Preparation of Ultrafine SnO_2 Powders by Spray-ICP Technique

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Abstract

The Spray-ICP technique uses the ICP(Inductively Coupled Plasma) of ultra-high temperature which is produced by r.f. power. The ICP is well-kwown as a clean heat source for the preparation of pure ceramic particles because the ICP is a electrodeless-thermal plasma without contamination.

In this study, SnO_2 particles were sythesized from metal salt solution by Spray-ICP technique. The effects of concentration of solution, collecting location of powders were investicated. The prepared SnO_2 particles from each concentration of solution had same crystalline phase(tetragonal SnO_2) and the mean size decreased in proportion to the increase of solution concentration. Each SnO_2 powders collected in reactor and electrostatic collector had same crystalline phase and morphologies. The mean size of SnO_2 particles prepared by Spray-ICP technique was below 30nm.

1. Introduction

Until now the nanosize ceramic powders have been synthesized by thermal plasma[1]. Thermal plasma is divided into two kinds on a large scale. One is a d.c. plasma(or arc plasma), the other is a r.f. plasma(or inductivily coupled plasma, ICP). A d.c. plasma have been used for the synthesis of oxide or nonoxide powders and thermal-spray coating, etc. However the synthesized powders were contaiminated by carbon electrode for ignition, and then the unreacted materials is formed because of a fast plasma stream. But a r.f. plasma is a electrodeless plasma and so the synthesized powders were high purity. This plasma have more slow stream-line and a homogeneous temperature distribution than a d.c. plasma. Therefore the products without unreacted materials can be obtained with a sufficient reaction of substances.

Ultrafine SnO_2 powders, in this research, were synthesized by ICP-spray technique. The effects of concentration, collecting location of powders were investicated.

2. Experimental Procedures

Figure 1 shows a schematic diagram of spray-ICP equipments[2]. A plasma gas(Ar gas, 1.4 ℓ min^{-1}) flow into a r.f. torch(quartz tube) which three-turned r.f. coil (55mm inner dia.) is placed around. The radio-frequency is a 6MHz and r.f. power of 5kW is applied to a r.f. coil. The formed ICP at these generating conditions is stabilized by a sheath gas(Ar gas, 30 ℓ min^{-1}). Figure 2 shows a experimental procedure for preparation of SnO_2 powder by spray-ICP technique. The tin chloride solution was prepared by dissolved tin metal in conc. HCl. The tin chloride solutions are atomized in a ultrasonic atomizer. The formed mist (solution droplets) are moved by carrier gas(Ar gas, 1.4 ℓ min^{-1}) and are sprayed into ICP(40mm dia., 160mm long) at narrow-tiped nozzle(1.5mm fine tip). These mist move from ICP to ICP tail flame. The SnO_2 powder in reactor(70mm dia., 500mm long) is produced by cooling and is collected with using an electrostatic collector. About the formed powder from tin chloride($SnCl_4$), the powder is prepared as the change of solution concentration(0.5, 0.3 and 0.1M) to discuss the extent of crystallinity.

The products are characterized by x-ray diffractometer(XRD, CuK_α target and Ni filter ; Rigaku Denki, Co., Japan), transmission electron microscopy(TEM, CM-2, Philips Co., Nertherland) and scanning electron microscopy(SEM, S-5000, Hitachi Co., Japan).

3. Result and Discussion

On synthesizing SnO_2 fine powder by Spray-ICP technique.The concentration of starting solution were changed 0.5, 0.3 and 0.1M for the effect on crystalline, morphology and size of fine powder.

Fig.3 shows the result of powders characterized by XRD. The prepared powders in solution of each concertration were SnO_2 fine powders having tetragonal structure.
As the concentration of starting solution increases, crystallization and grain size of SnO_2 powders increases.

Fig.4 shows the TEM photographs of SnO_2 fine powders synthesized from starting solution of each concentration.
SnO_2 fine powders were composed of spherical and bar-shape particles. the prepared SnO_2 fine powders from 0.1M solution was mainly observed spherical-shape particles and SnO_2 fine powders from 0.3M and 0.5M solution were mainly bar-shaped particles. That SnO_2 fine powder having rutile structure has a bar-shaped morphology corresponds to Kagawa[3, 4].
As the concentration of starting solution increases, the crystallization of SnO_2 powder

increases. Because of (110) and (101) planes of SnO_2 powders being densest, it is regarded that particles having grown (110) and (101) planes become bar-shaped. and large particles investigated in TEM photographs formed coalescene growth by coagulation before the solidfication.

Fig.5 shows the result measured mean size and size distribution of SnO_2 powders by TEM photographs.

Mean size of every sample is below 30nm. as the concentration of starting solution decreases, mean size decreased and the mean size of prepared fine powders from 0.1M solution was about 10nm and finer.

Table 2 shows that the lattice constant of prepared powder wsa investigated using unit cell of TSS(Thhuku university supercomputer service network). regardless of the concentration of solution, lattice constant was mainly constant. it is considered that temperature is constant among inner reaction conditions.

For the influence on collected position of prepared SnO_2 fine powders, the prepared SnO_2 powder from 0.3M solution was collected in reactor and electrostatic collector and then was investigated crystalline, morphology and grain size.

Fig.6 shows the XRD results of the SnO_2 prepared from 0.3M solution collected in reactor and electrostatic collector. every crystalline of SnO_2 is tetragonal and collected position has no effect on the crystalline of products.

Fig.7 shows the TEM photographs for the observation of particles. SnO_2 powders collected each position were mainly spherical and bar-shaped, especially fine powder collected reactor was chiefly bar-shaped. and the crystal growth progressed easily to (110), (101) planes. this is a cause that the reactor temperature is higher than elecrostatic reactor by ICP durig the synthesis of SnO_2.

The size distribution of synthesized SnO_2 powder is mainly in limits of 10~30nm and the mean size is chiefly below 20nm.

4. Conclusion

1. The crystalline structure of the synthesized SnO_2 fine powder by Spray-ICP technique is the tetragonal structure of rutile having the main peak of (110) plane.
2. The collected position of the synthesized SnO_2 fine powder by Spray-ICP technique did not bring the effect to crystalline and morphology of particles.
3. The synthesized SnO_2 fine powder by Spray-ICP technique is mainly bar-shaped, In the case of the concentration of starting solution being dilute, the distribution of spherical shape is high, the mean size of SnO_2 powders is below 30nm and finer.

5. References

[1] N. KURAMOTO, H. TANIGUCHI, "Transparent AlN Ceramics", J. Mat. Sci. Lett., 3, 1984, 471~74.

[2] AKITO, KATO, "Vapor Phase Synthesis of Ceramic Powders", pp. 181~92 in Advances in Ceramics, Vol. 12 : Ceramic Powder Science, Edited by G. L. Messing, K. S. Mazdiysni, J. W. McCauley and R. A. Haber, Am. Ceram. Soc., USA(1987)

[3] SOTIRIS E. PRATSINIS, "Vapor Synthesis of Ceramic Powders", pp. 227~38 in Ceramic Tranasctions, Vol. 12, Ceramic Powder Science Ⅲ, Edited by S. Hirano, G. L. Messing and H. Hausner, Am. Ceram. Soc., Nagoya-shi, Japan (1991)

[4] O. SCHULZ and H. HAUSNER, "Gas-phase Synthesis of Ceramic Powders", pp. 275~82, in Ceramic Powder Processing Science, Proceedings of the Second International Conference, Edited by H. Hausner, G. L. Messing and S. Hirano, Berchtesgaden, Germany(1988)

[5] ABHIJIT GURAV, TOIV KODAS et, al., "Aerosol Processing of Materials", Aerosol Sci. and Tech., 19, 1993, 411~52

[6] Y. C. LAU et. al., "Synthesis of Zirconia Powders in an RF Plasma by Injection of Organic Liquid Precusors", pp. 298~303 in Ceramic Transactions, Vol.1, Ceramic Powder Science Ⅱ, A, Edited by G. L. Messing, E. R. Fuller and Jr. H. Hausner, Am. Ceram. Soc., Ohio, USA(1987)

[7] Toyonobu Yoshida, "Thermal Plasma Synthesis of Ceramic Powders and Coatings", 328~339 in Combution and Plasma Synthesis of High-Temperature Materials, Edited by Z. A. Munir and J. B. Holt, VCH, 1990

[8] M. SUZUKI, M. KAGAWA et. al., "Powder Processing of Ultrafine Particles by the Spray-ICP technique", pp. 147~152 in Ceramic Tractions, Vol. 22, Ceramic Powder Science Ⅳ, Edited by S. Hirano, G. L. Messing and H. Hausner, Am. Ceram. Soc., USA(1991)

[9] M. SUZUKI, M. KAGAWA et. al., "Synthesis of Ultrafine Single-Component Oxide Particles by the Spray-ICP technique", J. Mat. Sci., 27, 679~84, 1992.

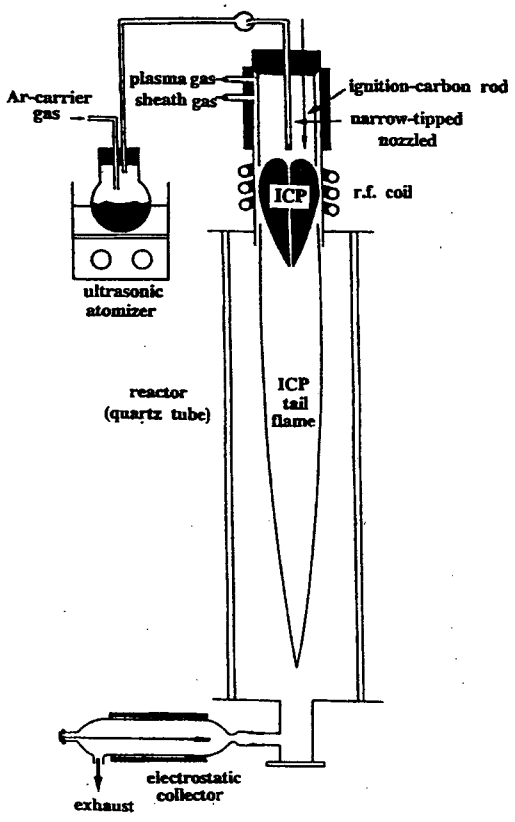


Fig. 1 Schematic diagram of apparatus for SnO_2 powders by spray- ICP technique.

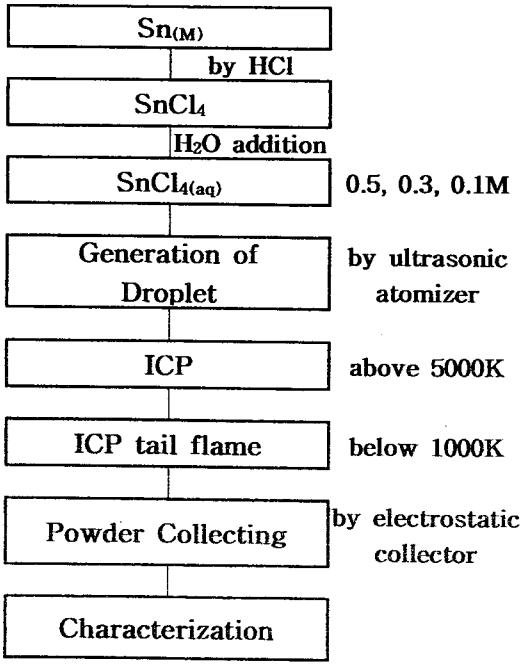


Fig.2 Experimental Procedure for preparation of SnO_2 powder by spray-ICP techniq

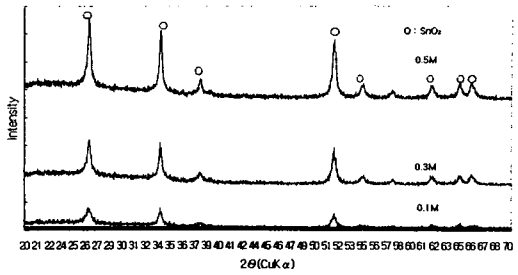


Fig. 3 XRD patterns of SnO_2 powders.

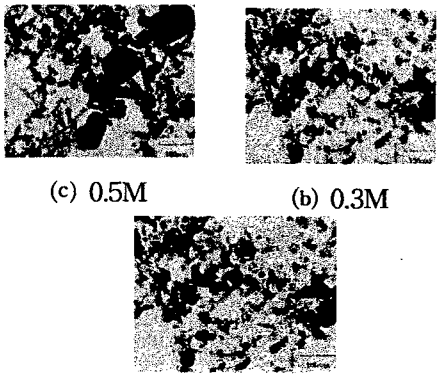


Fig. 4 TEM photographs of SnO_2 powders prepared by spray-ICP technique.

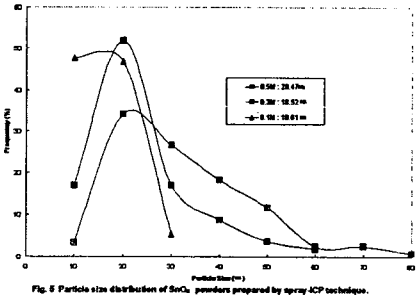


Fig. 5 Particle size distribution of SnO_2 powders prepared by spray-ICP technique.

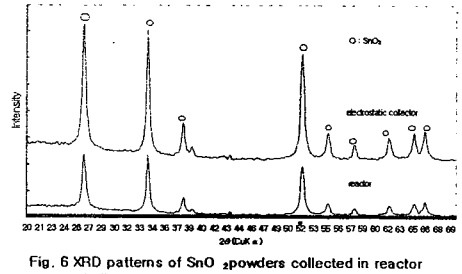
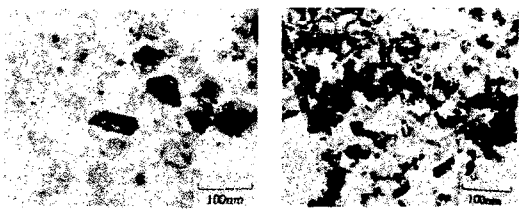


Fig. 6 XRD patterns of SnO ₂powders collected in reactor and ellectrostaticcollector.



(a) (b)

Fig.7 TEM photographs of SnO_2 powders collected in (a) electrostatic collector and (b) reactor.