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The study of process production of polishing powder based on cerium dioxide

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Abstract

Finely divided cerium dioxide powder is an excellent polishing agent for optical glass under intensive processing conditions. Cerium dioxide powder was produced from a mixture of rare earth carbonates by conversion to oxides, reacting with acid to separate a sediment of $CeO(OH)_2$ from solution containing the trivalent rare earth ions, washing the sediment, and drying and annealing it to produce finely divided CeO_2. Physical and chemical investigations of each stage of the processing were performed. A relation was established between the properties of $CeO(OH)_2$ (such as degree of fineness and crystal structure) and the properties of the REE oxides that were used. It was shown that very fine REE oxides generate fine $CeO(OH)_2$. It was also shown that to obtain CeO_2 powder with high specific surface area and perfect crystal structure, the $CeO(OH)_2$ must be annealed in two steps: (1) dehydration of intermediate $CeO_{1.5}(OH)$ to produce very fine powder, and (2) dehydration at 800–1050°C. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Cerium dioxide powder; Polishing agent

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1. Introduction

In the decade of the 1940s engineers who were processing optical glass began to use polishing powder made from rare earth elements (REE). The use of rare earth polishing powders achieved an improvement of the efficiency of the industrial polishing process 2–3 times in comparison with earlier used crocus cloth. Nowadays rare earth polishing powders are the best materials in the polishing process.

Numerous investigations have shown that the main feature of the highly productive polishing powder is the significant content of cerium dioxide (CeO_2). The crystal structure of CeO_2 defines such important properties as polishing ability, mechanical strength and wear resistance. Producers of polishing powder generally produce polishing powder with very high CeO_2 content.

Up to 1992 in the USSR (Kazakhstan Republic) two types of polishing powder with high cerium content were released – cerite and photopol, with CeO_2 content more than 90%. These products met the requirements of optical glass polishing processes used at that time.

In 1997 in Russia at Chepetskiy Mechanical Plant (ChMP), Russia, Glazov town, the production of new types of rare earth polishing material began with more high CeO_2 content in solid solution of REE oxides (70–85%) and with improved physical, chemical and technological features. But the problem remains to create a better polishing material with high cerium content that could be suitable for use under intensive operating regimes for optical glass processing with multiple usage of the polishing agent on a synthetic polishing underlayer. Another very important problem is to reduce the prime cost of the product in order to save resources, energy and time by improvement of the process.

2. Experimental

Resource-saving and low-waste technology is being developed for extracting CeO_2 out of the rare earth raw materials and producing highly effective polishing powders, using CeO_2 as the base. New in this technology is CeO_2 sedimentation by hydrolysis, which provides an opportunity to economize chemical agents, on one hand, and to produce highly pure CeO_2 with micron-sized particles, narrow range of granular composition and perfect crystal structure, on the other hand.

The initial raw material is a mixture of co-precipitated

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total REE carbonates which were produced during the processing of loparite, apatite or monazite concentrates with the content in mass% of about CeO_2 43.0–55.0%; Ln_2O_3 24.6–27.0%; Nd_2O_3 14.0–20.5%; Pr_6O_{11} 5.0–6.9%; and total REE concentrates of middle and heavy group 1.0–8.5%.

The technological scheme for making polishing powder with high CeO_2 content has the following main steps:

1. The annealing of the REE carbonate mixture to REE oxides;
2. Treatment of REE oxides with acid and production of $CeO(OH)_2$ sediment (Ce valence +4) and a solution of trivalent REEs;
3. Washing of $CeO(OH)_2$ sediment;
4. Drying and annealing of $CeO(OH)_2$ to CeO_2.

The mechanisms of the chemical processes on each technological stage were studied. The optimum regimes of their operation was determined.

3. Results

The annealing of REE carbonates to REE oxides was done with the aim to oxidize cerium up to the tetravalent state. It was found that during annealing of REE carbonates the oxidation of cerium was not always completed. The degree of oxidation depends on the annealing temperature and the ratio between the individual lanthanoids in carbonates. So during annealing of carbonates produced from loparite with the mole ratio of lanthanoids as follows Ce:(Pr,Tb):(La,Nd,Sm . . .)=4.0:0.6:3.4 the cerium oxidation begins at 160°C, achieves a maximum value of 90–95% in the temperature of 350–550°C and oxidation decreases to 78–80% at temperature 800–1050°C. (Fig. 1). The incompleteness of cerium oxidation is a function of the process of cerium reduction, because of electronic transitions in the oxide solid solution phase which take place at 300°C. It was found that reduction is possible only if at least one element with variable valence besides cerium (for instance Pr or Tb), and also at least one element with fixed valence (+3), are present in the REE oxide mixture. Elements with variable valence take part in electronic transitions but elements with valence (+3) create defect sites in the oxygen sub-lattice, allowing the oxidation–reduction process to proceed rapidly due to high mobility of anion vacancies. In the 350–550°C range the crystallization of solid solution of REE oxides is not yet completed. That is why the processes of reduction proceed slowly and the cerium oxidation state is at its maximum value.

The leaching step has the aim to separate Ce^{4+} from the other lanthanoids. For this purpose the REE oxide mixture is treated with acid solution after annealing. This treatment dissolves trivalent REEs but cerium remains in sediment as $CeO(OH)_2$. The process can be attributed to two subsequent reactions: dissolution of REE oxides in acid (reaction (1)) and hydrolysis of dissolved cerium(IV), reaction (2):

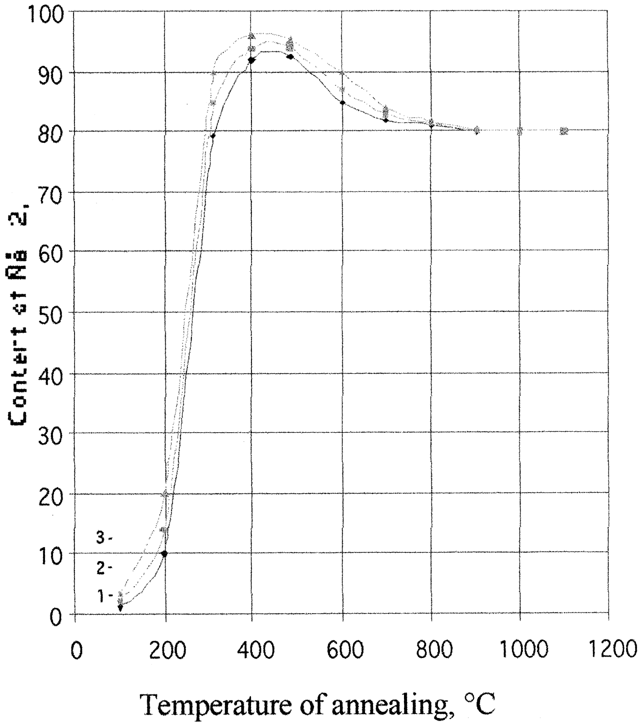

Fig. 1. Dependency of cerium oxidation degree from temperature of REE carbonates annealing. Time of annealing: 1) 1 h; 2) 2 h.

$$LnO_{1.5*}CeO_2 + 7H_3O^+ = Ln^{3+} + Ce^{4+} + 10.5H_2O \quad (1)$$

$$Ce^{4+} + 7H_2O = CeO(OH)_2\downarrow + 4H_3O^+ \quad (2)$$

Overall reaction:

$$LnO_{1.5*}CeO_2 + 3H_3O^+ = CeO(OH)_2\downarrow + Ln^{3+} + 3.5H_2O$$

Kinetic curves of the process are shown in Fig. 2. It is seen that the process passes through formation of the intermediate product – a salt of cerium(IV) (curve 3). At first the Ce^{4+} concentration in solution increases but afterwards decreases to zero. Formation of the intermediate product indicates that at least two reactions occur. Moreover, as can be seen from curve 2 the hydrolysis process does not start immediately because during the first two minutes the concentration of lanthanoids in solution is constant and corresponds to the content of lanthanoids in the solid phase.

Proton-magnetic resonance investigation shows that cerium is present in the final sediment as $CeO(OH)_2$. The acid treatment leaves trivalent REEs in solution but cerium remains in the sediment. In the sediment the cerium purity level is more than 99%. During hydrolysis additional purification from Fe, Ca and other elements also takes

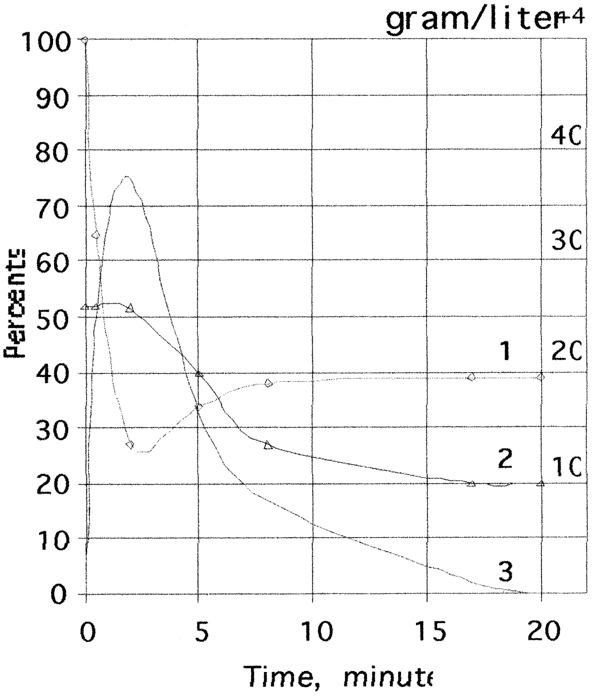

Fig. 2. Kinetics of acid treatment of REE oxides.

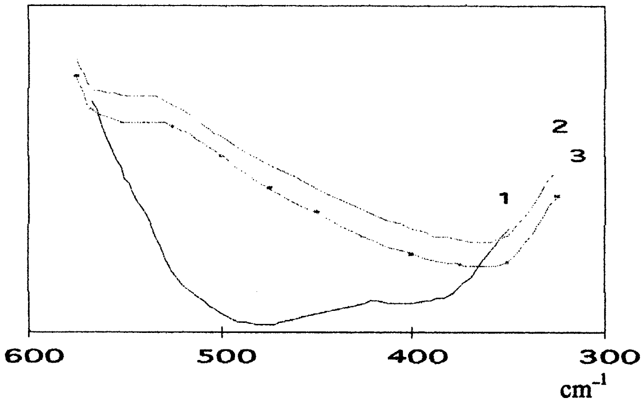

Fig. 3. Infrared spectrum of CeO_2 made from: 1) $CeO(OH)_2$; 2) REE carbonate; 3) REE oxalate.

place. The process of dissolution/hydrolysis causes considerable heat emission (about 300 calories per gram) that allows a decrease in energy consumption.

Washing the $CeO(OH)_2$sediment is conducted with water or, in order to avoid peptization, by electrolyte solutions, for instance NH_4NO_3.

Drying of $CeO(OH)_2$ sediment is conducted at 100–130°C. Before annealing the dry sediment is pulverized.

The dry $CeO(OH)_2$ product is a very fine crystalline powder with a structure similar to fluorspar. Depending on the production parameters the crystal lattice parameter of $CeO(OH)_2$ is 5.414–5.426 Å, close to the lattice parameter of pure CeO_2 (5.409 Å). This circumstance allows production of CeO_2 with more nearly perfect crystallinity than by annealing of REE carbonate or REE oxalate. The structure quality was evaluated by its infrared spectrum. The spectrum with intense absorbance in the range of 450–500 cm^{-1} corresponds to a more nearly perfect structure, which is related to valence oscillation of the Ce–O bond (see Fig. 3).

A relationship was found between properties (fineness, perfection of crystal structure) of $CeO(OH)_2$ and properties of REE oxides which were used. Very fine REE oxides generate very fine $CeO(OH)_2$ also. If defective REE oxides are used, defective $CeO(OH)_2$ is produced. From REE oxides with regulated structure, $CeO(OH)_2$ with the same regulated structure will be obtained (see Figs. 4 and 5. This relationship is evidence of continuity of structure and provides the opportunity to control properties of $CeO(OH)_2$ by variation of the annealing regime of REE oxides.

Annealing of $CeO(OH)_2$ is performed to dehydrate it and to produce cerium dioxide with perfect large-scale crystal structure. By investigation of the dehydration process of $CeO(OH)_2$ it was shown that thermal stability of $CeO(OH)_2$ is a function of the degree of perfection of its crystal structure. We have shown that samples having more perfect crystal structure are subject to dehydration at higher temperature. The scheme of thermal decomposition of $CeO(OH)_2$ with regular crystal structure, which is produced from REE oxides annealed at high temperature, is as follows:

$$\mathrm{CeO(OH)_2} \xrightarrow[-0.5\mathrm{H_2O}]{200\text{–}400^\circ\mathrm{C}} \mathrm{CeO_{1.5}(OH)} \xrightarrow[-0.1\mathrm{H_2O}]{400\text{–}800^\circ\mathrm{C}} \mathrm{CeO_{1.6}(OH)_{0.8}} \xrightarrow[-0.4\mathrm{H_2O}]{>800^\circ\mathrm{C}} \mathrm{CeO_2}$$

The scheme of thermal decomposition of $CeO(OH)_2$ with defective crystal structure, which was produced from REE oxides annealed at low temperature, is as follows:

$$\mathrm{CeO(OH)_2} \xrightarrow[-0.5\mathrm{H_2O}]{200\text{–}400^\circ\mathrm{C}} \mathrm{CeO_{1.5}(OH)} \xrightarrow[-0.4\mathrm{H_2O}]{400\text{–}650^\circ\mathrm{C}} \mathrm{CeO_{1.9}(OH)_{0.2}} \xrightarrow[-0.1\mathrm{H_2O}]{>650^\circ\mathrm{C}} \mathrm{CeO_2}$$

From the above schemes it follows that for $CeO(OH)_2$ with both defective and regular structure, the first stage of $CeO(OH)_2$ dehydration occurs in the same temperature range 200–400°C. This stage is completed by $CeO_{1.5}(OH)$ production. The second stage of dehydration associated with removing more firmly bound OH^- groups occurs in a different way. When defective $CeO(OH)_2$ is used, the dehydration of $CeO_{1.5}(OH)$ begins at about 400°C. When regular $CeO(OH)_2$ is used, the dehydration of $CeO_{1.5}(OH)$ begins at about 800°C. At temperatures above 800°C dehydration is complete in both cases.

The dehydration process is accompanied by destruction of crystal structure and modification of product fineness. Maximum destruction takes place during dehydration of intermediate product to $CeO_{1.5}(OH)$. Therefore, when

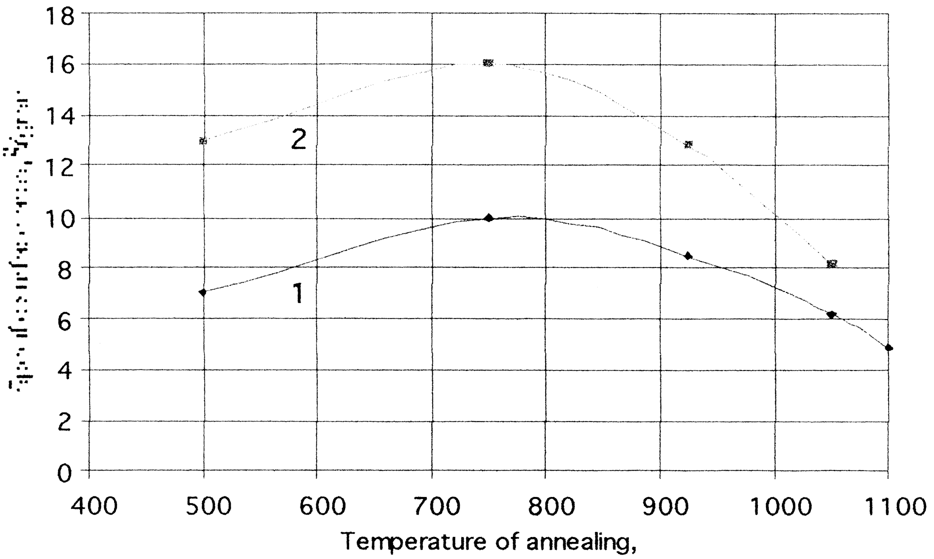

Fig. 4. Specific surface area of REE carbonates as function of annealing temperature: 1) REE oxides, 2) $CeO(OH)_2$.

defective $CeO(OH)_2$ is annealed, the maximum of annealed product specific surface area corresponds to 300–400°C, but for $CeO(OH)_2$ with regular structure it occurs at 700–800°C (Fig. 6).

We have found that in order to get cerium dioxide powder with high specific surface area and perfect crystal structure the annealing of $CeO(OH)_2$ needs to be conducted in two stages: first at a dehydration temperature of intermediate product to $CeO_{1.5}(OH)$ to provide maximum growth of fineness and then at temperature 800–1050°C to generate the perfect crystal structure of CeO_2.

Analysis of annealed cerium dioxide powder by electronic microscopy shows that the particles are nearly spherical, which is typical for material produced from oxides. A property of the synthesized powder is also the high homogeneity of its fineness. Studies performed by a SediGraph 5100 analyzer demonstrate that these powders contain 97% particles of size 0.5–10 μm. Thus the finished material possesses all the properties required for a polishing powder to be used in intensive polish regimes: high fineness, equal granule size and perfect crystal structure.

4. Conclusions

Resource-saving and low-waste technology has been developed to make CeO_2 from a mixture of REE oxides by hydrolysis. A real opportunity to control the properties of the CeO_2 product has been demonstrated.

Based on these studies a new grade of polishing powder

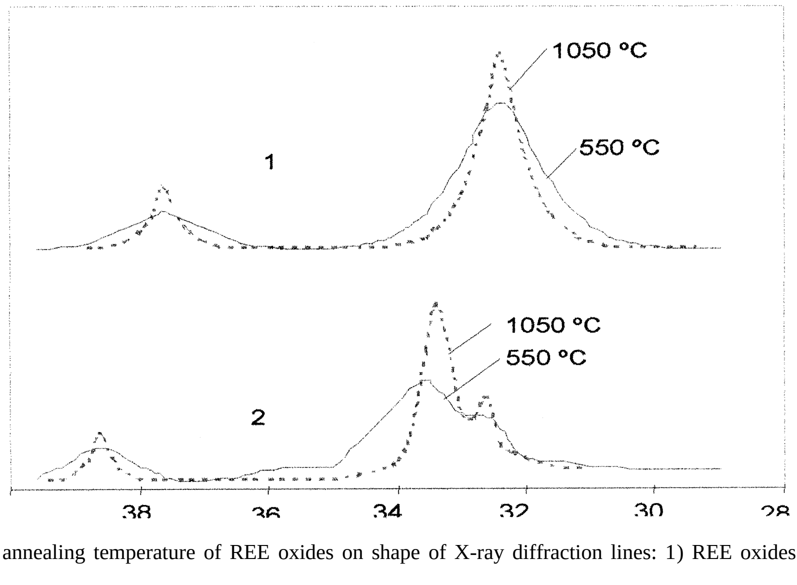

Fig. 5. Influence of annealing temperature of REE oxides on shape of X-ray diffraction lines: 1) REE oxides; 2) dry $CeO(OH)_2$.

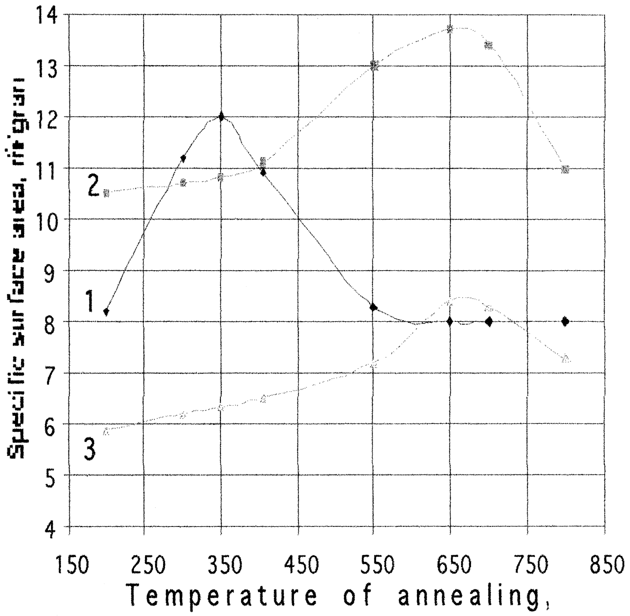

Fig. 6. Influence of annealing temperature of $CeO(OH)_2$ on CeO_2 specific surface area (m^2/gram). Herewith $CeO(OH)_2$ is prepared from oxides annealed at temperature as follows: 1) 550°C, 2) 800°C, 3) 1050°C.

has been produced. It is a powder named ''Ceripol'' with high CeO_2 content. At Chepetskiy Mechanical Plant, Glazov town, production of lots of the new powder has been made. It has the following physical and chemical characteristics and performance:

1. Cerium dioxide contents → 98–99% (weight),
2. Specific surface area → 3–5 m^2/gram,
3. Average particle size → 1.5–2 μm,
4. Polishing ability → 320 mg/30 min (the powder ''Ftoropol'' has 270 mg/30 min).

This powder differs from others by higher wear resistance: after 15 h the polishing ability was 260 mg/30 min. This powder is being tested by leading Russian optical enterprises.

For further reading

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