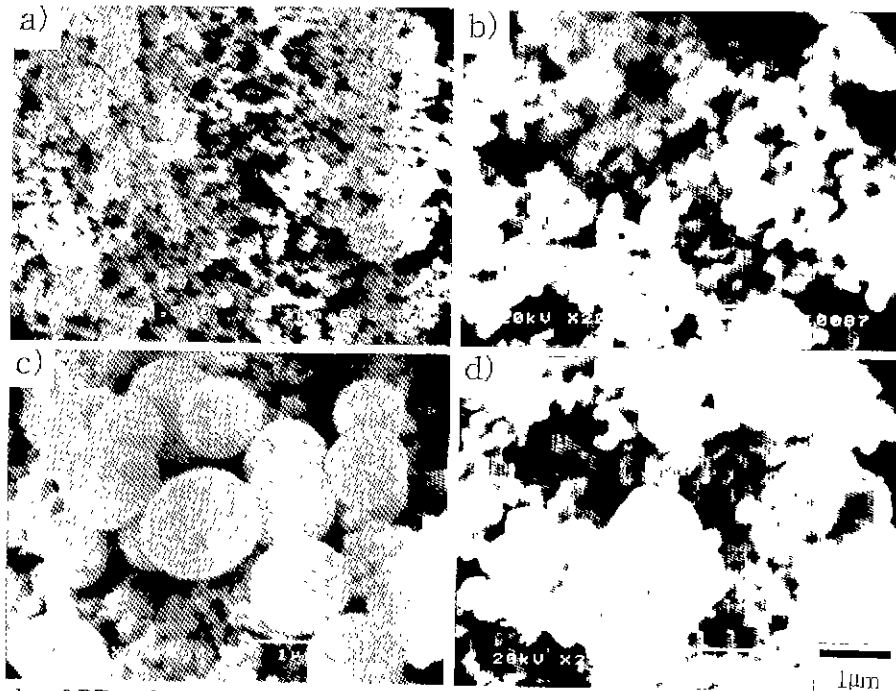


Fig. 5. SEM photographs of BT-oxalates with variation of aging time. a) 0 minute, b) 30 minutes, c) 60 minutes, and d) 90 minutes.

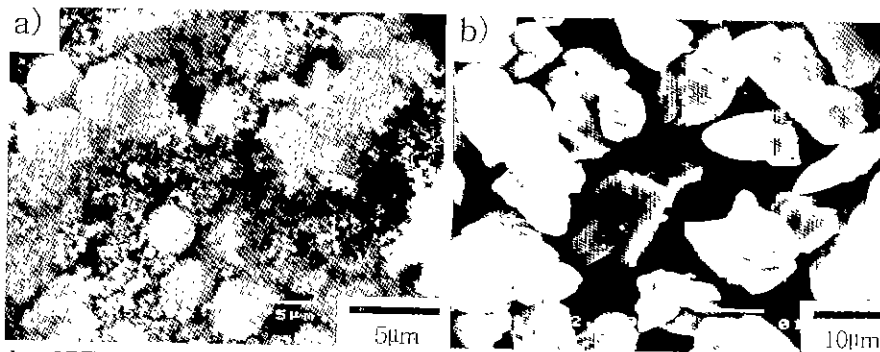


Fig. 6. SEM photographs of BT-oxalates aged for a) 3.5 hours, and b) 24 hours.

alates by burette-dropping method and two-flow-spraying method, respectively. These BT-oxalates were not aged. Primary particle sizes are about 0.2 μm in both

photographs, but sprayed particles shows more uniform arrangement. This figure also shows that it is necessary to control the size of liquid droplet and therefore all mix-

ed metal ion solutions were sprayed in the following experiments.

Figure 4 shows SEM photographs with condition of oxalic acid solution. a) is for 0.5 M oxalic acid solution, b) is for 2.0 M, and c) is for 1.0 M but in double volume. These BT-oxalates were aged for about 12 hours in water. Particle sizes in these photographs show much differences with condition of oxalic acid solution. It shows that the growth of BT-oxalates strongly depend on the concentration and equivalent of solutions. Furthermore, it can be thought that solubility of BT-oxalates in reacted solution is related to growth of particles and the solution and reprecipitation mechanism is the mechanism of particle growth.

To examine this assumption, BT-oxalates were aged in

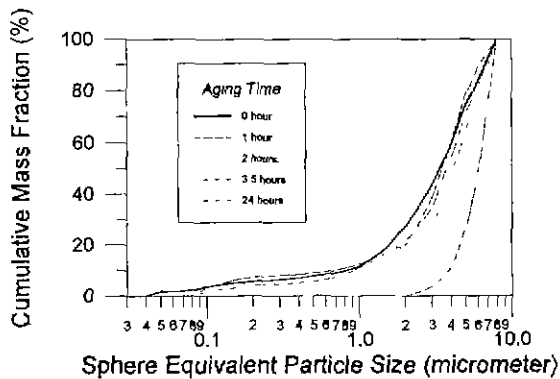


Fig. 7. Cumulative particle size distribution of BT-oxalates with variation of aging time.

distilled water, and were observed by SEM at every 30 minutes up to 90 minutes. Figure 5 shows the SEM photographs. In a), which is for BT-oxalates not aged, primary particle sizes are about 0.2 μm , and pretty uniform arrangement appears. After a 30 minute aging, particle grew to about 0.3 μm , and abnormal particle growth appeared in b). In c) and d), the abnormal particle grew more and the smaller particles remained not grown. These nonuniform size distribution is thought to be caused by nonuniform solubilities among primary particles leading to different growth rates.

BT-oxalates were aged for longer time. Figure 6 a) is SEM photographs after 3.5 hour aging, and shows similar state as in figure 5 c) and d). Figure 6 b) is SEM photograph after 24 hour aging, where every particle has grown to about 10 μm and the shapes are nonspherical. This indicates that mass transportation occurs from smaller particles to larger particles with solubility difference between those particles and therefore larger particles become larger, while smaller particles become smaller. It can be inferred that BT-oxalate grows in water during aging through abnormal particle growth.

Figure 7 is particle size distributions of BT-oxalates aged in water. Till 3.5 hours, little differences was observable, but after 24 hour aging, particle growth progressed markedly, which agrees well with figures 5 and 6. The agglomeration between fine primary particles is accounted for the large particle region over 1 μm in the cases of short aging time.

Precipitated BT-oxalates were aged in ethanol and

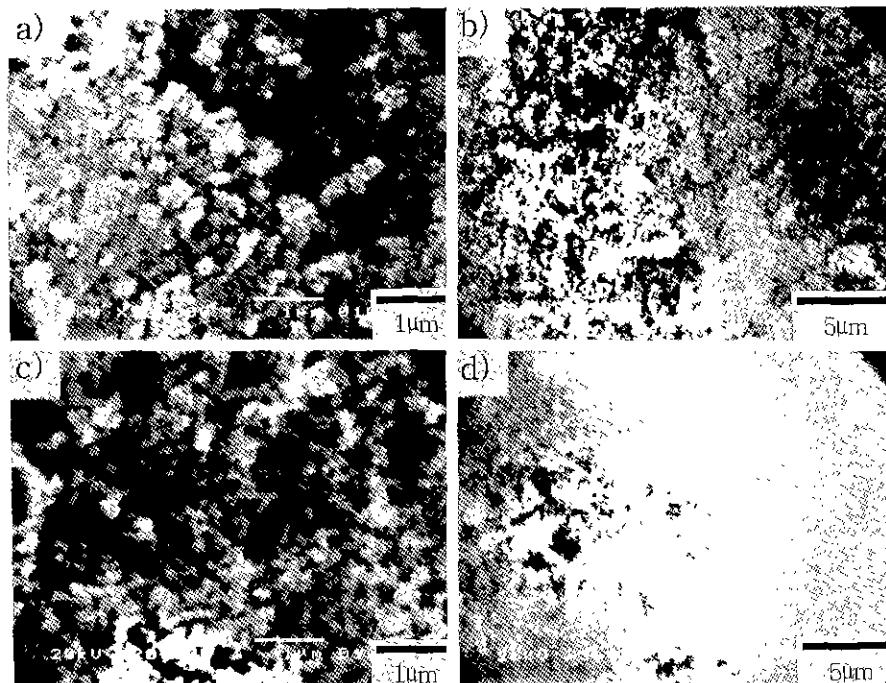


Fig. 8. SEM photographs of BT-oxalates with variation of aging fluids and aging time. a) 0 hour in ethanol, b) 2.5 hours in ethanol, c) 0 hour in methanol, and d) 2.5 hours in methanol.

methanol, and shown in figure 8. In both cases, there are no notable growth, and BT-oxalates may have proper solubility only in water.

Figure 9 is a model of growing particles in water. Small particles have high dissolving rate and large par-

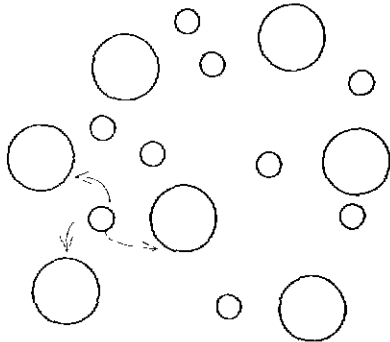


Fig. 9. Model of particle growth in water.

ticles have low dissolving rate. Hence, dissolved material moves through solution to large particles and then precipitates. A relation between supersaturation and particle size was proposed as eqn. (1).⁸⁾

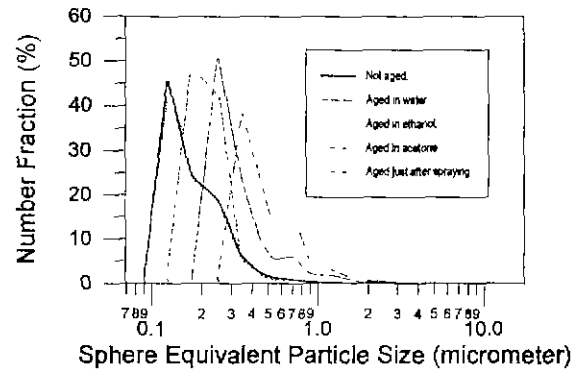


Fig. 11. Particle size distribution of ST-oxalates aged in various fluids for 4 hours.

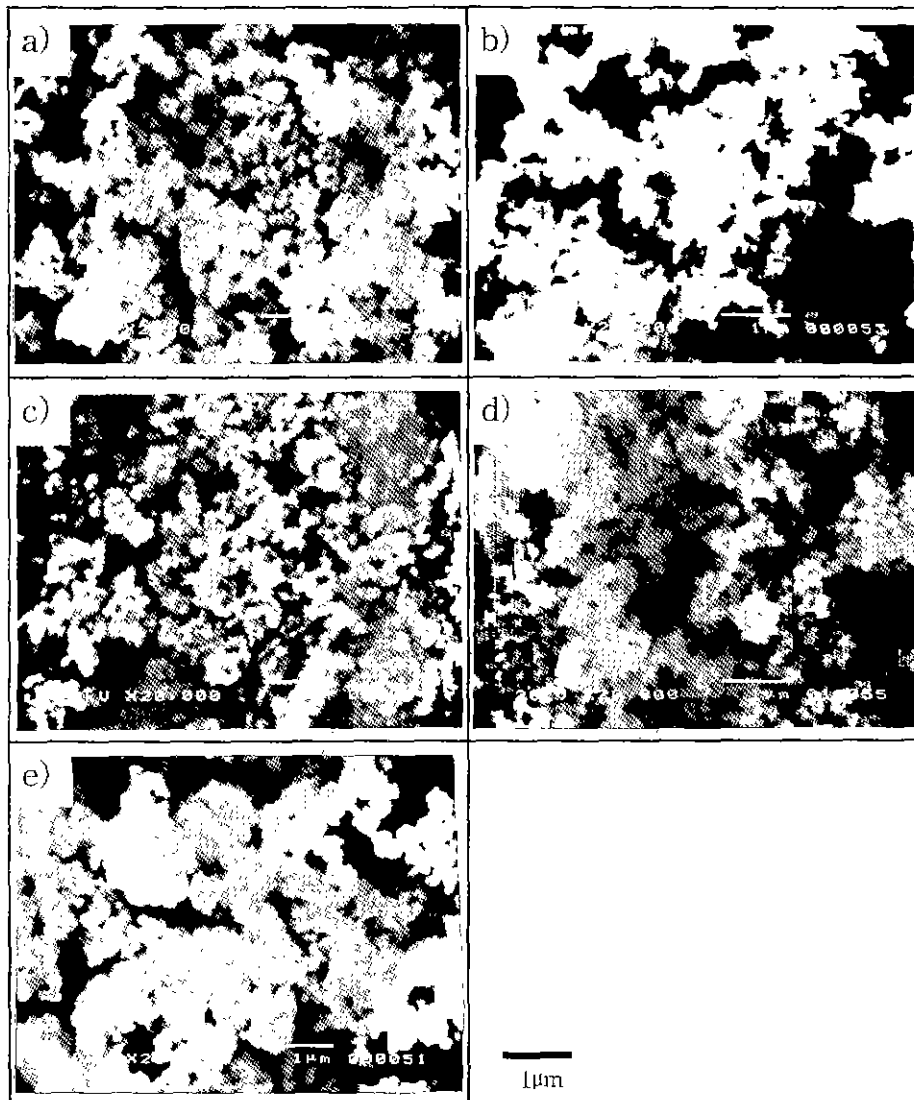


Fig. 10. SEM photographs of ST-oxalates. a) not aged, and aged in b) water, c) ethanol, d) acetone, and e) without any fluid.

$$\delta = \ln \frac{C_s}{C_\infty} = \frac{\gamma M}{RT\rho} \cdot \frac{2}{r} \quad (1)$$

δ = degree of supersaturation

C_s = concentration of particle

C_∞ = concentration of infinitely large plate

γ = liquid-solid interface energy of the material

M = molecular weight

R = ideal gas constant

T = absolute temperature

ρ = density of material

r = radius of particle

Degree of supersaturation is inversely proportional to particle size in the same material, so the smaller the particles, the better they solve. This explains mass transportation through liquid phase and particle growth.

2. ST- and CZ-Oxalates

Precipitated ST-oxalates were aged in various fluids,

and shown in figure 10. There is no notable growth in water, ethanol, acetone, compared with ST-oxalates not aged. ST-oxalates solved in methanol completely. For the case of ST-oxalate, where the solvent was composed of water and methanol, particles have grown a little. This can be verified in particle size distributions of these ST-oxalates, figure 11. In the cases of water and methanol, fractions over 1 μ m appear to increase. For aging in water, ST-oxalates are known to have considerable solubility in water, so ST-oxalates may grow in water, too. As a result, ST-oxalates appear to grow in water and methanol through the solution and reprecipitation mechanism.

Figure 12 shows SEM photographs of CZ-oxalates aged in various fluids. There is a notable growth only in the case of e), where solvent is composed of water and methanol by the mixed solvents from the starting precursors. CZ-oxalates solved in water completely. CZ-oxalates appear to grow in water. In figure 13, particle size distributions of CZ-oxalates, this can be approved.

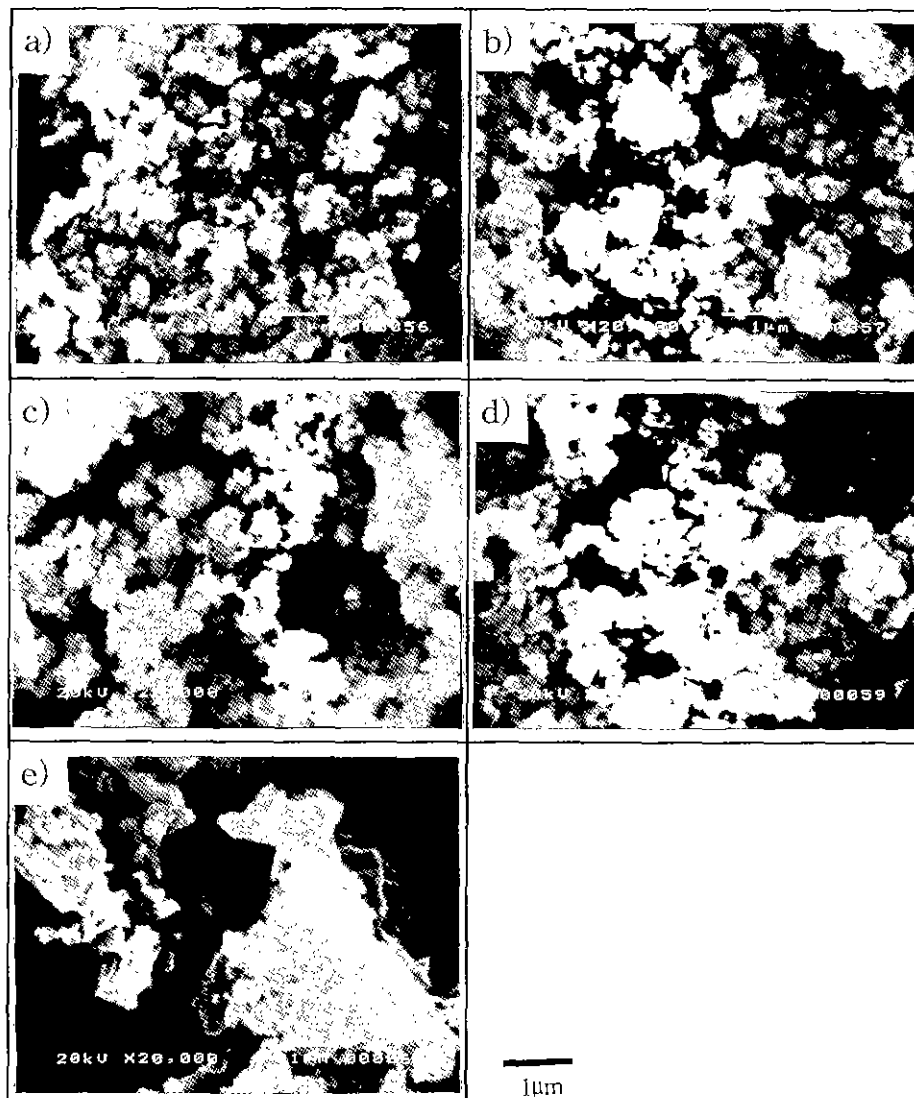


Fig. 12. SEM photographs of CZ-oxalates. a) not aged, aged in b) methanol, c) ethanol, d) acetone, and e) without adding any fluid.

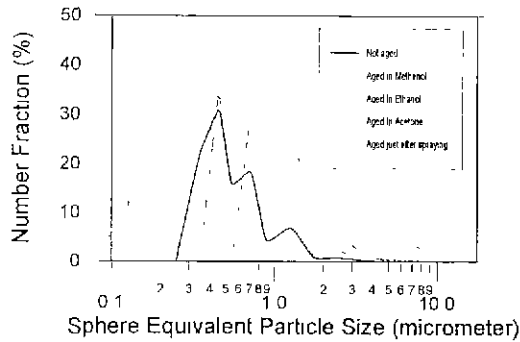


Fig. 13. Particle size distribution of CZ-oxalates aged in various fluids for 4 hours

Agglomerated particles appear in these particle size distributions for short aging times. CZ-oxalates grow in water through the solution and reprecipitation mechanism.

IV. Conclusion

Oxalates grow in fluids in this experiment as follows; BT-oxalates grow in water, ST-oxalates grow in both water and methanol, and CZ-oxalates grow in water. All of them grow through the solution and reprecipitation mechanism. Nonuniform distribution of particles in

fluids leads to nonuniform particle growth.

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