

Synthesis and Properties of Y_2O_3 Powder Obtained by Different Methods

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Abstract

Three different wet chemical methods for the preparation of fine yttrium oxide powders from chloride solutions were compared: (a) precipitation with ammonia, (b) precipitation with urea, and (c) precipitation from an Y–organometallic complex. Powders with widely different morphological characteristics resulted. Ammonia precipitated powder was strongly agglomerated. Urea precipitated powder consisted of spherical particles with narrow size distribution (mean size $\approx 0.4 \mu\text{m}$), whereas powder obtained from the Y–organometallic complex had a ‘foamy structure’ and consisted of soft agglomerates very sensitive to mechanical treatment. Powders were characterized by SEM and TEM techniques, and it was observed that agglomerates consist of randomly oriented crystallites with nearly spherical shape.

Drei verschiedene naßchemische Verfahren zur Herstellung feinkörniger Y_2O_3 -Pulver aus chloridischen Ausgangslösungen wurden miteinander verglichen: (a) Fällung mit Ammoniak, (b) Fällung mit Harnstoff und (c) Fällung aus einer Y–organometallischen Verbindung. Die erhaltenen Pulver wiesen äußerst unterschiedliche Morphologien auf. Das mit Ammoniak gefällte Pulver zeigte einen hohen Agglomerationsgrad. Die mit Harnstoff gefällten Pulver bestanden aus kugelförmigen Teilchen mit einer engen Korngrößenverteilung (mittlerer Durchmesser $\approx 0.4 \mu\text{m}$). Das Pulver aus der Y–organometallischen Verbindung hatte eine ‘schwammige Struktur’ und wies weiche, durch mechanische Behandlung leicht zerstörbare, Agglomerate auf. Die Pulver wurden mittels REM und TEM charakterisiert. Dabei zeigte sich, daß die Agglomerate aus nahezu kugelförmigen Kristalliten mit statistischer Orientierung bestehen.

On compare trois différentes méthodes de préparation de poudres fines d’oxyde d’yttrium, à partir de solutions de chlorures, par voie chimique humide: (a) précipitation avec de l’ammoniaque, (b) précipitation avec de l’urée et (c) précipitation à partir d’un complexe organo-métallique d’yttrium. Il en résulte des poudres possédant des caractéristiques morphologiques très différentes. La voie (a) donne une poudre très agglomérée, la voie (b) une poudre formée de particules sphériques présentant une granulométrie resserrée (taille moyenne d’environ $0.4 \mu\text{m}$), tandis que la voie (c) produit une poudre à la structure ‘en mousse’, formée d’agglomérats mous, très sensibles à un traitement mécanique. Les poudres ont été caractérisées par une étude MEB et MET, montrant que les agglomérats consistent en des cristallites, de forme pratiquement sphérique, orientées de façon aléatoire.

1 Introduction

During the processing of ceramic powders, especially in the formation stage, reaction parameters, such as metal salt concentration, pH, temperature, etc., significantly influence the particle size, shape and size distribution. Ceramic powders may be produced in a number of ways.¹ In general, the aim is to obtain ceramic powder with small particle size and narrow size distribution, as well as to reach high purity. Hard agglomerates cause differential sintering and limit the final densities.

In recent papers^{2–4} the influence of the kind of precursors and the preparation conditions on the properties of the Y_2O_3 powders was demonstrated. It was reported that by adding the acidic $Y(NO)_3$ solution to NH_4OH solution an Y_2O_3 powder sinterable to high density could be produced.²

Micheli⁴ used an organic polymer as a precursor for preparing weakly agglomerated Y_2O_3 powder which had to be milled. Matijević & Hsu⁵ described a method for the preparation of monodispersed colloidal particles of the lanthanide compounds. A method for the preparation of colloidal dispersions of uniform spherical particles of yttrium basic carbonate and rod-like particles of yttrium amine carbonate in the presence of urea was described by Aiken *et al.*⁶ The role of processing variables such as concentrations of specific ions, pH, temperature and aging time was studied by Sordelet & Akinc.⁷

The present paper describes the preparation of fine Y_2O_3 powder by thermal decomposition of the Y-organometallic complex. Advantages of the method are illustrated by comparing the powder characteristics with characteristics of powders obtained by other methods. Emphasis was on morphological and texture characteristics.

2 Experimental Procedure

Yttrium chloride hexahydrate ($YCl_3 \cdot 6H_2O$) (Strem Chemicals Inc., Newburyport, MA 01950, USA), ammonium hydroxide (NH_4OH) (Zorka-15000 Šabac, Yugoslavia), urea (CON_2H_4) (Kemika-41000 Zagreb, Yugoslavia) and glucose ($C_6H_{12}O_6$) (Kemika-41000 Zagreb, Yugoslavia) were used. All chemicals were PA grade. Y_2O_3 powders were synthesized by three different methods, designated here as (A), (B) and (C).

Method (A) used for the preparation of Y_2O_3 powder by precipitation with ammonia is presented in Fig. 1. Ammonium hydroxide was added dropwise to the yttrium chloride with concentration

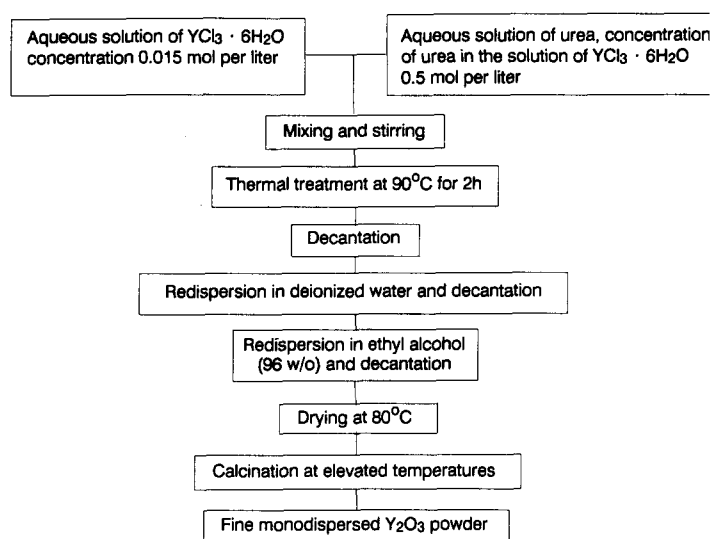


Fig. 2. Flow diagram of the synthesis of Y_2O_3 powder according to method (B).

1.5×10^{-2} mol/litre, to reach $pH = 10-10.5$. The resulting precipitate was flocky, voluminous and settled out quickly. After separation from the mother solution, the precipitate was washed by dispersion in deionized water and finally in ethyl alcohol (96 vol.%) to remove chloride ion and then dried at $80^\circ C$ in air for several hours. An aqueous solution of $AgNO_3$ was used to control the precipitate washing.

Method (B) for the preparation of monodispersed Y_2O_3 powder in the presence of urea is presented in Fig. 2. An aqueous solution of yttrium chloride and urea was prepared so that the concentrations of the yttrium chloride and urea were 1.5×10^{-2} mol/litre and 0.5 mol/litre, respectively. The solution was heated in a water bath at a heating rate of $40-50^\circ C/h$, to a temperature of $90^\circ C$. The solution was aged at this temperature for 2 h. The originally clear solution became milky at about $82^\circ C$. After aging the solution was left overnight and the precipitate was separated by decantation. Washing with deionized water, ethyl alcohol and drying were carried out as described in method (A).

Method (C) for the preparation of Y_2O_3 powder from an Y-organometallic complex is summarized in Fig. 3. An aqueous solution of the yttrium chloride with concentration 1 mol/litre was heated to the boiling temperature and mixed with an organic base (Schiff's base with excess urea). The molar ratio of the yttrium chloride, the urea and the glucose was 1:2:1, respectively. The synthesis of the organic base was carried out by melting glucose and urea at $150^\circ C$, as described in detail earlier.⁸ The clear dark-red solution was boiled for 1 h at $90-100^\circ C$ to dryness. The resulting solid black-coloured

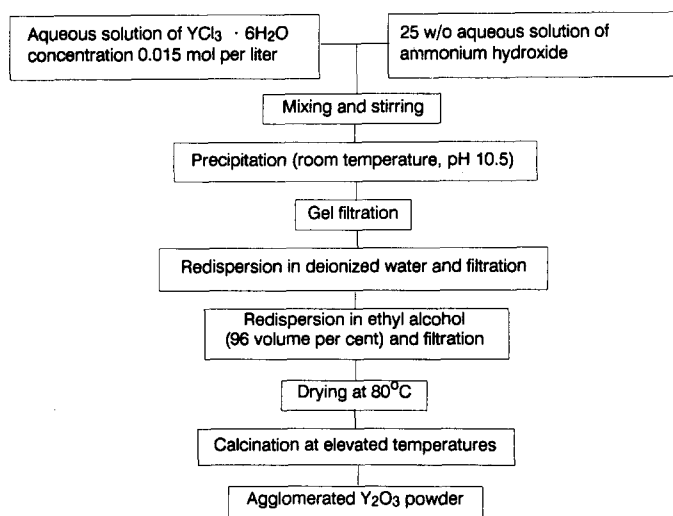


Fig. 1. Flow diagram of the synthesis of Y_2O_3 powder according to method (A).

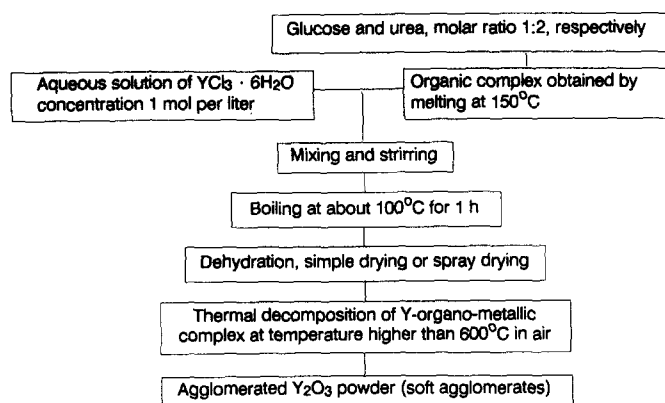


Fig. 3. Flow diagram of the synthesis of Y_2O_3 powder according to method (C).

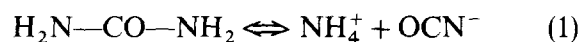
foamy mass was further pyrolysed in air. At about $350^\circ C$ chloride ion was removed by sublimation of ammonium chloride. A further increase in temperature up to $600^\circ C$ resulted in a white Y_2O_3 powder with a remnant 'foamy structure'.

The pH of the solutions containing the precipitates was measured by pH meter at room temperature. The thermal decomposition characteristics of the precipitates were determined by DTA apparatus (Perkin-Elmer 1700) at a heating rate of $10^\circ C/min$ in air. The solids were also characterized by infrared technique (Perkin-Elmer 783) using KBr pellets. Specific surface area was determined by the BET apparatus (Perkin-Elmer Sorptometer 212D), using nitrogen as an absorbent. The powder particle size and morphology were examined by scanning electron microscope (SEM, Leitz AMP 1600T). Phase composition of the calcined samples was examined by X-ray using nickel-filtered CuK_α radiation (Phillips APD 1700). Mean crystallite size was calculated from the width of the half peak height of the (222) Y_2O_3 reflection using the Scherrer relationship.⁹ A correction for instrumental broadening was done using Warren's formula⁹ and a crystalline quartz standard. Crystallite shape and orientation were examined by transmission electron microscopy (TEM, Jeol 2000F). Particle size distribution was measured by a granulometer apparatus (Cilas-Alcatel HR 850).

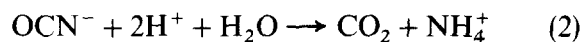
3 Results and Discussion

The morphological characteristics of the Y_2O_3 powders obtained by different methods are very dissimilar (Fig. 4(a)–(e)). The Y_2O_3 powder produced by method (A) contains aggregates of irregular shape (Fig. 4(a)). The Y_2O_3 powder produced by method (B) has a narrow size distribution of spherical particles (Fig. 4(b) and (c)). Some agglomerates are discernible (Fig. 4(b)); however, they are easily de-agglomerated by an ultrasonic mixer. Figure 5 illustrates the particle size distribution after ultrasonic mixer treatment for 240 s. The mean particle size after ultrasonic treatment was $0.43 \mu m$. A characteristic feature of the Y_2O_3 powder produced by method (C) is its 'foamy' appearance (Fig. 4(d) and (e)). This foamy morphology is sensitive to mechanical treatment. As shown in Table 1, powder C has the highest specific surface area. Results in Table 1 correspond to powders calcined at $700^\circ C$ for 1 h. The results indicate the 'soft' nature of C agglomerates.

The principal difference between methods (A) and (B) concerns homogeneity. In method (A) the precipitation process occurs under inhomogeneous conditions, as a high concentration gradient exists between the surface of base droplet and solution. On the other hand, in method (B) the homogeneity of chemical composition is on the molecular scale. Decomposition of urea at elevated temperatures plays an essential role in the particle formation, as shown earlier.⁵ At temperatures below $100^\circ C$ the aqueous solution of urea yields ammonium and cyanate ions:^{6,10}



In acid solution cyanate ions react rapidly, according to



whereas in neutral and basic solutions the carbonate ions and ammonia are formed:

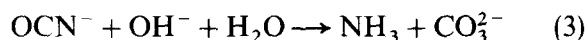


Table 1. Some properties of Y_2O_3 powders prepared in this research

Y_2O_3 powders	Temperature and calcination time ($^\circ C/h$)	Morphological characteristics	BET area ^a (m^2/g)	Mean crystallite size (nm)
A	700/1	Strongly agglomerated	1.5	20
B	700/1	Spherical particles, narrow sized, mean particle size $0.43 \mu m$	4.8	25
C	700/1	'Foamy structure', sensitive to mechanical treatment	22.3	20

^a Samples were calcined at $800^\circ C$ for 1 h in air.

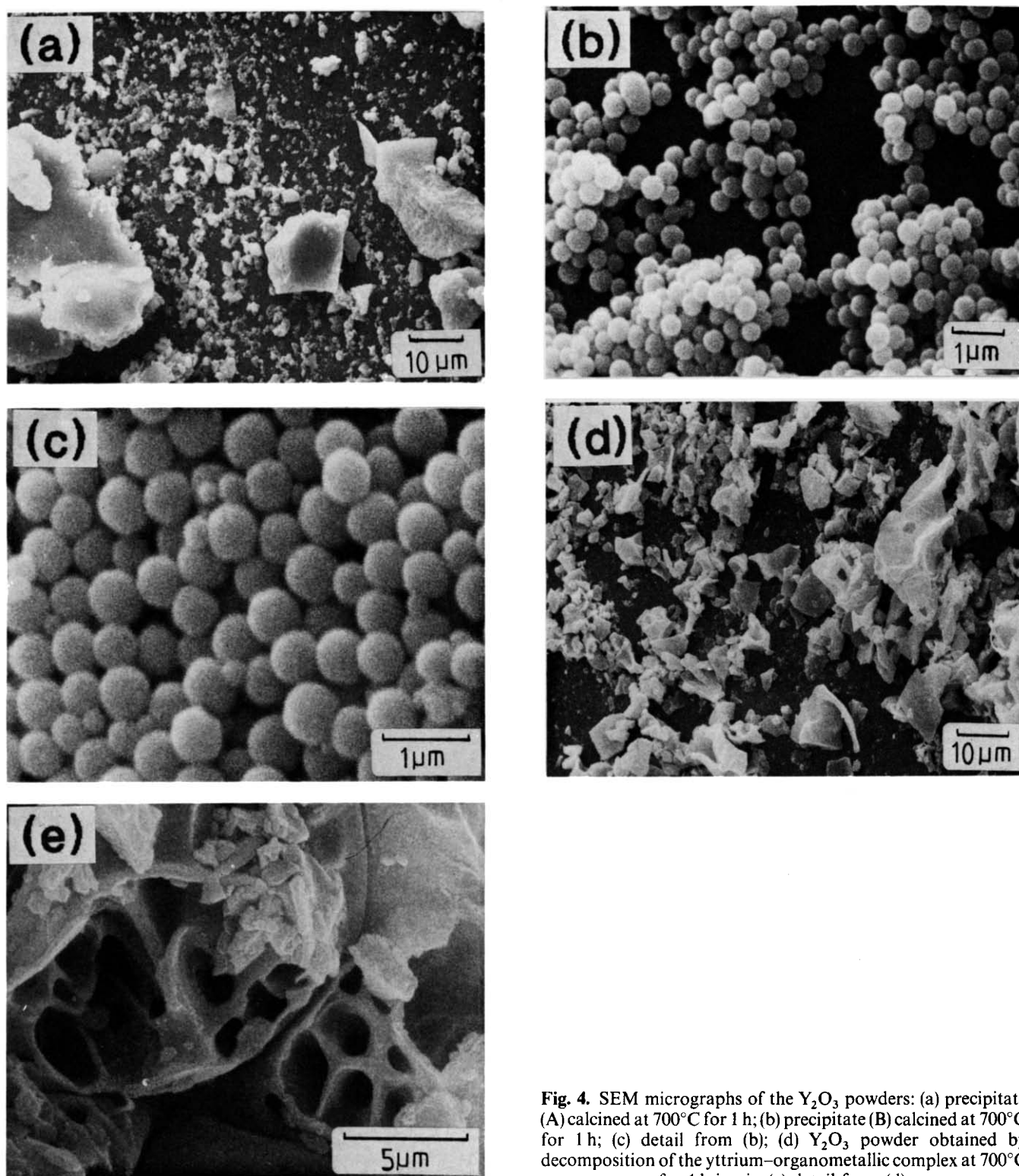
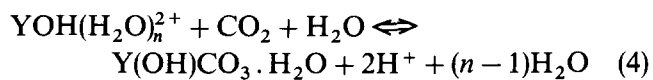


Fig. 4. SEM micrographs of the Y_2O_3 powders: (a) precipitate (A) calcined at $700^\circ C$ for 1 h; (b) precipitate (B) calcined at $700^\circ C$ for 1 h; (c) detail from (b); (d) Y_2O_3 powder obtained by decomposition of the yttrium-organometallic complex at $700^\circ C$ for 1 h in air; (e) detail from (d).

The yttrium ions are weakly hydrolysed in water into $YOH(H_2O)_n^{2+}$.¹¹

The resulting release of hydronium ions accelerates the urea decomposition (eqn (2)). The precipitation of the basic carbonate can be described by the following overall reaction:¹⁰



According to eqns (1)–(4), the reaction parameters, such as pH, the concentration of ions, temperature and heating rate, are factors which control the precipitation process from the embryonal stage to nucleation, nucleus growth, formation and growth of particles. Particle size distribution is a consequence of homogeneity, but other factors such as cation concentration and type of anions have a strong influence on the particle morphology.⁷ The

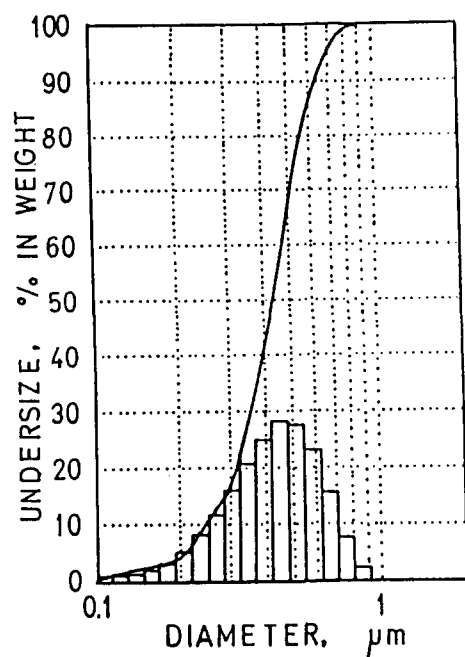


Fig. 5. Particle size distribution for Y_2O_3 powder (sample (B) calcined at $700^\circ C$ for 1 h) after ultrasonic treatment for 240 s.

pH increases stepwise, from about pH = 6 at the outset to pH = 8.6 at the end by thermal decomposition of the urea.

The characteristic of method (C) is the formation of the Y-organometallic complex. The chemical and structural composition of this complex is not known. By dehydration and then by thermal decomposition at elevated temperatures the organic substance combusted and resulted in pure Y_2O_3 powder. The 'foamy structure' of the calcined powder (Fig. 4(d)) the dehydration and the decomposition of the organic substance, due to the formation of gaseous reaction products. The sensitivity to mechanical treatment is related to the collapse of the residual 'foamy structure' of the calcined powder (Fig. 4(d) and (e)).

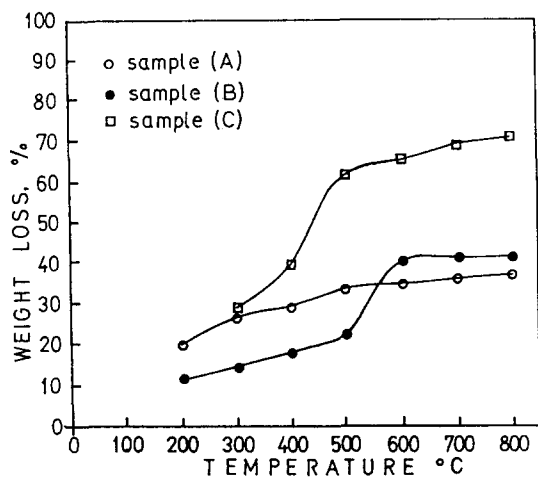


Fig. 6. Relationship between weight loss and temperature for 1-h soaks.

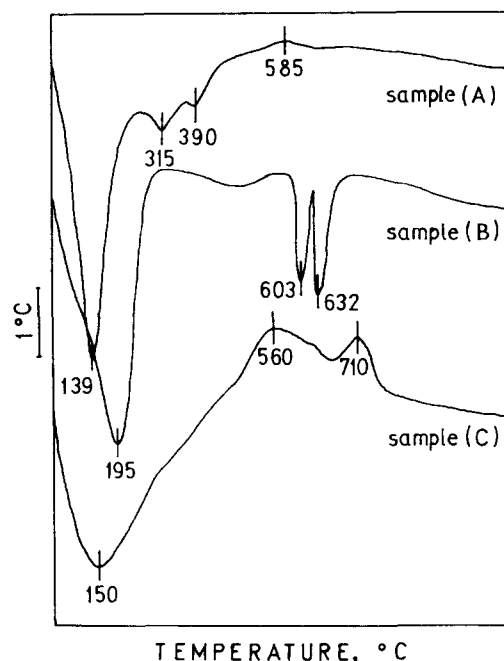
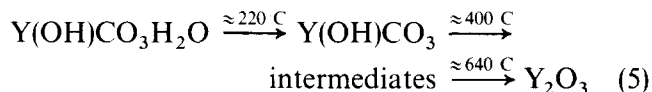


Fig. 7. DTA curves of samples (A), (B) and (C) heated at the rate of $10^\circ C/min$ in air.

The calcination process of the three representative powders was followed by thermogravimetric analysis (Fig. 6). The weight losses after 1 h at the calcination temperature of $800^\circ C$ for samples (A), (B) and (C) were 38, 42 and 71 w/o, respectively. The large weight loss of sample (B) at temperatures $500\text{--}600^\circ C$ is apparently a consequence of the thermal decomposition of $Y(OH)CO_3$ into Y_2O_3 ,⁶ according to



The highest weight loss of sample (C) is a consequence of the combustion of the organic substance. The DTA curve for sample (A) (Fig. 7) shows an endothermic peak at about $140^\circ C$ corresponding to the release of the water of hydration. An endothermic peak (the characteristic doublet) at $270\text{--}480^\circ C$ shows a two-step dehydroxylation similar to that described earlier.^{5,12} The broad exothermic peak at about $580^\circ C$ accompanies crystallization of Y_2O_3 . The DTA of sample (B) does not show any double endothermic peaks corresponding to dehydroxylation (Fig. 7), as in sample (A). The endothermic (doublet) peak is at 603 and $632^\circ C$. The doublet may be due to the simultaneous process of crystallization and chemical decomposition of the carbonate or to the decomposition of oxycarbonate to dioxycarbonate, and finally the change to the oxide as a final product.⁶ The DTA curve of sample (C) shows a broad endothermic peak at about $150^\circ C$ corresponding to the release of the

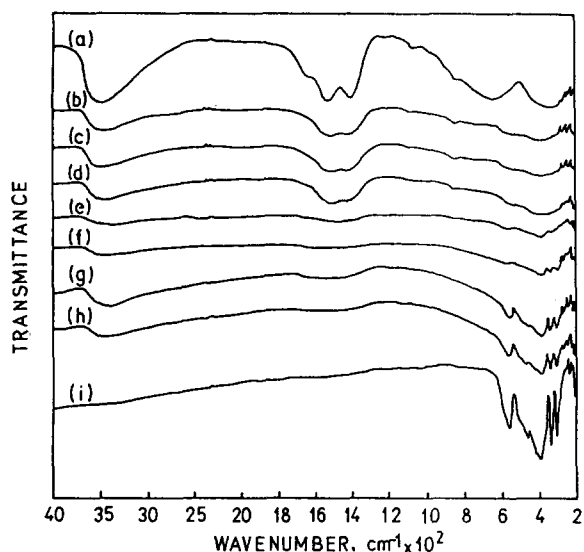


Fig. 8. IR spectra of sample (A) calcined at: (a) 80°C; (b) 200°C; (c) 300°C; (d) 400°C; (e) 500°C; (f) 600°C; (g) 700°C; (h) 800°C for 1 h in air; (i) commercial sample (Strem Chemicals Inc., Newburyport, MA 01950, USA).

water of hydration. The broad exothermic peak with a maximum at about 560°C corresponds to oxidation of organic matter. The exothermic peak with a maximum at 710°C is a consequence of the crystallization of the Y_2O_3 after removing the carbon.

The broad absorption band on the IR spectra (Figs 8–10) at 3480 cm^{-1} and the absorption peak at 1620 cm^{-1} are due to OH stretching and bending, respectively. The broad absorption peaks at 1530 and 1390 cm^{-1} , and intense peaks at 1080 and 840 cm^{-1} may be due to CO band stretching and bending. Absorption peaks at 1530 and 1390 cm^{-1} (Fig. 9) indicate the presence of the carbonate or of the carboxylate group. The chemical bond responsible for the sharp peak at 1630 cm^{-1} (Fig. 10) is not clear. It may be due to $-\text{CONH}_2$ (CO 'amide group') at $1650\text{--}1640\text{ cm}^{-1}$ (Ref. 13) and/or $\text{C}=\text{N}$

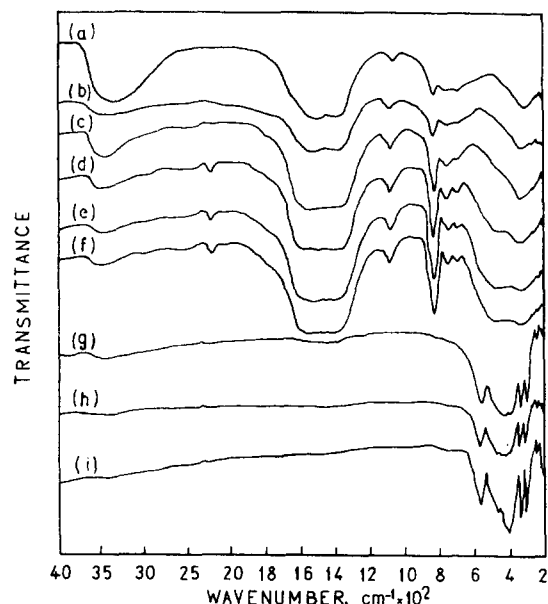


Fig. 9. IR spectra of sample (B) calcined at: (a) 80°C; (b) 200°C; (c) 300°C; (d) 400°C; (e) 500°C; (f) 600°C; (g) 700°C; (h) 800°C for 1 h in air; (i) commercial sample.

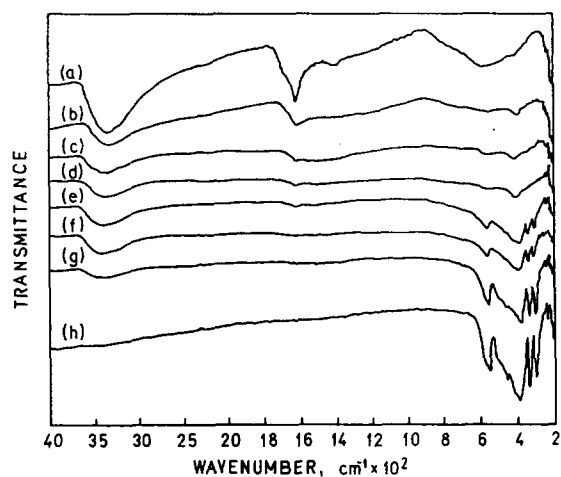


Fig. 10. IR spectra of sample (C). Yttrium-organometallic complex calcined at: (a) 300°C; (b) 400°C; (c) 500°C; (d) 600°C; (e) 650°C; (f) 700°C; (g) 800°C for 1 h in air; (h) commercial sample.

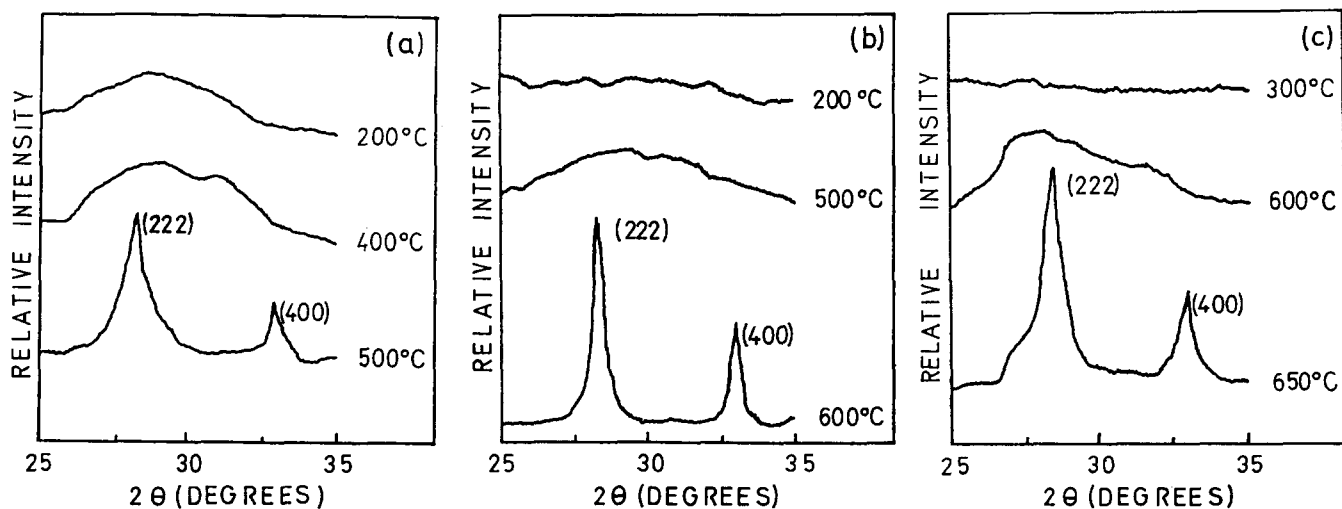


Fig. 11. XRD traces of (a) sample (A); (b) sample (B); (c) sample (C).

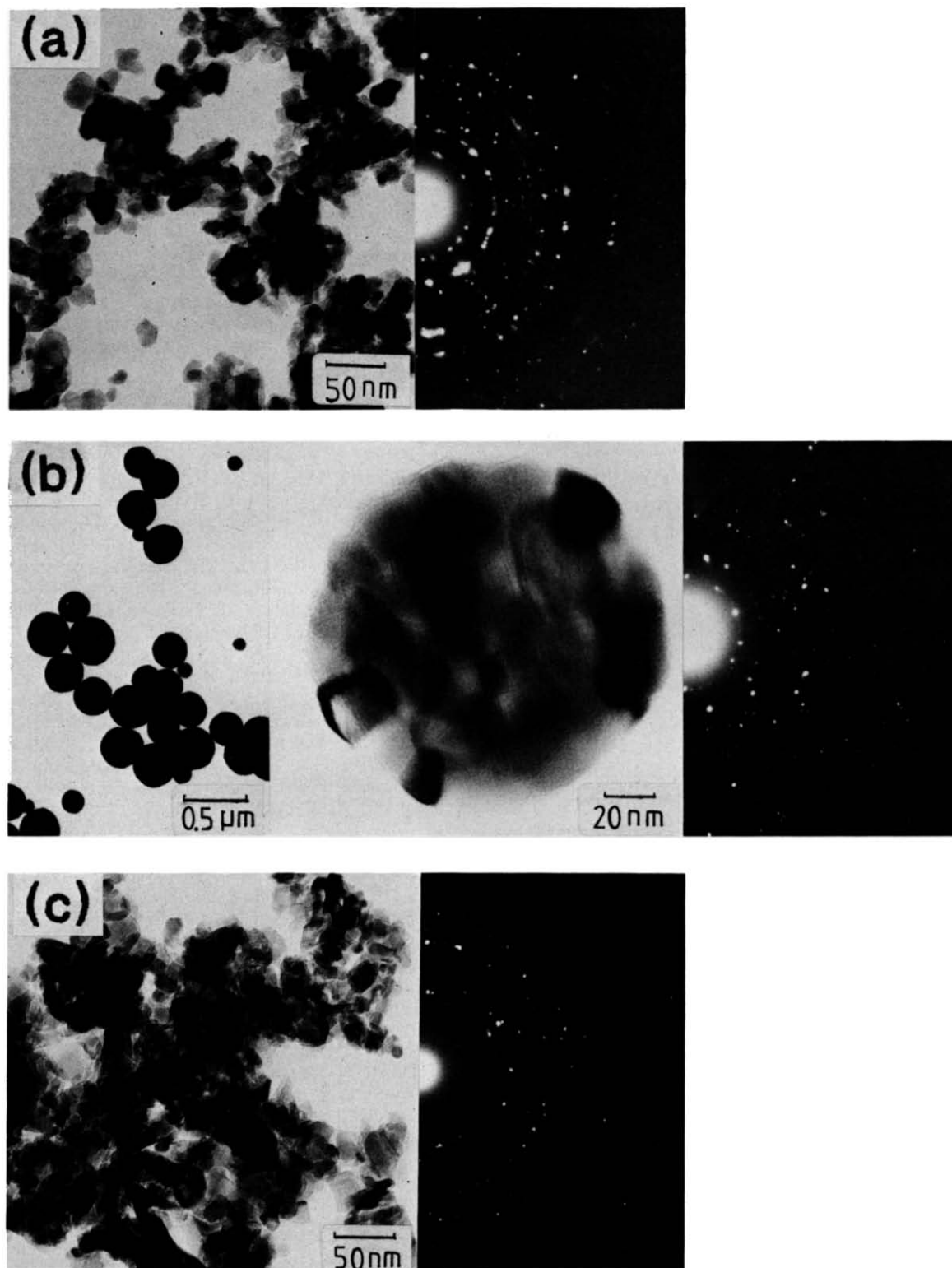


Fig. 12. TEM micrographs with diffraction patterns of the Y_2O_3 powders: (a) precipitate (A) calcined at 800°C for 1 h; (b) precipitate (B) calcined at 800°C for 1 h; (c) Y_2O_3 powder obtained by decomposition of the yttrium-organometallic complex at 800°C for 1 h in air.

group, which has an absorption peak at $1690\text{--}1640\text{ cm}^{-1}$. The IR spectra of the calcined powders are in accordance with the published data.¹⁴ The disappearance of the absorption peaks by calcination of the samples at elevated temperatures is in agreement with the DTA examination.

The XRD data (Fig. 11(a)–(c)) show that the samples (A), (B) and (C) remain amorphous until the calcination temperature exceeds 400 , 500 and 600°C , respectively. The powders treated at higher temperatures exhibit XRD patterns of crystalline, body-centred-cubic Y_2O_3 . The crystallization tempera-

tures for samples (B) and (C) are higher than for sample (A). Sample (B) contains hydroxocarbonate, which decomposes at a temperature of about 600°C. Crystallization of Y_2O_3 in sample (C) is related to the loss of the organic substance.

Figure 12 illustrates the crystallite size, shape and size distribution. Crystallites in all samples have a nearly spherical shape and a narrow size distribution. From X-ray line broadening the mean crystallite size was estimated to be 20, 25 and 20 nm of the calcined samples (A), (B) and (C), respectively (Table 1). There was no significant difference in crystallite size estimated by this method and by TEM examinations. Diffraction patterns of the calcined powder (Fig. 12) show that the crystallites within agglomerates have random orientation. The spherical particles (sample B) are polycrystalline and the characteristic substructure is illustrated in Fig. 12(b).

4 Summary

Precipitation of Y_2O_3 from aqueous chloride solution with ammonia produced strong agglomerates. By precipitation in the presence of urea a narrow sized Y_2O_3 powder with spherical particles (mean size 0.42 μm) was obtained. Practically, this powder contained no agglomerates. Particles were polycrystalline, with a random orientation of the crystallites within agglomerates. The Y_2O_3 powder obtained from the Y-organometallic complex had a 'foamy structure' which is sensitive to mechanical treatment, and it is possible to obtain fine sinterable powder with soft agglomerates. Agglomerates consist of randomly oriented crystallites with nearly spherical shape.

Precipitation in the presence of urea is potentially a method for the production of Y_2O_3 powder of high

purity, controlled morphology (spherical particles) and narrow size distribution.

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