SONOCHEMICAL PROCESSING OF CERAMIC POWDERS
~ Ultrasonic Effects on Oxalate Precipitation in Water-Ethanol Solution ~

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ABSTRACT

Ceramic powder preparation through precipitation from solution (or, wet-chemical processing) was performed through *Concerted Amplification* using the peculiar high-energy field of power ultrasound. In this paper, various effects of ultrasound on oxalate precipitation in water-ethanol solution are presented. In the precipitation of titanium oxalate, the initial precipitate was not a stable phase and ripened to be $Ti_2O_2(C_2O_4)(OH)_2 \cdot H_2O$. The ripening process was fastened by ultrasound. In the precipitation of lead oxalate, a sonochemical switching was observed between anhydrous lead oxalate (PbC_2O_4) and lead oxalate nitrate hydrate ($Pb_2C_2O_4(NO_3)_2 \cdot 2H_2O$). Low frequency ultrasound promoted the formation of the latter. In addition, this paper proposes a brand-new application of ultrasound concerning the structure of the starting solutions in this process.

Keywords: Wet-chemical Processing, Sonochemistry, Oxalate Precipitation, Solution Structure

1. INTRODUCTION

In the past, sonochemistry progressed mainly in organic synthesis.[1] The reason for this is presumably that most of organic reactions are conducted at moderate temperatures (<100 °C) in liquid phase, which is the only phase for the ultrasonic cavitation to occur. On the contrary in the history of ceramic synthesis, the conventional route is to react solid materials at high temperatures (>1000°C). Both the 'solid state' and the 'high temperature' must be lofty barriers against sonochemistry because cavitation never occurs in a solid and an ultrasonic transducer is not durable at high temperatures. In recent several decades, however, ceramists have been paying their attention to liquid phase processing, such as coprecipitation method, hydrothermal method, sol-gel method, polymerized complex method, and so forth. In order to further advance an advanced ceramic material, the liquid phase processing (or, *soft solution process*[2]) would be the indispensable route in that they are highly qualified, productive, and environmentally benign.

Wet-chemical powder process (or, the precipitation route) involves various physico-chemical phenomena such as dissolution, chemical reaction, nucleation & growth, and dispersion & agglomeration. It has been found by the authors that stimulation (or, *Concerted Amplification*) of these phenomena in the ultrasonic field results in *fastening* and/or *switching* of the processes.[3-5]

This paper concerns the oxalate precipitation in a water-ethanol solution. Metal oxalate salts are attractive materials as ceramic precursors due to their high crystallinity, low decomposition temperature, and formability of complex precursors.[6] Some of oxalates, however, have a solubility that cannot be ignored and therefore they do not sufficiently precipitate in an aqueous solution. In order to improve this, Yamamura *et al.*[7] employed an ethanolic solution of oxalic acid. This successful process is based on the facts that oxalic acid is soluble in ethanol and oxalates are insoluble in ethanol.

This paper presents experimental results on the precipitation of Ti and Pb oxalates, where the fastening and the switching effects of ultrasound are observed, respectively. In addition, this paper proposes a brand-new application of ultrasound concerning solution structure.

2. EXPERIMENTAL

Titanium source was an aqueous solution of $TiO(NO_3)_2$ prepared by dissolving $Ti(OH)_4$, which was previously precipitated by the hydrolysis of commercial $TiCl_4$, into conc. HNO_3. While, commercial $Pb(NO_3)_2$ was dissolved in distilled water. Cation concentration of the aqueous solutions was fixed at $0.028 mol/dm^3$. They were precipitated with the $0.028 mol/dm^3$ ethanolic solution of $H_2C_2O_4$ at the composition for $[C_2O_4^{2-}]/[TiO^{2+}]=1$ and

$[C_2O_4^{2-}]/[Pb^{2+}]=1$.

As for the Ti case, the reaction temperature was fixed at 60°C and the ultrasonication was made by using an ultrasonic homogenizer (Branson, model 450) with Ti horn. As for the Pb case, the reaction temperature was 20-60°C and extra ammonia was added to stabilize the precipitates. Bakelite protected PZT transducers (Tokin Co., Ltd.) were used for the ultrasonication in the Pb case. The precipitation products were filtered and washed, and then dried at room temperature.

3.RESULTS AND DISCUSSION

3-1. In the Titanium System

The initial precipitate with lower crystallinity, as shown in the lower part in Fig.1 (ex. the pattern for 1h), was not identified in the JCPDS cards. Ion-exchange chromatography revealed that about 4% of NO_3 is involved in this initial precipitate. As it was ripened in the mother solution, more crystalline phase appeared. Ripened phase was registered as $Ti_2O_2(C_2O_4)(OH)_2 \cdot H_2O$ (denoted as TOCO).

The formation of the TOCO phase completed within 4 hours at the sonication of 2 W/cm² (the result shown in Fig.1) and within <1 hour at 20 W/cm². In the absence of ultrasound, on the other hand, the formation rate of the TOCO phase was approximately 1/3 as much as the case of the 2 W/cm² sonication. This is a typical result of the fastening effect. Judging from the morphological changes of the precipitates by using electron microscopy, it is suggested that this ripening process proceeds with the dissolution of the initial precipitate.

Figure 2 shows the particle size change, which was measured by a centrifuge method (Shimadzu, SA-CP2), of the precipitates during the ripening. Gradual decrease of the particle size in the non-sonicated case would be due to the dissolution of the initial precipitate. And, slight increase from 5 to 6 hour corresponds to the formation of the TOCO phase. In the presence of ultrasonication, the particles size is always kept much lower than the control. At the initial stage, the smaller particle size under sonication is due simply to the dispersion effect, since the initial particles are an agglomerate of ultrafine particles. After the formation of the TOCO phase, the smaller particle size under sonication may be related to the enhanced nucleation of the TOCO phase, because its particles are rigidly shaped.

3-2. In the Lead System

Precipitates after 5 minutes' precipitation were a mixture of anhydrous lead oxalate (PbC_2O_4; denoted as PC) and lead oxalate nitrate hydrate ($Pb_2C_2O_4(NO_3)_2 \cdot 2 H_2O$; denoted as PCN). The PC/PCN formation ratio estimated by X-Ray Diffraction is shown in Figs. 3 and 4. It is in short concluded that the PCN phase is likely to form at lower temperature, at lower pH, with
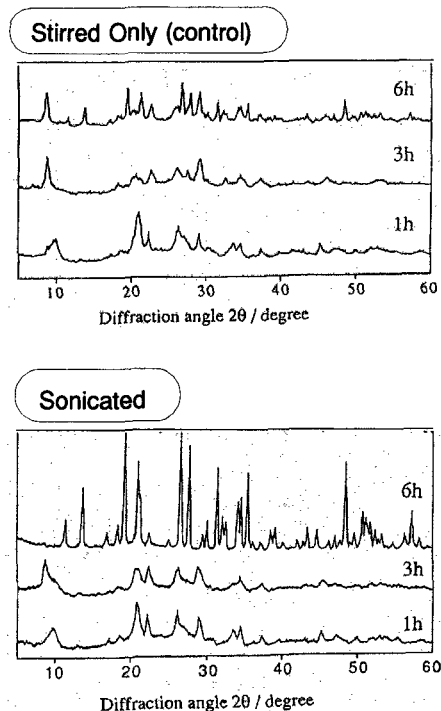

FIG.1   XRD patterns showing the formation of $Ti_2O_2(C_2O_4)(OH)_2 \cdot H_2O$ from the initial precipitate with or without ultrasound (2 W/cm2).
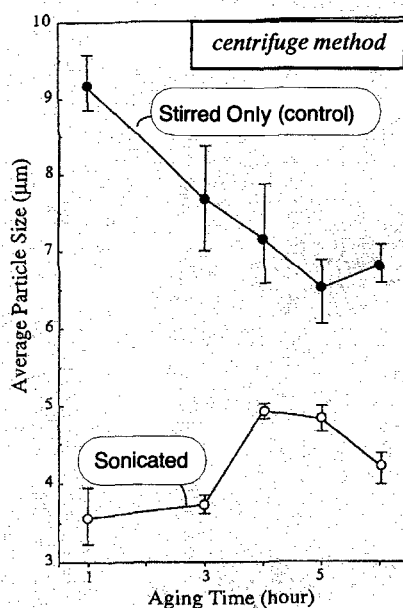

FIG.2   Particle size changes of the precipitates from $TiO(NO_3)_2$ aq. and $H_2C_2O_4$ /EtOH solution, involving formation of $Ti_2O_2(C_2O_4)(OH)_2 \cdot H_2O$ and ultrasonic effect (2 W/cm2).
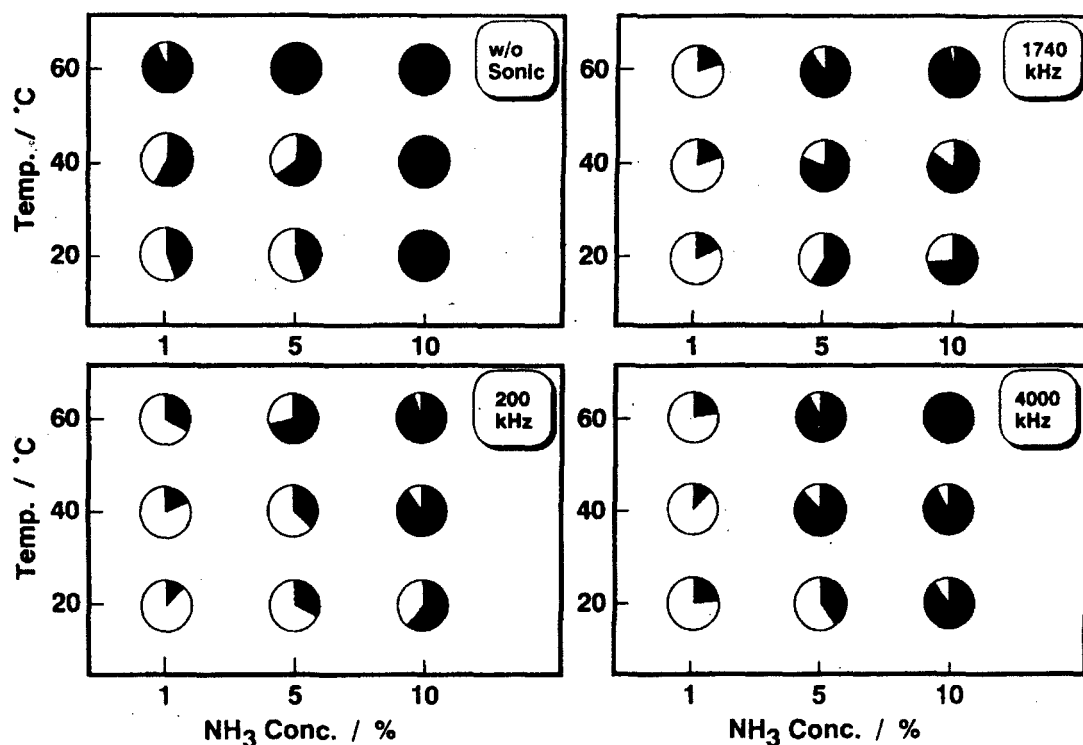
FIG.3 *Formation ratio of PbC_2O_4 (Black Part) and $Pb_2C_2O_4(NO_3)_2·2H_2O$ (White Part) under various ultrasonications. (Reaction Time = 5 min)*

longer reaction time, and ultrasonication especially at lower frequency. This is a switching effect of ultrasound from PC to PCN.

It is often found in the similar switching cases that an ultrasound enhances "high temperature phase". In the present case, however, it is interesting that the low temperature phase, PCN, was promoted by the ultrasound. Considering that the PCN increases with reaction time (Fig.4), PCN is thermodynamically stable. Electron microscopy on the morphological changes suggests that this is due to the dissolution-precipitation process just as was in the case of the Ti system. If we assume that the semi-stable phase (PC) is likely to dissolve at lower pH, and that its solubility decreases with increasing temperature, the formation of PCN is enhanced at lower pH and lower temperature. And lower frequency ultrasound may well enhance the formation of PCN because it has higher dispersion effect than high frequency ultrasound. However, it is not simply interpreted when we look at the result at 60°C and 1% NH_3 for example; i.e., in the absence of ultrasound, the PCN amount increased up to only 10% after 5 hours' aging, while the PCN amount increased more than 70% by sonication in spite of very short reaction time of 5 minutes. It is therefore infered that the ultrasonic effect here is not a mere enhancement of dissolution but maybe the promotion of PCN nucleus.
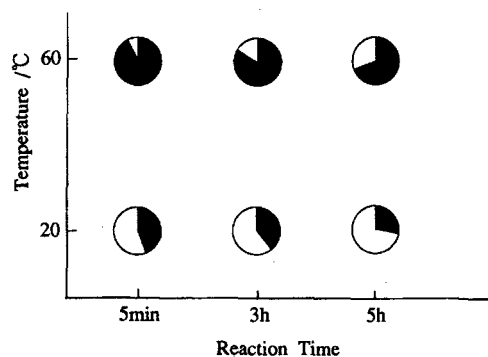

FIG.4 *Phase change from PbC_2O_4 (Black Part) to $Pb_2C_2O_4(NO_3)_2·2H_2O$ (White Part) with aging time in the absence of ultrasound (1% ammonia)*

4. SERENDIPITY ~ NOVEL POSSIBILITY OF ULTRASONICATION

As a serendipity in the oxalate precipitation experiment, we found curious phenomenon and have reported recently[9] ; i.e., when the starting solutions are aged for a long peoriod, the precipitation rate is dramatically lowered with increasing aging time. It is at first sight unfavorable to decrease the reaction rate.
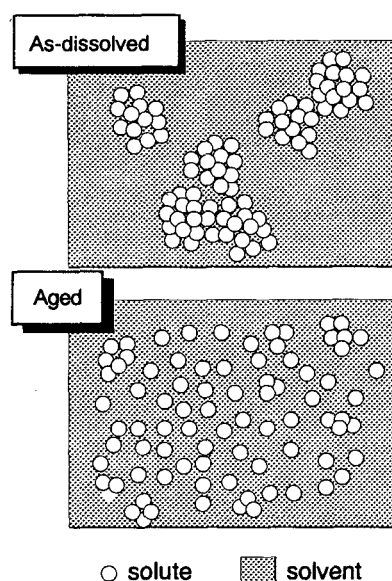
○ solute   ▨ solvent

FIG. 5 *Conceptional schematic of the structural change during aging of starting solution, which should be enhanced by weak ultrasonication ; (I) Change of Dissolution Level.*
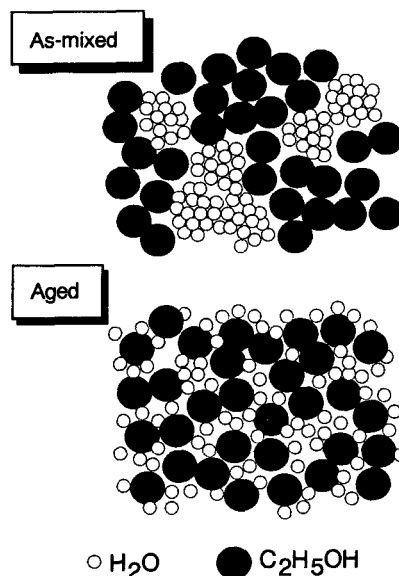

○ H₂O   ● C₂H₅OH

FIG.6 *Conceptional schematic of the structural change during aging of starting solution, which should be enhanced by weak ultrasonication ; (II) Microscopic Mixing of Water and Ethanol.*

But, considering that some of wet-chemical power syntheses are too fast to control, we found it interesting to change the precipitation rate merely by aging the starting solutions and are thinking of the application of ultrasound to the aging of them.

Because the starting solutions for precipitation are of course tranparent and look homogeneous, we scarcely notice that their structure changes with aging. But if we note that tranparency of a solution only means that the dissolved particles in the solution are scattering-free from visible lights (λ~hundreds of nm), it does not at all guarantee the homogeneity of ions, molecules, and clusters.

As for the changes during the aging of the clear solutions, we propose Figs. 5 and 6, which may reasonably explains the delay of precipitation. Figure 5 suggests that it takes a certain time to dissolve a dissolved material more uniformly. In the as-dissolved structure, there are many nucleus for the precipitation to fasten the reaction. Aging of it would reduce the number of nucleus. Figure 6 indicates that water and ethanol, which is known as the most miscible pair in science, may not be homogeneous at molecular level. Because water has higher dielectric constant than ethanol, a solute is likely to be ionized in water. Considering that the precipitation is likely to occur when ionized, the change described in Fig.6 is related to the decrease of the reactive site in the solution. These structural changes are gradually prooved by NMR measurement.[9,10] And finally, it is emphasized that these changes should be surely enhanced by ultrasonication.[10]

REFERENCES

1) S.V.Ley and C.M.R.Low, *"Ultrasound in Synthesis"*, Springer-Verlag, Berlin, Heidelberg (1989)
2) M. Yoshimura and W.Suchanek, *Solid State Ionics*, 197-208 (1997).
3) N.Enomoto, M.Katsumoto, Z.Nakagawa, *J.Ceram. Soc.Jpn.*, 102 [12] 1105-1011 (1994).
4) N.Enomoto, J.Akagi, Z.Nakagawa, *Ultrasonics Sonochemistry*, 3 [2] 97-103 (1996).
5) N.Enomoto, S.Maruyama, Z.Nakagawa, *J.Mater. Res.*, 12 [5] 1410-1415 (1997).
6) W.S.Clabaugh, E.M.Swiggard, and R.Gilchrist, *J.Res.Natl.Bur.Stand.*, 56 [5] 289-291 (1956).
7) H.Yamamura, A.Watanabe, S.Shirasaki, Y.Moriyoshi, and M.Tanada, *Ceram.Intl.*, 11 [1] 17-22 (1985).
8) H.L.Choi, N.Enomoto, N.Ishizawa, Z.Nakagawa, *Powder Diffraction*, 9 [3] 187-188 (1994)
9) N.Enomoto, J.Shiihara, T.Hongo, Z.Nakagawa, *J. Ceram. Soc. Jpn.*, 107 [3] 285-288 (1999).
10) T.Haseba, K.Matsushita, T.Asakura, K.Kameyama, T.Tamaki, S.Okouchi, T.Watanabe, and H.Uedaira, *Alcoholism: Clinical and Experimental Research*, 5 [17], 963-967 (1993)