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Preparation of nanometer yttrium oxide^{*}

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Abstract: The nanometer yttrium oxides were obtained through precipitation in aqueous solution by reaction with ammonium bicarbonate. The reaction between yttrium chloride and ammonium bicarbonate, the effect of surfactants on particle size and the methods of controlling agglomeration were studied. Compared to other methods, the method of controlling the agglomeration by adding surfactant is one of the best methods for controlling the agglomeration of nanometer particles in wet-chemical process. Increasing surfactants in process of precipitation deduced particle size, obtained narrow size distribution of primary particles. As for the concentration range studied, excess surfactants increased the particle size on the contrary. Characteristics of the thermal decomposition of yttrium carbonate were studied. It indicated that the approximate chemical composition of the precipitate was $Y(OH)Cl_x(CO_3)_{(1-x/2)} \cdot 3H_2O$, the cubic Y_2O_3 was obtained above $600^\circ C$, the specific surface and the remain chloride of nanometer Y_2O_3 was decreased with calcinating temperature rising. The spherical nanometer yttrium oxide was gained with primary particles < 50 nm, agglomerate distribution $D_{50} < 150$ nm, $BET > 35$ m²/g, agglomerate constant $(D_{50}/D_{BET}) < 6$.

Key words: nanometer; yttrium oxide; agglomeration

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1 Introduction

Nanometer yttrium oxides show distinct properties, for the nature of the atomic structure in the interfacial regions. When the grain size becomes smaller than the critical scale that is associated with certain properties, such properties can change; many of these properties can be engineered through particle-size and grain-size controlling. The small grain size of the nano-materials has a pronounced effect on many physical and chemical properties^[1-3]. So they are widely used in high-technology material, such as MLCC, Solid oxide fuel cells (SOFC), electrolyzers, and amperometric oxygen monitors, FED, PDP phosphor ($Y_2O_3:Eu$), super conducting materials, advanced structural ceramics application *et al.*^[4-8].

There is current interest in using wet chemical precipitation routes to synthesize nanometer powders. The wet chemically synthesized powder has excellent homogeneity and particle uniformity. But wet chemical precipitation routes have some disadvantage, such as a strong tendency for hard-aggregate formation

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during drying and calcinating the precursor powder^[9-13]. The main objective of this work was to investigate the influence of experimental variables on the yttrium oxide particles and provide an economic method to produce nanometer yttrium oxide.

2 Preparation procedure

2.1 Preparation

Yttrium oxide source for fabrication was 99.99% pure oxide obtained from rare earth plant. Other reagents employed in the process, such as hydrochloric acid, ammonium bicarbonate, surfactant, were all industry grade, and were used without further purification.

A yttrium stock solution was prepared as follows: yttrium oxide (purity > 99.99%) were dissolved in a stoichiometric amount of hydrochloric acid and diluted to 0.35 mol/L with respect to yttrium ion and had a pH of 3 to 5. The stock solution was filtered through two layers qualitative filter paper. Adding 40 L of stock solution and some surfactants to 100 L vessel. An amount of ammonium bicarbonate was dissolved in water and filtered through two layers qualitative filter paper. The ammonium bicarbonate reactants were introduced dropwise at rates of no more than 2 L/min to constantly stirred yttrium stock solution at 350 rpm during the whole reaction period at room temperature. Then the resulting precipitate was vacuum filtered and washed with distilled water and dispersed and calcined at 860°C for 4 h. The preparation process was described in Fig1.

2.2 Measurements

The crystalline phase identification was performed by the X-ray diffraction (XRD) (SEIMENS D/max-1200X, German) method using $\text{CuK}\alpha$ radiation. The precipitate morphology and size were examined by TEM (Model JEM-1010, JEOL, Japan) and SEM (Model X-650, HITACHI, Japan). Specific surface areas of the nanometer powders were determined by the BET (Model Coulter SA3100, USA) method. The distribution of the agglomeration was determined by the laser scatter particle analyzer (Model Coulter Ls-230, USA). The thermogravimetry (TG) was examined at rate of 10°C/min in air by NETZSCH TG209 (German).

3 Result and discussion

3.1 Procedure of precipitation

The Value of pH of yttrium solution was examined every two minutes during the precipitation. The variation of the pH value with the molar ration $[\text{NH}_4\text{HCO}_3]/[\text{Y}^{3+}]$ is shown in Fig. 2. Based on the change of pH and observation in precipitation, when the pH value of solution is above 4, a little of precipitate liking snow forms in yttrium stock solution when ammonium bicarbonate being added, the pH value of solution is slowly rising and a flat roof of the pH value appears. After the molar ration $[\text{NH}_4\text{HCO}_3]/[\text{Y}^{3+}]$ is above 3, the pH value of solution is rapidly rising. The analysis of precipitation (Table 1) shows

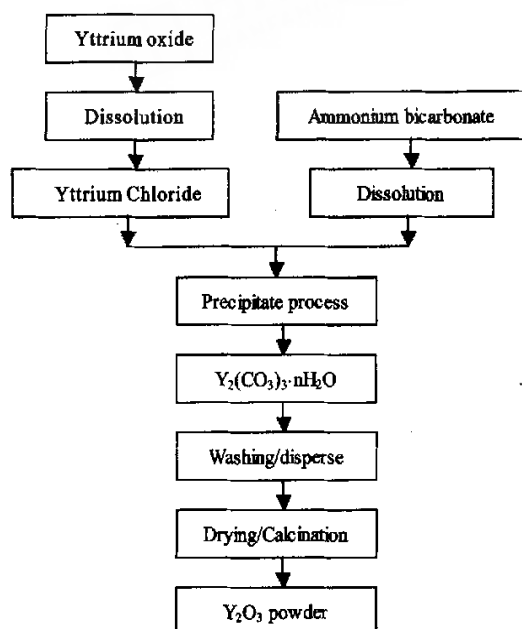
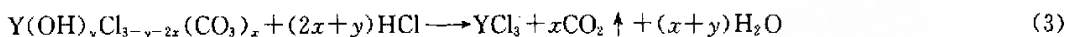
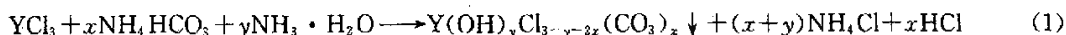


Fig. 1 The Flowchart of the preparation procedure

the amorphous precipitation is not entirely yttrium carbonate, $[\text{CO}_3^{2-}]/[\text{RE}^{3+}] < 1.5$. Basing on equation of positive and negative electric charge, there are some negative ions except CO_3^{2-} . There are so much Cl^- in yttrium chloride stock solution that the Cl^- is easy to enter the precipitation. The analysis of precipitation approves there are much Cl^- in precipitation. At the same time ammonia bicarbonate with some ammonia was decomposed by ammonia bicarbonate, so the OH^- can enter precipitate. According to reference [14,15], the reaction between yttrium chloride and ammonium bicarbonate can be expressed as follows,



So the total equation of reaction is:

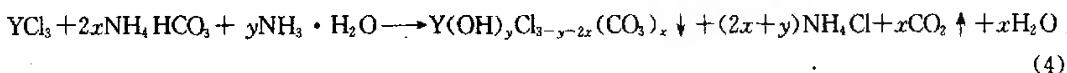


Table 1 The chemical analysis of precipitate $w/\%$

Element	C	Cl	Y	Y ₂ O ₃
Amorphous	7.5	1.7	41	52

The molecular formula was generally expressed as $\text{Y}(\text{OH})_y\text{Cl}_{3-y-2x}(\text{CO}_3)_x \cdot n\text{H}_2\text{O}$.

The Fig. 2 shows the loss of weight of precipitate of yttrium is 48% (mass fraction). Based on Table 1 and Fig. 3, the molecular formula of precipitate is $\text{Y}(\text{OH})_{0.1}\text{Cl}_{0.1}(\text{CO}_3)_{1.4} \cdot 2\text{H}_2\text{O}$.

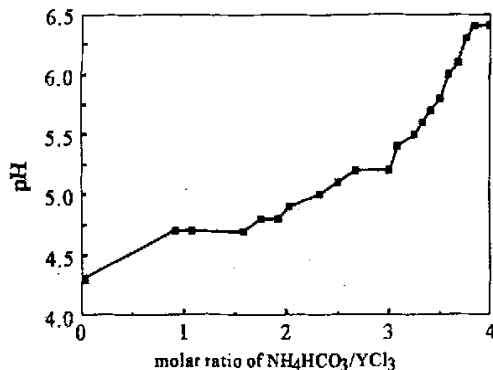


Fig. 2 Relationship between pH value and $n(\text{NH}_4\text{HCO}_3)/n(\text{Y}^{3+})$

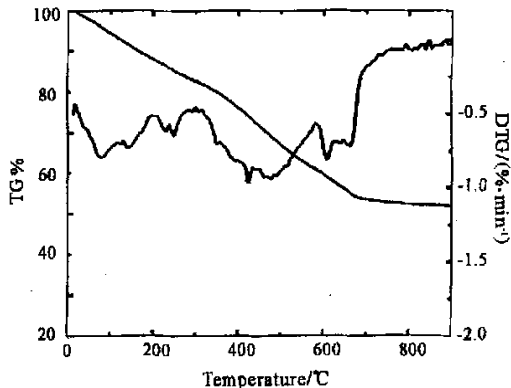


Fig. 3 The TG of precipitate of yttrium

3.2 Influence of surfactant concentration on particle size and shape

Fig. 4 gives some useful information in the influence of surfactant concentration on particle size. Increasing surfactants in process of precipitation, deduced particle size and narrow size distribution of primary particles are obtained. For that Gzrar A is macromolecular polymer, its shape in solution likes snake. GzrarA absorbed by particles forms a film of hydrophile on the surface of particles, the film can block the agglomeration of particles. The function enhances as the content of surfactant added, but over the concentration range studied, excess surfactants increased the particle size on the contrary. We thought some particles grow on the surface of polymer as polymer is added enough, excess polymer is the moulding board of

particle growing, so some strip particle forms.

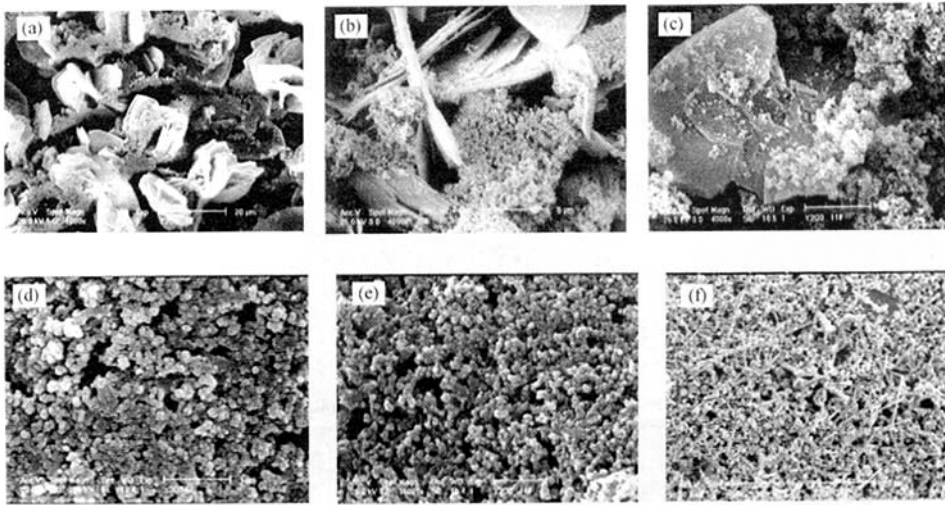


Fig. 4 SEM micrographs of yttrium oxide obtained by adding surfactant
(a)–1%; (b)–5%; (c)–8%; (d)–10%; (e)–15%; (f)–20%

3.3 The study on the controlling of agglomeration

After filtering, some surfactants were dropped into the precursor of rare-earth carbonate (followed as Table 2). The precursor was stirred for some hours at a certain temperature, then the precursor change in- to solid foams, drying and calcinated at 860℃.

Table 2 The effect on agglomeration by quantity and different surfactants

No	The amount of rare- earth carbonate	The amount and type of surfactant	The result of dispersing
1	12	Tween-80 200 mL	Bad, light yellow mass
2	12	Tween-80 400 mL	Bad, yellow mass
3	12	PVA 300ml 10 g/L	Bad, small sandy
4	12	GzrarA 300ml 5 g/L	Bad, mass
5	12	GzrarA 300ml 10 g/L	Preferable, small powdery
6	12	GzrarA 300ml 20 g/L	Preferable, small powdery
7	12	GzrarB*500ml 100 g/L	Preferable, some mass
8	12	GzrarB 1200ml 100 g/L	Bad, elasticity gluey particle
9	12	GzrarA 300ml 10 g/L +GzrarB 500 mL 100 g/L	Very good, puff powder

Fig. 5 shows the particle size distribution curves of yttrium oxide obtained by different agglomeration- controlling methods. The yttrium oxide obtained by milling and washing with alcohol^[16,17] show some large particles. The mean particle size of agglomeration by the milling and washing with alcohol is larger than those by heterogencous azeotropic distillation[18], the mean particle size of agglomeration by this method is the smallest. It also proves that this method is economic.

When GzrarA was added and absorbed on particles, double electric layer was incrsassated and the space of particles was enhanced. And GzrarA can easily form foams, it also enhances the space of particles. The

surface tension of GzrarA in water is small. Based on equation of capillary pinch, decreasing surface tension and enhanced aperture can decrease the force of capillary. So adding GzrarA has two main functions: (1) enhancing repulsion force of particles; (2) decreasing the capillary pinch. But it is the best by just using GzrarA. It is possible the GzrarA can't repel the pinch of particles, and some particles touch together, some particles form hard agglomeration by the hydroxide of water. Because macromolecule surfactant has space baffle function, GzrarB was added to baffle the touch of particles. And strong stirring can disperse the particle, the mechanism can explain by the action between macromolecule surfactant and particles.

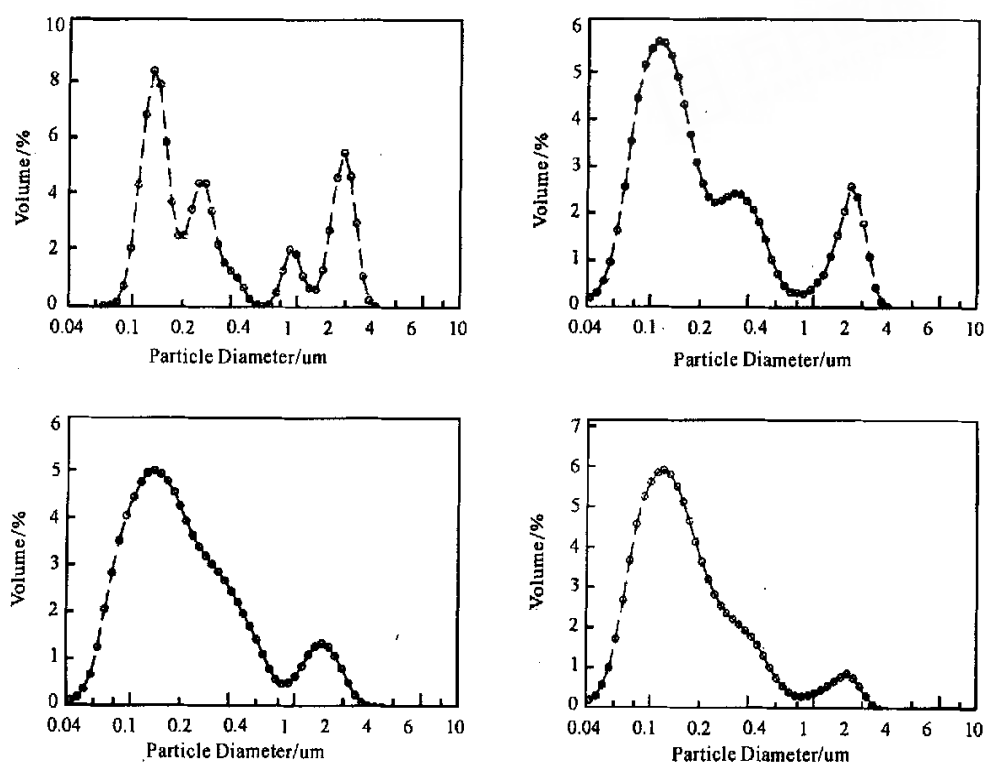


Fig. 5 Particle size distribution curves of yttrium oxide obtained by different methods

(a)—milling; (b)—washing by alcohol; (c)—heterogeneous azeotropic distillation; (d)—the method studied

In the end the mechanism of controlling agglomeration in this study is: making particles, surfactant and air to form the mixture foams of solid, liquid and gas to enhance the space of particles, and using the baffle and stabilization of macromolecule surfactant to control the agglomeration of particles.

3.4 The decomposition of yttrium carbonate

The calcination has important influence on the properties of yttrium powder. If we raise the temperature of calcinations, the specific surface area is reduced, the particle size is increased and energy is wasted. Otherwise the yttrium can not entirely decompose. So the decomposition of yttrium carbonate were analysed by thermogravimetry (TG). The TG result (Fig. 2) shows yttrium carbonate entirely decompose before 700°C. Fig. 6 shows the temperature and time of calcinations have a signify effect on crystalline phase of yttrium oxide. But the calcinations temperature was determined at 860°C in order to gain unitary crystalline phase and decrease the loss on ignition of yttrium oxide.

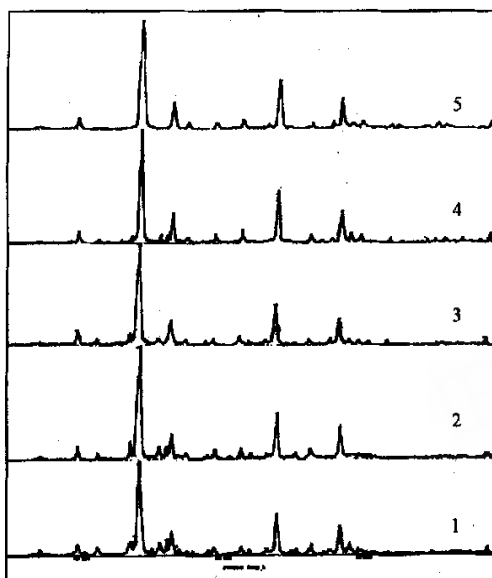


Fig. 6 The XRD for yttrium oxide prepared under calcinate conditions at 600°C for 3 h (1), 700°C for 3 h (2), 800°C for 3 h (3), 860°C for 1 h (4) and 860°C for 3 h (5)

Table 3 Quantitative analysis of yttrium oxide of Fig. 6 by XRD

Sample	No.					w/%
	1	2	3	4	5	
Y ₂ O ₃	86.71	87.42	90.58	93.38	100.00	
Y ₃ O ₄ Cl	13.29	12.58	9.42	6.62	0	

3.5 The characteristics of nanometer yttrium oxide

Optimizing the parameters of preparation, the uniform, nanometer size, spherical yttrium oxide particles were gained, the main characterizations of nanometer yttrium oxide were shown in Fig. 7, Table 4.

Table 4 Main properties of nanometer yttrium powder

Sample	BET/(m ² · g ⁻¹)	d _{BET} /nm	d ₁₀ /nm	d ₅₀ /nm	d ₉₀ /nm	AF-(50) (d ₅₀ /d _{BET})
Y ₂ O ₃	37.41	32.0	74	138	650	4.3

4 Conclusion

Uniform, nano-meter size, spherical yttrium oxide particles were prepared by precipitation in aqueous solution reacted with ammonium bicarbonate. Increasing surfactants in process of precipitation deduced particle size, obtained narrow size distribution of primary particles. Over the concentration range studied, excess surfactants increased the particle size on the contrary. The cubic Y₂O₃ was obtained above 600°C, The spherical nanometer yttrium oxide is gained with primary particles < 50 nm, agglomerate distribution D₅₀ < 150 nm, BET > 35 m²/g, agglomerate constant (D₅₀/D_{BET}) < 6.

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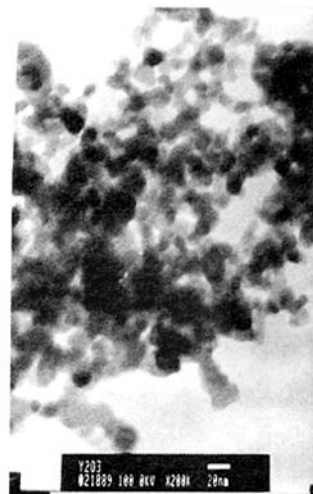


Fig.7 TEM micrographs of yttrium oxide