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Preparation of ceria-based polishing powders from carbonates

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The preparation of Ce(IV) oxide-based polishing powders by thermal decomposition of carbonates was studied and the effect of the calcination process conditions on the properties of product was examined. High-grade polishing powders can be produced at calcination temperatures 700–1200 °C, the maximum polishing efficiency is achieved by calcining at 1000–1100 °C. The observed dependences were interpreted from the standpoint of the present mechanochemical theory of glass polishing.

1. Introduction

Polishing powders based on cerium oxide are reckoned among the most efficient and most widely used means for polishing glass [1, 2]. As may be seen from the designation, the active constituent of this type of polishing agents is cerium (IV) oxide but normally non-negligible amounts of oxides of the other rare earth elements (La_2O_3, Nd_2O_3, etc.) may be present as well. The presence of these oxides, however, does not reduce the efficiency of the polishing powders (providing that the content of CeO_2 remains higher than about 45% [3]), which is due to the formation of ceria-based solid solutions [4].

The respective oxides are prepared by a thermal decomposition of oxalates, hydroxides or carbonates of the rare earth elements (REE) [2, 3]. The course of the calcination process influences in a decisive way the properties of a polishing agent. Dependences of the polishing efficiency (and, in sporadic cases, of other characteristics) on the conditions of calcination were measured during the thermal decomposition of oxalates and hydroxides of REE [2, 3, 5] and, less frequently, of REE carbonates [6].

In addition to polishing efficiency polishing powders are characterized by a number of other properties such as bulk density, granulometric composition, specific surface area, pH of aqueous extract, aqueous suspension stability, and others [2, 3, 7]. Until recently there has not been established any explicit correlation among these characteristics (or other physical quantities) and the polishing efficiency of a polishing powder except for some rules formulated generally by Kaller [8, 9]. One reason for this situation is the comparatively complex nature of the process of mechanical polishing of glass that has not yet been elucidated in detail.

The theories explaining the mechanism of the polishing process may be divided into three groups: (i) microabrasion theory, regarding polishing as continuation of the process of grinding on a micro-scale; (ii) the theory of thermal softening and creeping of the surface of glass; and (iii) chemical theories of polishing.

Nowadays it may be taken as proven that in the course of glass polishing both physical and chemical processes are taking place.

The polishing efficiency depends to a high degree both on the dynamic conditions during polishing (velocity, pressure) and on chemical conditions (pH of the suspension of a polishing powder, presence of chemical accelerators, etc.) [10, 11].

In the present work we were concerned with the preparation of ceria-based polishing powders from carbonate precursors. We studied the effect of calcination on the polishing efficiency and other characteristics of the polishing agents and attempted to find out the correlations among the measured quantities and to interpret them from the standpoint of today's mechano-chemical theory of glass polishing.

2. Experimental procedure

2.1. Preparation of polishing powders

Three series of polishing powders were prepared:

Series A: The raw material was reagent-grade cerium (III) nitrate

Series B: The raw material was a cerium-containing fraction as obtained from a bastnasite concentrate by extraction with tributylphosphate.

Series C: The raw material was a cerium-containing fraction as obtained from a REE concentrate from the Kola apatite by conventional processes – selective precipitation and dissolving.

The above starting materials were used for the preparation of nitrate solutions at the concentration of 0.2 mol dm^{-3} of REE and 0.1 mol dm^{-3} of free nitric acid. The respective REE carbonates were precipitated from these solutions by a gaseous mixture of carbon dioxide and ammonia. The precipitation took place at 30–35 °C; the procedure has been described in greater detail in our previous paper [12]. The precipitate was separated by filtration and dried at 110 °C. Thus prepared carbonates did not have an exactly defined composition, they were a mixture of

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normal, basic and oxo carbonates. Using the X-ray diffraction analysis a crystal phase of the $Ce_2O(CO_3)_2 \cdot nH_2O$ type was identified. Besides, further unidentified crystalline and amorphous components were present (see Fig. 1).

Samples of polishing powders were prepared by calcining the REE carbonates in an open crucible in a muffle furnace under controlled conditions (temperature, time).

Chemical composition of the prepared polishing powders is given in Table I.

2.2. Measuring methods

The polishing efficiency of polishing powders may be assessed in accordance with two aspects: (a) the quality of the polished surface of glass, and (b) the rate at which the mass of glass is being removed.

The degree of the glass surface roughness was evaluated with the aid of a microprofile meter Hommel Tester T-20. This instrument, however, enables only greater unevenesses to be measured. At present there is no objective method available for measuring the unevenesses of a well polished glass surface. In keeping with practice, the quality of polishing was, therefore, evaluated visually.

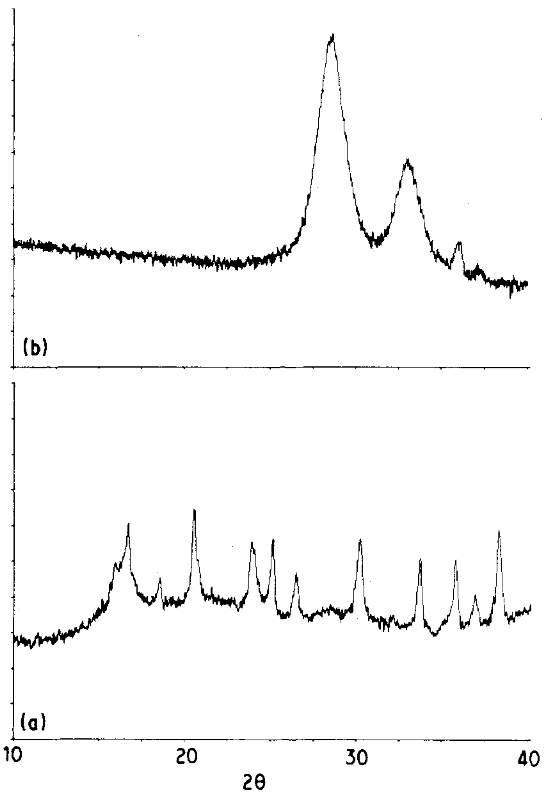

Figure 1 X-ray diffraction patterns of (a) cerium (III) carbonate and of (b) the product obtained by calcination at 300 °C for 1 h for Series B.

TABLE I Chemical composition of polishing powders

Sample[a]	Series A	Series B	Series C
CeO_2 (%)	99.95	98.24	82.19
La_2O_3 (%)	0.01	0.84	7.41
Pr_6O_{11} (%)	0.01	0.18	1.89
Nd_2O_3 (%)	0.01	0.26	7.01

[a] The content of higher lanthanoids in the Series B and C samples fluctuates between 0.1–0.2%. The content of admixtures in Series A is negligible.

The rate of glass removal was assessed gravimetrically in accordance with the relation

$$r = m/(S_g t_p \rho_g) \qquad (1)$$

where r is the linear rate of glass removal, m the loss in weight of glass in the course of polishing, S_g the surface area of polished glass, t_p the time of polishing and ρ_g the density of glass. The measurements were conducted on a polishing machine Kärger.

The particle size distribution was measured by the photosedimentation method using a centrifugal particle size analyser Shimadzu SA CP-2. Based on the Rosin-Rammler-Sperling-Bennet (RRSB) distribution the particle size characteristic x_d and grain size exponent n were calculated. It holds

$$R(x) = 100 \exp[-(x/x_d)^n] \qquad (2)$$

$$R(x_d) = 100/\mathrm{e} \qquad (3)$$

where e is the basis of natural logarithms (2.718) and $R(x)$ is the weight per cent of particles whose size is equal or larger than x.

The value of the apparent or "outer" specific surface area S_v was calculated from the RRSB distribution characteristics

$$S_v = \left(\frac{kn}{\rho_p x_d}\right) \int \exp(-x)^n x^{n-2} \mathrm{d}x \qquad (4)$$

where k is the shape factor and ρ_p the density of the polishing powder.

The X-ray diffraction measurements were carried out on a Philips PW 1140 spectrometer. The size of crystallites was calculated from the diffraction lines broadening according to the Sherrer formula [13]

$$a = K\lambda/\beta \cos\theta \qquad (5)$$

where K is the shape factor, λ the wavelength of the applied radiation, β the broadening of the diffraction line, and θ the diffraction angle. The procedure of measuring the cerium oxide crystallites size is described in a greater detail elsewhere, for example, in [14].

Besides, specific surface area S_s of the polishing powders was measured by the dynamic sorption method with the aid of a Geotest instrument (VÚEK, Hradec Králové, Czechoslovakia).

The methods of assessing the properties of polishing powders have been described in more detail in our previous paper [7].

3. Results and discussion

The dependence of the polishing efficiency of polishing powders (expressed as linear rate of glass removal) on temperature and time of calcination is shown in Fig. 2. It may be seen that the effect of calcination time on the polishing efficiency is considerably lower than that of polishing temperature. The dependences of the polishing removal rate on calcination temperature exhibit

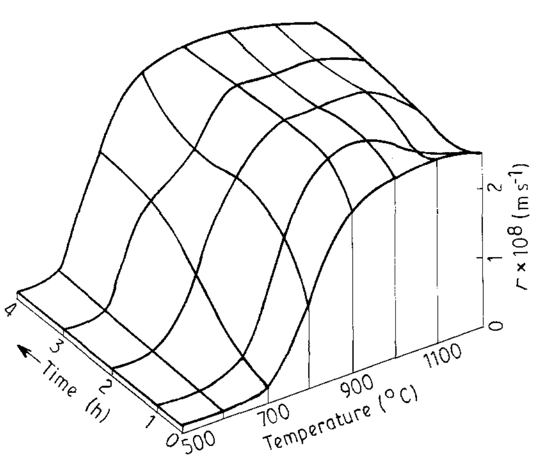

Figure 2 Dependence of polishing efficiency (linear rate of glass removal) on temperature and time of calcination (Series B).

the maximum in the temperature range of roughly 1000–1100 °C. A steep decline in the polishing efficiency begins when the calcination temperature decreases to below 700 °C and, at the same time, also the polished surface quality deteriorates markedly.

In Fig. 3 is demonstrated the dependence of the removal rate and glass surface roughness on the calcination temperature (300–800 °C, time of calcination 1 h). When samples of polishing agents prepared at lower temperatures are used, not only the removal rate is low but so is also the quality of the polished surface, and this is true even in the cases when the glass was previously polished with some other, high-grade polishing agent. Scratches and, particularly, defects of the "orange skin" type appear on the treated surface, witnessing a chemical attack on the glass surface.

The X-ray diffraction patterns of polishing agents samples as prepared by the calcination at 300 °C show that only cerium(IV) oxide is present. See Fig. 1 (compare e.g. [15, 16]). It has been known that the decomposition of Ce(III) carbonates is a complex process accompanied by oxidation of cerium and formation of a number of intermediate products [15, 17, 18]. According to Savin *et al.* [16] the decomposition and oxidation of Ce(III) carbonates are complete at the temperature of 460 °C; Perry *et al.* [17], however, demonstrated that Ce(III) was present even in samples calcined at 500 °C. Hence it seems that preparations calcined at temperatures lower than roughly 700 °C contain some intermediate products of the decomposition that have a marked negative effect upon the polishing properties.

High-grade polishing powders can be prepared by calcination at 700–1200 °C. More detailed measurements were conducted with two series of samples: pure cerium(IV) oxide and mixtures of CeO_2 with other REE oxides (content of CeO_2 82%).

Samples from both the series calcined at 700–1200 °C enable to attain a good quality of the polished surface; the dependence of the glass removal rate on the temperature of calcination exhibits the maximum at 1050 °C [6].

The values of the specific surface area S_s in samples of the A and C series were measured by the sorption method; the obtained dependences (Fig. 4) are of similar character as those assessed when studying the thermal decomposition of cerium(III) oxalate [19] or hydroxide [16]. Besides, the particle size distribution of the samples was measured and the values of apparent specific surface area S_v were calculated from the RRSB distribution characteristics. The values of S_v and S_s differ considerably and the differences cannot be attributed only to deviations of the real shape of the particles from a spherical form as presumed in the calculation of S_v. It is necessary to assume that the polishing agent particles have a more complex – microporous – character. The ratio S_v/S_s may be regarded as a measure of compactness or mechanical resistance of the particles [20]. The dependence of the ratio S_v/S_s on temperature of calcination is also demonstrated in Fig. 4.

The sizes of the polishing agents crystallites were measured by the X-ray diffraction method (Fig. 5).

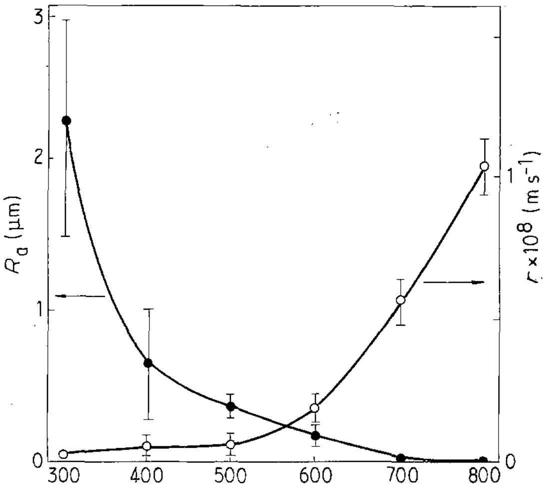

Figure 3 Dependence of removal rate and roughness of the polished glass surface on temperature of calcination (Series B, time of calcination 1 h). R_a is the mean arithmetic deviation of profile.

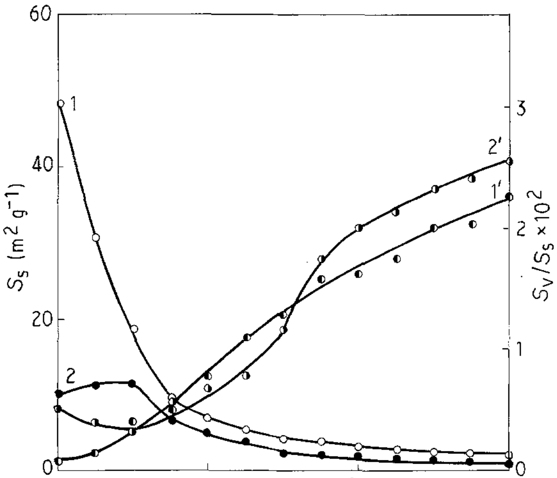

Figure 4 Dependence of specific surface area S_s (curves 1 and 2) and of the S_v/S_s ratio (curves 1' and 2') on calcination temperature. 1 and 1' for Series A, 2 and 2' for Series C.

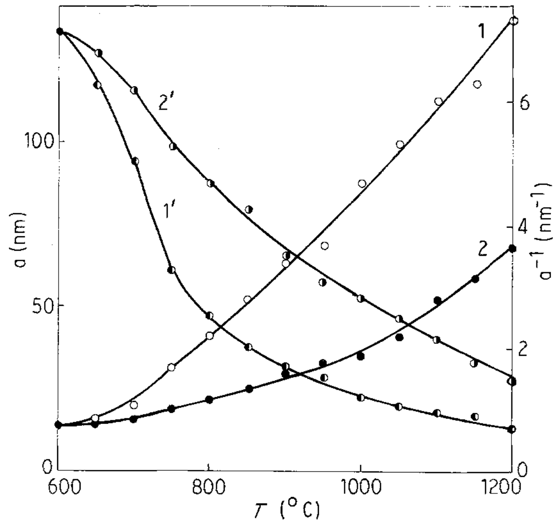

Figure 5 Dependence of the size of polishing agent crystallites on calcination temperature. 1 and 2 for dependence of a on T. 1′ and 2′ for dependence of a^{-1} on T. Time of calcination 1 h.

The dependences obtained make it possible to interpret, at least qualitatively, the correlation between the polishing efficiency (rate of glass removal) and temperature of calcination.

It has been known that both the mechanical and chemical aspects play a role in the polishing process. Let us assume for simplicity that the overall rate of removal r is a sum of the mechanical (r_m) and chemical (r_c) actions. The contribution of the mechanical action is proportional to mechanical resistance of particles of the respective polishing agent, i.e. to the S_v/S_s ratio. The chemical contribution depends on the polishing agent ability to create new, chemically active surfaces in the course of the polishing process. It is, therefore, a function of the crystal lattice order (size of crystallites, number of crystal lattice defects). When we calculate the value of specific surface area S_u according to

$$S_u = \text{constant}/a \qquad (6)$$

(where a is the size of crystallites and the constant incorporates the shape factor and polishing agent density), S_u may be considered specific surface area "utilizable" for polishing and r_c is then proportional to this specific surface area S_u.

The dependence of r_m on calcination temperature has a similar shape as the dependence for S_v/S_s (Fig. 4), the dependence of r_c on calcination temperature has a similar character as the curves 1 and 2 in Fig. 5. The curves are shown schematically in Fig. 6. The shape of the cumulative curve $r_m + r_c$ corresponds to experimentally ascertained dependence of the glass removal rate on the temperature of calcination (Fig. 2).

Based on the results of laboratory investigations conditions for the preparation of polishing powders in a pilot plant scale were specified. In spite of the fact that the process of calcination was carried out in a different type of equipment (rotary kiln), good quality polishing powders were produced whose properties did not differ substantially from those of the laboratory samples as prepared in a muffle furnace (see Table II).

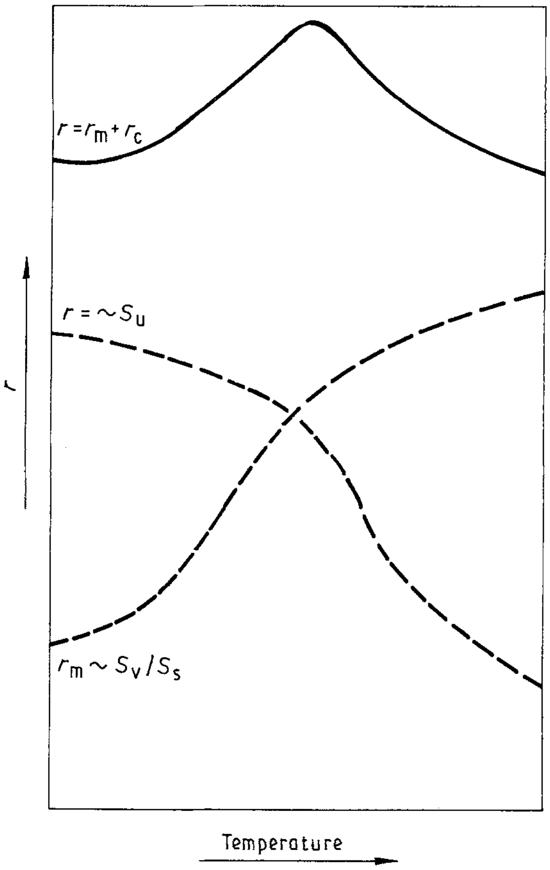

Figure 6 Schematic presentation of the contributions of mechanical (r_m) and chemical (r_c) actions to the overall rate of glass removal (r) (see the text).

TABLE II Properties of the prepared polishing powders

Property	Sample I[a]	Sample II[b]
Bulk density (kg m^{-3})	403	475
Particle size characteristic (μm)	7.2	7.6
Grain size exponent	1.05	1.29
Specific surface area S_s (m^2 g^{-1})	2.64	3.45
Linear rate of glass removal (m s^{-1})	1.84×10^{-8}	1.76×10^{-8}

[a] Prepared in a laboratory muffle furnace (1050 °C, 1 h).
[b] Prepared in a rotary kiln (1050 °C, mean residence time 1 h).

4. Conclusion

Good quality polishing powders can be prepared by thermal decomposition of cerium (III) carbonate (or in a mixture with a certain amount of other REE) at temperatures ranging from 700 to 1200 °C. The highest rate of glass removal was observed with samples prepared at 1000–1100 °C. Although the rates of removal achieved with polishing agents made at 700 °C and at 1200 °C are virtually the same, the mechanism of the process of polishing obviously is somewhat different in these two cases, which may affect the properties of the polished surface of glass (chemical resistance, rate of ageing, etc.). An experience known in the practice has been confirmed: polishing agents with high removal rate produce also polished surfaces of good quality, and vice versa. Besides the polishing efficiency the temperature of polishing affects primarily the value of the specific surface area S_s and size of the crystallites, and these quantities can be used for estimating the polishing agent quality. The other characteristics (bulk density, particle size distribution, behaviour of the agent in aqueous suspensions) depend on the conditions of calcination to a much lesser degree [6]. The calcination temperature influences all the properties of a polishing agent in a greater extent than the time of calcination.

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