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Crystallization of Yttria Under Hydrothermal Conditions

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Abstract

The effect of precursor type and hydrothermal crystallization conditions on the morphology of yttria grains was studied. Yttrium nitrate and yttrium chloride were used as yttrium salts soluble in water. Yttrium hydroxide obtained by the reaction of the chosen salt with ammonia was subjected to hydrothermal conditions (200–270°C, 0–120 min) in an autoclave. The shape of the yttria grains was strongly dependent on the crystallization temperature and the type of precursor used. With yttrium chloride as a precursor and at crystallization temperatures up to 498K, yttria grains are isometric in shape. Above this temperature yttria grains get elongated with a needle-like shape. The size of the needles depends on the crystallization time. For the case of the yttrium nitrate precursor, the critical temperature of crystallization, above which extended yttria grains appear, is about 25°C higher. From the results a model mechanism for the hydrothermal crystallization of yttria is proposed. © 1996 Elsevier Science Limited.

Introduction

Yttria crystallizes in a cubic form which is stable up to the melting point (2430°C). Because of its chemical stability and refractory nature, yttria has a wide range of applications, e.g. high-temperature chemical-resistant substrates, crucibles for melting reactive metals and nozzles for jet-casting of molten rare-earth-iron magnetic alloys.[1] A new application of yttria are crucibles used as an yttria source in the YBCO monocrystallization process.[2] Pure commercial-grade yttria powder is difficult to sinter to high density without going to temperatures in excess of 1800°C.[1] This is the reason why a lot of research is performed to produce active yttria powder.[1–4] A significant decrease of sintering temperature (about 200°C) was found by using micropowders obtained by crystallization under hydrothermal conditions.[2] Recently it was observed that the morphology of yttria grains produced by the hydrothermal process is dependent on crystallization conditions. Under certain conditions yttria grains change their shape from isometric to elongated, needle or rod-like shape (rods=needles with a greater diameter).

Hydrothermal crystallization is a technique widely used for preparation of active powders of yttria or calcia-stabilized zirconia,[5–6] $BaTiO_3$[7] and chromia.[8] However very little is known about the processes involved in hydrothermal crystallization. In recent research publications the general approach to understand the processes is either qualitative (by observing morphology)[8–11] or thermodynamic.[12] The aim of this work was a study of the effect of hydrothermal conditions (temperature and time) on the shape and size of yttria grains.

Experimental Procedures

The starting point of powder preparation was precipitation of yttrium hydroxide by reaction of 0·1 M yttrium salt water solution with ammonia. Two types of yttrium salts were used: yttrium chloride obtained by dissolution of 99·99% purity yttria in chloric acid and commercial, pure yttrium nitrate produced by ZOCh Lublin (Poland). For a complete precipitation reaction the pH of the solution was controlled and maintained at pH = 9. Precipitated gels were washed with distilled water and decanted up to pH = 7·5. Yttrium hydroxide gels from different precursors were separately subjected to hydrothermal conditions in an autoclave (type LA500 produced by Kombinat MLW in Leipzig, Germany) at temperatures of 200–270°C and holding times of 0–120 min. Crystallized yttria

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powders were again separately washed with distilled water and dried at 120°C. The powders were characterized with a scanning electron microscope (OPTON DSM 950) and powder size and shape were analysed. The powder size was estimated from experimental distribution of its diameters approximate to the simple log-normal distribution with a median and geometrical deviation as estimators.[13] Median was defined as the value at which 50% of the material is greater than, and 50% smaller than the stated size. On the other hand geometrical deviation was the ratio of the size at 15·87% probability to that at 50%, or the ratio at 50% probability to that at 84·13%.

When dealing with elongated grains, the length of a grain was taken as a measure of its size. When treating the grains as rectangles, the ratio of the length of the shorter side to the diagonal was a measure of the 'relative elongation'. For a square-like shape this ratio equals 0·7 which means that smaller values are due to a significant elongation of the grains. In this way it was possible to quantify the elongation aspect of the grains. The measurements of yttria particles were carried out from the photos earlier prepared by SEM and a minimum of 300 particles were measured in each sample.

Results and Disscusion

Effect of hydrothermal treatment temperature

As can be seen from the data shown in Table 1, the shape and size of yttria grains are distinctly dependent on the crystallization temperature (holding time was stable and equalled 120 min in that case) and the type of yttrium salt used as well. In the case of a chloride precursor at 200 and 225°C grains are isometric in shape and 0·8 μm in size (Fig. 1). The increase of temperature up to 250°C leads to a change of grain shape from isometric to needle-like (Fig. 2), which is confirmed by the relative elongation values listed in Table 1.

Fig. 1. Isometric yttria grains obtained from a chloride precursor at 225°C (crystallization time 120 mm).

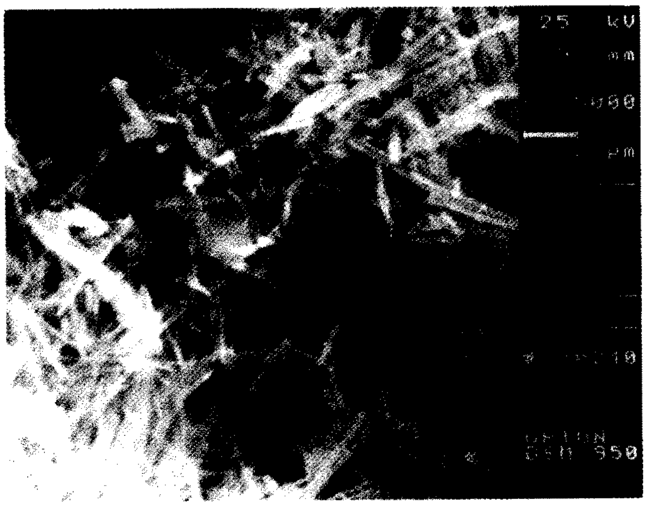

Fig. 2. Needle-like yttria grains obtained from a chloride precursor at 250°C (crystallization time 120 min).

The crystallization temperature affects differently the shape and size of yttria grains obtained from a nitrate precursor. Only at 200°C (see Table 1) is the isometric shape of grains maintained. However at 225°C, yttria grains are getting elongated and rod-like in shape (Fig. 3). They are distinctly longer as compared with the grains obtained from the chloride precursor (see Table 1). Further increase of crystallization temperature up to 250°C decreases the length of rod-like grains and increases the values of the relative elongation.

Table 1. Mean size and elongation of yttria grains as a function of crystallization temperature (crystallization time 120 min) and precursor type

Crystallization temperature (°C)	*Precursor type*			
	Yttrium chloride		*Yttrium nitrate*	
	Grain size (μm)	*Relative elongation*	*Grain size (μm)*	*Relative elongation*
200	0·81±1·42	0·71±1·10	0·63±1·60	0·69±1·08
225	0·77±1·60	0·65±1·16	10·89±1·32	0·06±1·50
250	3·34±1·47	0·17±1·91	2·30±1·49	0·14±1·34
270	—	—	2·31±1·66	0·38±2·43

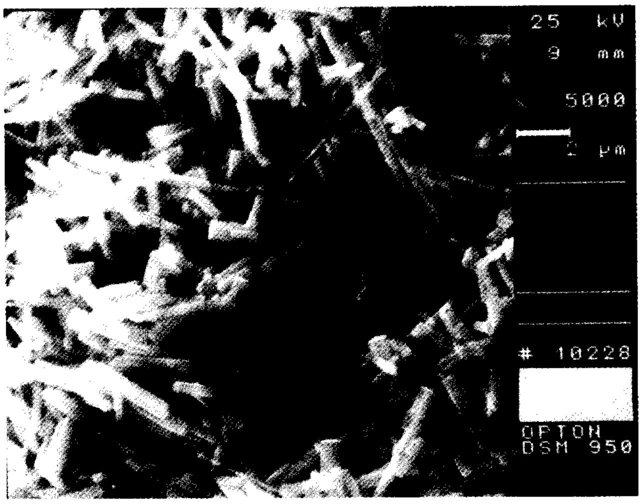

Fig. 3. Rod-like yttria grains obtained from a nitrate precursor at 225°C (crystallization time 120 min).

Effect of hydrothermal treatment time

In the case of a chloride precursor and at temperatures of 225°C no effect of crystallization time was observed on the shape of the yttria grains (see Table 2). After 15 min of crystallization, the grains are isometric in shape and have a mean size of 0·69 μm. After 120 min, the grains maintain the isometric shape and have a mean size of 0·77 μm. The values of relative elongation confirm their isometric shape (0·7 and 0·65, respectively). However at 250°C the crystallization time distinctly affects the size and shape of the yttria grains. At this temperature, all crystallization times give rise to grains with an elongated shape. As can be seen from Table 2, the longer the crystallization time, the longer the size of the grains. The relative elongation reaches a minimum value at 90 min crystallization time showing the most needle-like aspect to occur at that temperature.

As it was mentioned earlier, at 225°C the crystallization of yttria from the nitrate precursor leads to an elongated and rod-like shape of the grains. When increasing the crystallization time while keeping the temperature constant at 225°C the grains elongate from 3·3 μm for 15 min to about 11 μm for 120 min (see Table 3). The most distinct increase of grain length is observed between 60 and 120 min of crystallization time.

Different results were obtained at 250°C. The length of the grains decreases from 4 μm for 15 min to 2·3 μm for 120 min. However the values of relative elongation are practically unchanged for crystallization periods longer than 30 min. For crystallization times longer than 15 min, the needle-like aspect of the grains changes in favour of rod-like grains. At the same time the standard deviation of the relative elongation shows a tendency to decrease leading to a more homogeneous distribution.

Model mechanism for the hydrothermal crystallization of yttria

From the results a qualitative model mechanism for the hydrothermal crystallization of yttria can be proposed. At temperatures up to 200°C the

Table 2. Mean size and elongation of yttria grains obtained from a chloride precursor as a function of crystallization time and temperature

Crystallization time (min)	*Crystallization temperature (°C)*			
	225		*250*	
	Grain size (μm)	*Relative elongation*	*Grain size (μm)*	*Relative elongation*
15	0·69±1·60	0·69±1·08	1·70±1·78	0·32±2·08
30			2·67±2·00	0·24±2·73
60			3·55±1·51	0·16±1·50
90			3·60±1·59	0·15±1·46
120	0·77±1·57	0·65±1·16	3·72±1·47	0·17±1·91

Table 3. Mean size and elongation of yttria grains obtained from a nitrate precursor as a function of crystallization time and temperature

Crystallization time (min)	*Crystallization temperature (°C)*			
	225		*250*	
	Grain size (μm)	*Relative elongation*	*Grain size (μm)*	*Relative elongation*
15	3·34±2·29	0·33±2·42	4·14±1·48	0·17±1·82
30	3·07±1·86	0·14±1·42	3·50±1·59	0·14±1·61
60	3·89±1·84	0·14±1·44	3·32±1·55	0·14±1·92
90	5·53±1·92	0·12±1·82	2·92±1·60	0·15±1·64
120	10·89±1·32	0·06±1·50	2·30±1·32	0·14±1·34

first stage of crystallization is always the growth of isometric yttria grains independent of time and precursor type. A change of grain size without change in shape as a function of crystallization time suggests a classical mechanism of dissolution of the smallest grains combined with the crystallization of the dissoluted material on the larger ones.

When the temperature increases up to 225°C for the case of a nitrate precursor and up to 250°C for the case of a chloride one, the growth of elongated yttria grains is observed. According to Nishizawa[14] and Bucko,[15] the appearance of elongated forms of yttria can be the result of spontaneous connection of aligned isometric yttria particles due to an earlier creation of phase contacts between neighbours. Again dissolution and recrystallization is the only available mechanism for enhancing the contact area and for filling voids between neighbouring particles. However as the cubic structure, in which yttria crystallizes, has no preferential direction, it is difficult to accept that there is only one crystallization mechanism (dissolution and crystallization). From the experiments it follows that there is an influence of the type of precursor on the kinetics of the dissolution and crystallization process (creation of active complexes). In the case of the nitrate precursor, the critical temperature above which extended yttria grains appear is about 25°C higher than compared with the chloride precursor. For the moment the reason of this different temperature behaviour is unclear.

Conclusions

This study demonstrated that the temperature and time of hydrothermal crystallization strongly affect the kinetics of yttria grain growth and also their morphology. The proposed model for the hydrothermal growth of yttria relies on a dissolution–crystallization mechanism and coalescence which lead to a preferential growth of elongated shapes. A distinct effect of the precursor type on the crystallization temperature of needle and rod-like forms of yttria grains was also observed. The difference in temperature is about 25°C. The origin of this temperature difference is unclear.

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