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Ultrasound Effects on Cerium, Praseodymium, and Terbium Oxides

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The behavior of intermediate higher rare earth oxides, such as Pr_6O_{11} and Tb_4O_7, and $Ce_{1-x}Pr_xO_2$ compounds as powders has been studied by a new experimental procedure. They have been subjected to ultrasound irradiation (20 kHz) during immersion in a 5% dilute acetic acid solution. Pure PrO_2 and TbO_2 oxides (yield 100%) can be formed within sonication periods of 7–8 and 15–24 hr, respectively (instead of 3 days and 1 month through classical methods). Electron microscopic images and granulometry measurements show that the grain size has decreased greatly after sonication. The results are discussed in terms of cavitation phenomena and of chemical species (H_2, O_2, HO_2, OH, H_2O_2, . . .) formed during sonolysis of water and acetic acid.

INTRODUCTION

For about 15 years ultrasound (US) irradiations have been used either to generate new chemical reactions or to accelerate reaction kinetics. Up to now this procedure has mainly been utilized for organic and organometallic syntheses (1–4). In the field of solid state chemistry one can mention the works of Suslick (5–9) relative to the study of fine metallic particles and clusters, of Roy *et al.* (10) on catalyzing reactions with alumina precursors, of Chartier *et al.* (11) on deagglomeration and dispersion of $BaTiO_3$ and Al_2O_3 ceramics, of Glenmie and Konsztowicz (12) on the activation of large MnO_2 crystals in various solvents, and of Lorimer *et al.* (14) on the encapsulation of TiO_2 pigments.

The aim of this study is to illustrate that US irradiation is a powerful procedure to promote solid state reactions and to obtain very fine particles in the case of rare earth oxides with a fluctuant oxidation state (*R* = Ce, Pr, and Tb).

THE SONOCHEMISTRY

The understanding of the phenomena which govern US–liquid or US–solid/liquid interactions is not yet definitively established. Indeed, one of the most important problems is linked to the cavitation phenomena. Sonochemistry derives from this intense nonlinear acoustic process. Several review articles and books have pointed out the historical developments and modern aspects of sonochemistry (1–3, 15–18). It is not our purpose here to develop such a broad subject. One can mention that Richards and Loomis (19) reported in 1927 the first chemical and biological effects of US.

The first mathematical model for the cavitation phenomenon was theoretically established in 1917 by Lord Rayleigh (20). Since that time numerous other theories and calculations have been developed. They involve a large number of parameters which either add to, or compete with each other. This requires very complex mathematical models. However, some basic phenomena are now known and allow us to understand why application of US can be such a powerful energetic procedure.

When a liquid is irradiated by US there is nucleation, growth, and implosive collapse of micro- and nanobubbles. The last stage produces powerful shock waves, and tremendous energy results from the implosion. The bubbles can be filled with a gas, the vapor of the liquid, or be almost empty. When they collapse, temperatures of about 5200 K in the gas phase volume and 2200 K in the

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liquid film around the bubble can be produced. Such "hot spots," which produce shock waves with pressures in the 10^7–10^9 Pa range, have lifetimes of about 10^{-8}–10^{-9} sec (heating and cooling rates of 10^8–10^9 K $\sec^{-1}$). Another hypothesis is that the bubbles could be electrically charged. Consequently, at the moment of the implosion, intense multipolar electric fields of about 10^{11} eV cm^{-1} are likely to be generated.

In the case of a solid–liquid medium, cavitation can occur through two mechanisms which are still a matter of debate. The first is linked to microjet impact due to an asymmetric collapse of the bubbles attached to, or near, the surface of the solid. High-speed microcinematographic sequences (21) or flash microphotography (22) have allowed the determination that, at the moment of the collapse, a liquid microjet (with a velocity of more than 100 m/sec and impact pressure of about 10^8 Pa) is formed. This jet is directed toward the surface of the solid, the period of the impact being about 10^{-8} sec. The second mechanism, associated with the shock wave phenomenon, results from the collapsing cavity. The relative importance of these two mechanisms depends on the method by which cavitation is produced (7). It seems difficult, in fact, to dissociate the two phenomena. Indeed, when a fine powder is immersed into a liquid, the grains are strongly shaken during US irradiation. Consequently, there is a high probability that the small particles are subjected to the two mechanisms. Moreover, shock waves can create high-velocity interparticle collisions (7). Such collisions, which may be either frontal or grazing and are associated with microjets and bubble implosions, can induce microcracks or can pull away microroughnesses. All of these phenomena lead either to phase transitions or to the formation of very fine particles. One can assert that numerous parameters must be taken into account: frequency and output power of the US irradiation; liquid density, viscosity, purity, reactivity (water, dilute acid, organic solutions, etc.); size, toughness, roughness, density, etc. of the grains; and also nature of the material (metals, alloys, oxides refractories, etc.). Finally, as claimed by Suslick (1), US is a new means of studying chemical reactions because the irradiation process differs from classical chemistry reactions in duration, pressure, and energy per molecule.

EXPERIMENTAL PROCEDURE

US irradiations were produced by means of two different apparatuses. The first one consists of a US generator (frequency within 30–80 kHz) fitted to a vat half filled with water, in which test tubes are immersed. The second one is an industrial apparatus (Branson Sonifier Model 450, frequency 20 kHz, input power 450 W) of which the titanium horn, fitted to an electrostrictive element (a lead zirconia–titania material), is immersed in a liquid. Two kinds of solutions have been used: dilute acetic acid (5%) in water, and water. The experiments consist of putting the powder (4–21 g) in a container filled with a liquid (200 cm^3) and irradiating the mixture by means of US for varying times, depending on the chemical species. In the case of dilute acetic acid solutions small amounts of dilute acid were added during treatment; this compensates for the loss of acid due either to slow evaporation or to reaction with R^{3+} ions. After irradiation the powder is separated from the liquid either by filtering by means of a sintered glass or by long-time centrifugation for colloid solutions. Then the precipitates are rinsed either with a 5% dilute acetic acid solution or with distilled water, and finally dried at 373 K for 12 hr.

The powders were characterized before and after sonication by different methods: X-ray diffraction, transmission electron microscopy (TEM), scanning electron microscopy (SEM) fitted to an energy dispersive X-ray spectrometer (EDX), and X-ray absorption spectroscopy (XAS). The grain size distribution was studied by means of granulometers, and the abrasive capacity by an atomic force microscope (AFM).

RESULTS

The Synthesis of Rare Earth Dioxides

Among the R series, three elements (cerium, praseodymium, and terbium) are characterized by a fluctuant valency in their oxide form. It is now known that they can form a great number of ordered higher oxide phases which do not systematically obey the basic R_nO_{2n-2} law ($4 \leq n < \infty$) (23–26). This causes the two limiting oxides R_2O_3 ($n = 4$) and RO_2 ($n = \infty$) to be sometimes difficult to synthesize in a pure 3^+ or 4^+ oxidation state. This is particularly important since obtaining pure PrO_2 and TbO_2 require long chemical treatment times.

(*a*) *Praseodymium dioxide.* Since the early sixties it has been known that selective dissolution (or slow leaching) of a mixed-valence compound such as Pr_6O_{11} in a 5% dilute acetic acid solution produces PrO_2 (27, 28). The procedure requires mechanical stirring, for more than 3 days, of the oxide powder immersed into the bath. The beginning of the reaction is easily detected because the solution takes a characteristic green color due to the dissolution of the Pr^{3+} ions into the acetic acid. In a previous paper it has been shown that, under ambient conditions, an acoustic emission ($\approx$45 dB) in the US acoustic field ($\approx$200 kHz) can be recorded when the reaction starts (29). When the leaching process is entirely achieved, the acetic solution is intense green, and the black powder is oxidized to PrO_2.

This procedure has been repeated by replacing mechanical stirring with US irradiations. The first experiments were carried out with the ultrasonic vat apparatus. As function of the bath temperature the appearance of the green color has been observed after the following sonication periods: at 278 K, 90 min, at 293 K, 25 min; and at 333 K, 05 min. In general (at ambient temperature) the reaction is completed after a 7–8-hr treatment. A yield of 100% in PrO_2 is reached with the Branson apparatus for this time period. The X-ray diffraction patterns (XDP) show only one structure. The back X-ray lines such as (620), (533), and (622) allow accurate determination of the fcc lattice parameter of the fluorite cell: $a_F = 0.53920 \pm 0.00003$ nm. This value is slightly smaller than the one given previously (25).

Remarks concerning impurities:

1. In a few cases the starting powders showed the coexistence of $Pr(OH)_3$ and Pr_6O_{11} phases (30). After sonication the hydroxide was not always destroyed, but sometimes remained in coexistence with the PrO_2 phase.

2. The addition of formic acid (2%) to acetic acid (3%) leads to formation of praseodymium formate ($C_3H_3PrO_6$) characterized by a rhombohedral structure, equivalent to that of neodymium (31).

(*b*) *Terbium dioxide.* The preparation of TbO_2 (actually $TbO_{1.95}$ (25)) by leaching Tb_4O_7 with a 5% dilute acetic acid solution requires at least 1 month. After such a period the yield does not exceed 20–25%. It is difficult to detect the beginning of the reaction because the liquid remains colorless. We have repeated this experiment according to the classical procedure. After a week it was not possible to detect the formation of TbO_2. In fact the reaction,

$$Tb_4O_7 + 6H^+ \rightarrow 2TbO_2 + 2Tb^{3+} + 3H_2O$$

is very slow, compared that of Pr_6O_{11} (32).

Performing the same experiment assisted by US irradiation has allowed us to obtain the exclusive presence of TbO_2 after about 24 hr of treatment. XDP reveal that the dioxide begins to form after 9 hr of sonication. This result provides evidence that US accelerates the chemical reaction significantly. The fluorite fcc parameter has been calculated from six XDP. The accurate measurements of the interplanar spacings of the back diffraction X-ray lines (620), (533), and (622) leads to the parameter $a_F = 0.5217 \pm 0.0001$ nm. This value is slightly lower than the one reported for $TbO_{1.95}$ as $a'_F = 0.5220 \pm 0.0001$ nm (25). However, it can be compared to the one recently reported by Kang and Eyring (32) as $a''_F = 0.5215 \pm 0.0002$ nm. This indicates that US irradiations favor the pronounced tetravalent character of terbium in its oxide form. This has been corroborated by XAS: the M_{IV-V} edge reported in Fig. 1 shows clearly that the cation valency is 4+ (26).

(*c*) *Cerium dioxide.* Sonication of pure CeO_2 powder (only Tb oxide traces have been detected by EDX analyses) does not reveal a phase transition. XDP were indexed as fluorite with $a_F = 0.54109 \pm 0.0001$ nm (25). Moreover, an XAS procedure showed that the M_{IV-V} edge was identical before and after sonication (Fig. 2).

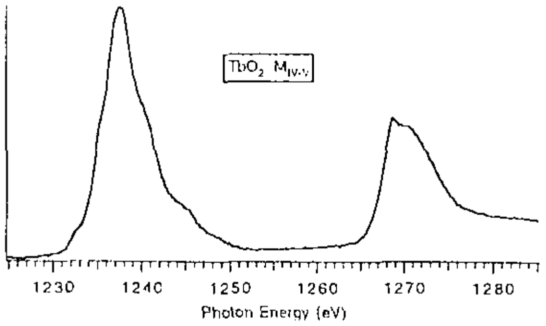

FIG. 1. M_{IV-V} absorption edge characteristic of the tetravalent terbium ions.

Oxidation State of Mixed Oxides

To study the influence of US on the oxidation state of mixed oxides, various $Ce_{1-x}Pr_xO_2$ samples have been prepared, with increasing x values such as x = 1, 2, 3, 4.4, 5, and 10%. For the lower ratios (up to 5%) the following procedures has been followed in our laboratory. First, a cerium acetate (Ce^{3+}) powder (10 g) and a Pr6O11 powder are separately dissolved in water and dilute HCl, respectively. Then the two components are mixed and added to oxalic acid heated to 440 K. This leads to the coprecipitation of cerium and praseodymium oxalates (Ce^{3+} and Pr^{3+}). Finally, the mixture is filtered, dried, and calcinated for 12 hr at 1273 K.

Accurate EDX analyses have been carried out on various crystallites of the $Ce_{1-x}Pr_xO_2$ (x = 4.4%) compound. They show that the Pr content varied between 4.40 and 6.10%. XDP indexations of the back X-ray lines as (620), (533), and (622) have revealed the lattice parameter ($a_F = 0.5409 \pm 0.0001$ nm) to be very slightly smaller than that

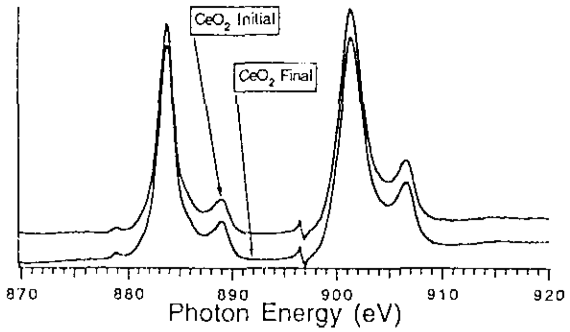

FIG. 2. M_{IV-V} absorption edge characteristic of the tetravalent cerium ions.

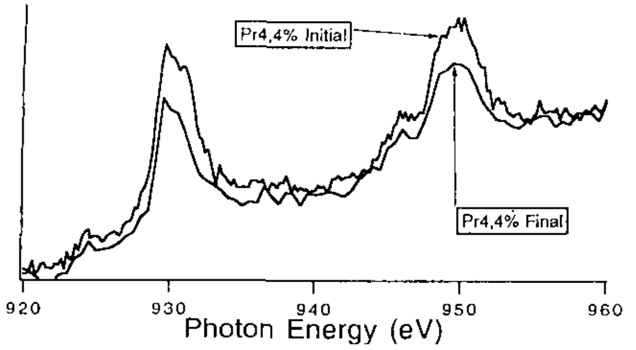

FIG. 3. M_{IV-V} absorption edge of praseodymium ions within the CeO_2 : 4.40% Pr matrix.

of pure CeO_2. This indicates that the Ce^{4+} ions have been substituted by Pr^{4+}. For the higher Pr content, the PrO_2 diffraction lines are also absent. In order to obtain more information XAS experiments have been carried out. It is clear that the M_{IV-V} edge of Ce^{4+} is well characterized (Fig. 2). For the praseodymium it is more difficult to obtain accurate measurements because the Pr ratio is too small. The background is relatively too high to allow precise deconvolution calculations. As an example, the M_{IV-V} edge of the $Ce_{1-x}Pr_xO_2$ (x = 4.40%) sample does not seem to vary greatly before and after US treatment (Fig. 3). However, compared to other spectra carried out for different PrO_x samples (26), the aspect of the edge is close to those of Pr_9O_{16} or $Pr_{10}O_{18}$. This would indicate that small amounts of Pr^{3+} ions are always present in the matrix.

The Grain Size Distribution

(*a*) *Praseodymium oxides.* To compare the effects on grain size distribution of US irradiations with or without the leaching reaction, two different experiments have been carried out. The first one was done with a Pr_6O_{11} powder immersed in water without acetic acid. Before US treatment the average diameter of the grains is close to 8.55 μm, with lower and upper particle sizes of 3 and 30 μm. After a rapid sonication period (10 mn) the median diameter decreases to 6.60 μm, and the extremal grain sizes to about 2 and 20 μm. For the second procedure, the powder was immersed in a 5% dilute acetic acid solution. The grain size distribution of the initial powder shows the presence of two types of grains with average diameters of 6.5 and 20 μm, respectively. The grain size extrema are close to 2.5 and 40 μm, respectively (Fig. 4a). After a first sonication period od (7 hr) the distribution is always characterized by two kinds of particles, with median diameters close to 2.2 and 10 μm, and extremal sizes of about 1.9 and 20 μm (Fig. 4b). After a longer irradiation period (9 hr) the size of the particles did not exceed 0.8 μm, and the average diameter is close to 0.4 μm, as illustrated by an SEM micrograph (Fig. 4c).

(*b*) *Terbium oxides.* Two terbium oxide powders have been studied. EDX analyses have allowed the detection of Ce, Pr, and Dy as impurities within some grains. The first powder was irradiated in a 5% dilute acetic acid solution for 11 hr. The initial grain size distribution is characteristic of a coarse powder with an average diameter of about 16.54 μm (Fig. 5a). After sonication the size decreases greatly to a median diameter close to 0.41 μm with no particles over 7 μm. The second maximum should indicate that the reaction is not complete (Fig. 5b). The second sample presented an initially more regular grain size distribution with an average diameter close to 2.25 μm and a maximum size of about 10 μm (Fig. 6a). After a sonication period of 35 hr, the distribution curve (Fig. 6b) exhibits a regular distribution with a median diameter of 0.36 μm and a maximum size close to 1 μm. One can assert in this case that the leaching reaction is nearly complete. SEM observations confirm that the size of most of the scattered particles is between 0.2 and 0.6 μm (Fig. 7).

(*c*) *Cerium and cerium–praseodymium oxides.* Ceria material is well known for its toughness properties. The grain size distribution of the initial sample is nearly regular with an average diameter close to 1.65 μm (Fig. 8a). After sonication (9 hr) of the powder immersed in water, the median diameter decreases to about 0.36 μm, with the maximum size decreasing from about 10 μm (initial powder) to 0.9 μm (Fig. 8b). SEM photographs (too poor in contrast to be published) show that the initial powder is composed of particles the size of which varies from 0.1 to 10 μm. After sonication (9 hr) the grain size was broadly reduced. The SEM image (Fig. 9) reveals first, that the grain size is between approximately 0.075 and 7.5 μm, and second, that some aggregates are formed. Such an observation is in good agreement with the distribution reported in Fig. 8b.

In the same way, SEM and TEM photographs of the sonicated $Ce_{1-x}Pr_xO_2$ (x = 4.40) powder reveal the coexistence of small crystallites (0.20–0.60 μm in size) and aggregates composed of small grains (maximum size of 1.2 μm) (Fig. 10).

The Abrasive Capacity of PrO_2 Powders

In order to evaluate the effect of US on the abrasive capacity of fluorite-type powders on glass, the effects of two PrO_2 powders have been compared by means of an AFM apparatus. The first sample was prepared under US irradiations. The second one was obtained by way of the classical reaction; i.e.; the Pr_6O_{11} powder was stirred for 15 days in a dilute acetic acid bath. Borosilicate glasses, specially prepared for high-performance mirrors, have

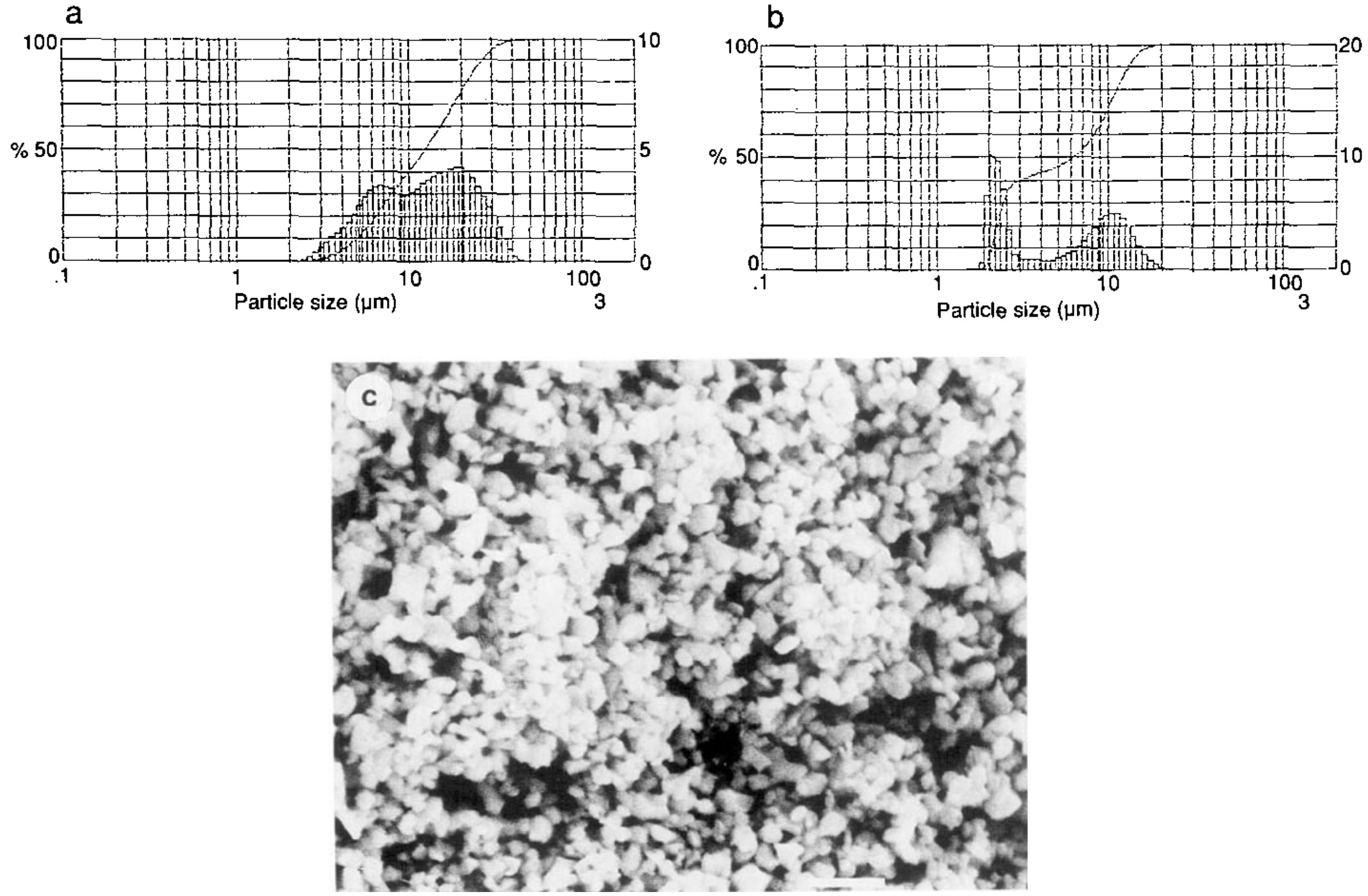

FIG. 4. Grain size distribution of a Pr_6O_{11} powder dipped in a 5% dilute acetic acid solution: (a) initial material; (b) after sonication (7 hr); (c) SEM micrography (×9500) after sonication (9 hr) (the white bar is equal to 1 μm). Lines on (a) and (b) show cumulative distribution of particle sizes.

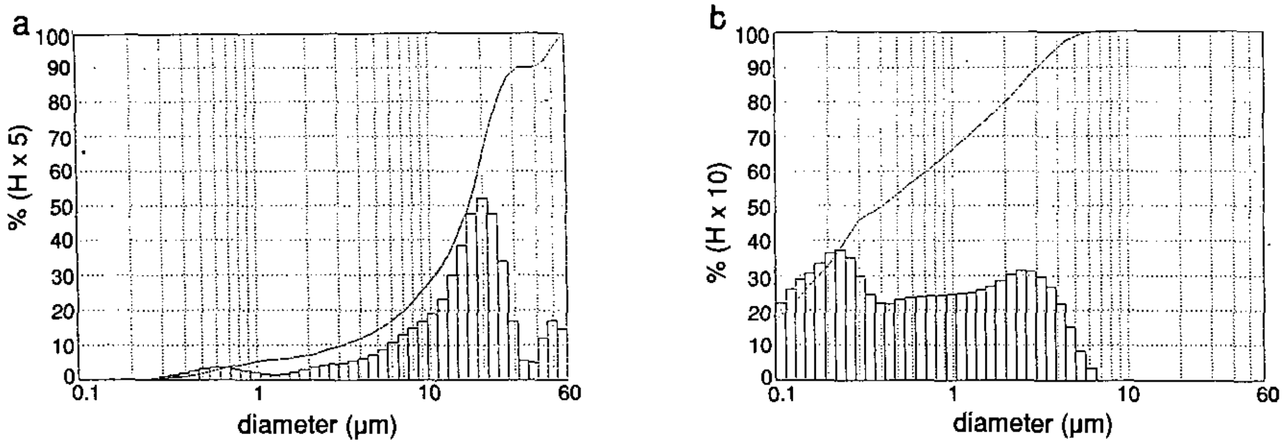

FIG. 5. Grain size distribution of the first series of terbium oxide powder: (a) initial Tb_4O_7 material; (b) after US irradiation (11 hr). Lines show cumulative distribution of particle sizes.

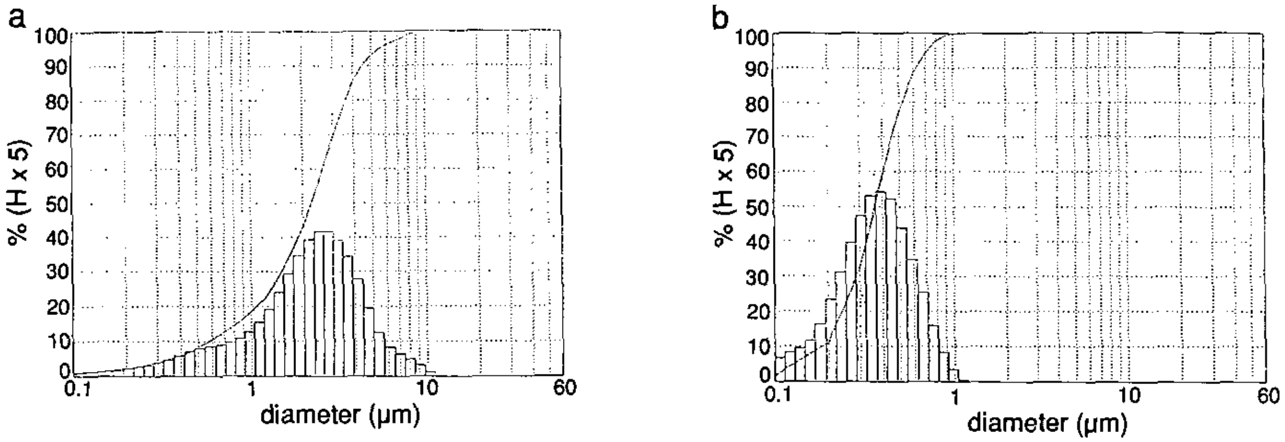

FIG. 6. Grain size distribution of the series of terbium oxide powder: (a) initial powder; (b) after US irradiation (35 hr). Lines show cumulative distribution of particle sizes.

been abraded with these two powders. AFM images show that the resulting two surfaces are completely different (Figs. 11 and 12). The first one (Fig. 11) is abraded by means of the leached powder. One can observe a network of near parallel trenches, with a maximum depth that does not exceed 2 nm, the angle of repose being at most 1°. It has been verified that the whole glass surface remains absolutely flat. The second surface (Fig. 12), abraded by the sonicated powder, is very different. It is characterized by smooth hills and a deceptive stalagmite appearance due to the drawing scale (indicated by arrows on the figure). However, the whole surface does not remain absolutely flat, and is characterized by large smooth hollows.

The glass surfaces have been analyzed by means of an X-ray fluorescence apparatus (detection limit 1%). The main result allows one to conclude that the two surfaces are free of Pr ions. Such a procedure does not, however, permit one to detect the presence of a thin film possibly attached to the glass substrate. On the other hand, the

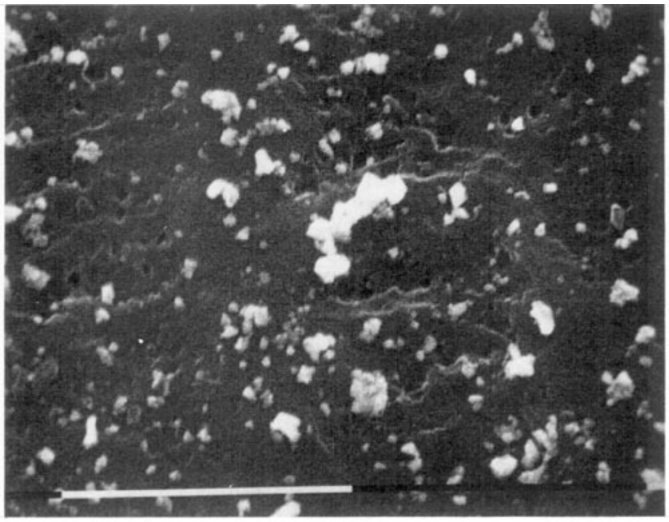

FIG. 7. SEM picture (×8000) of a TbO_2 powder after a sonication period of 35 hr (the white bar is equal to 1 μm).

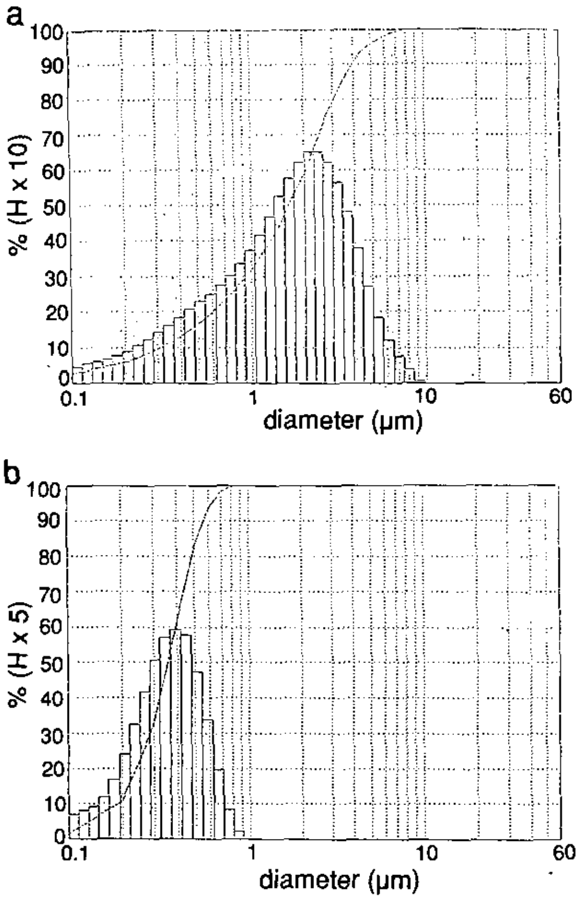

FIG. 8. Grain size distribution of a CeO_2 powder dipped in water: (a) initial powder; (b) after US treatment (9 hr). Lines show cumulative distribution of particle sizes.

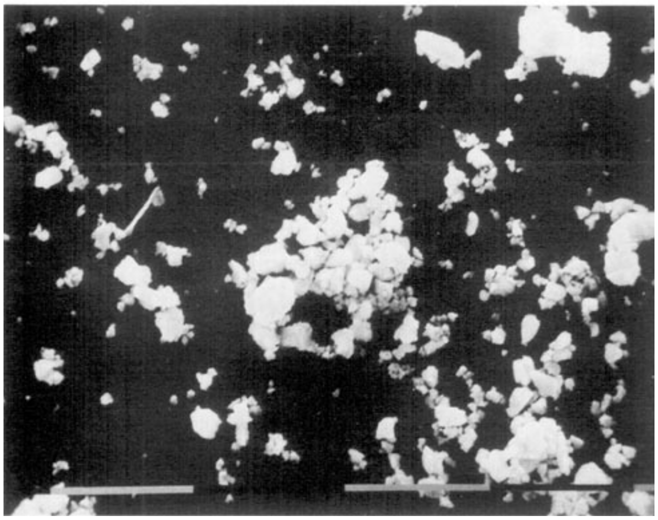

FIG. 9. SEM micrograph (×2000) of a CeO_2 powder after sonication (9 hr) (the white bar is equal to 10 μm). One can observe the coexistence of very small grains and agglomerates composed of small crystallites.

same substrates have been used to deposit boron and tungsten thin films (20–30 nm thick). AFM observations show that the surfaces are strongly similar whatever the abrasive powder used.

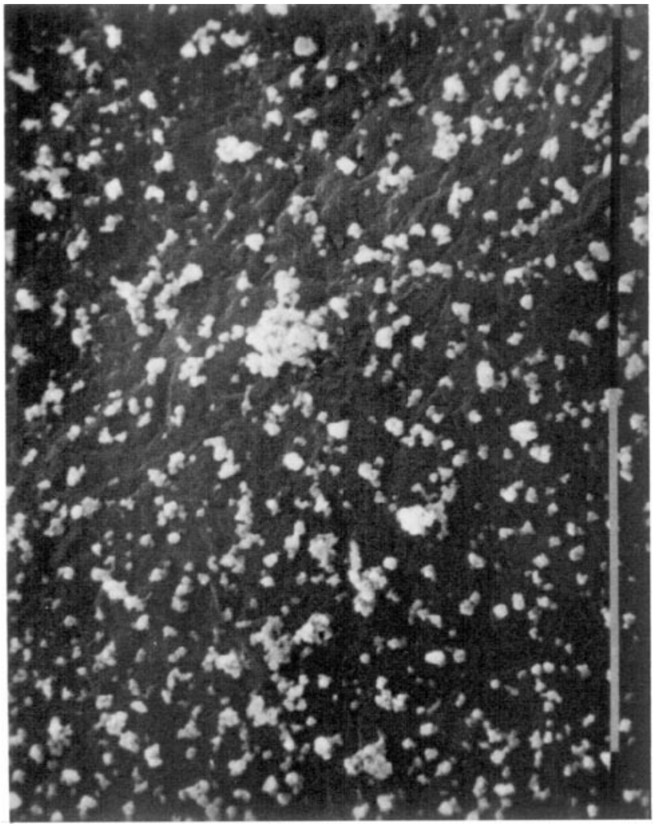

FIG. 10. SEM image of microparticles relative to the $Ce_{1-x}Pr_xO_2$ (x = 4.40%) compound (×5000) (the white bar is equal to 10 μm).

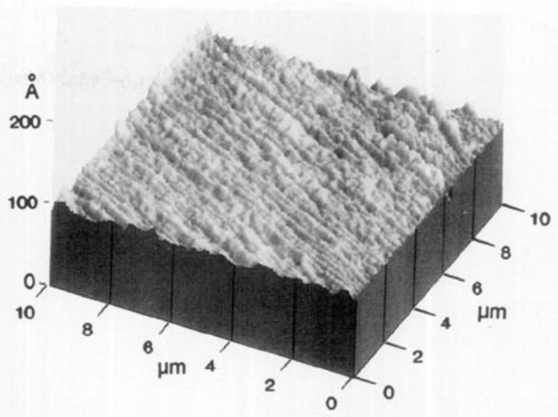

FIG. 11. AFM image of a glass surface abraded with a PrO_2 powder prepared according to the leaching procedure.

DISCUSSION

US irradiations of Pr_6O_{11} and Tb_4O_7 powders immersed in a 5% dilute acetic acid solution have produced PrO_2 and TbO_2. The main results relate to the duration of the treatment and to the final yield in RO_2. Compared to the classical methods, one can assert that the experiment does not require special procedures involving complex inorganic products, high temperature, long heating and/or long strirring periods (27, 28, 30, 32). Indeed, at ambient atmosphere, yields of 100% are reached after sonication periods of 7–8 hr for PrO_2 and 15–24 hr for TbO_2. Kang and Eyring (30, 32) have demonstrated that PrO_x oxides have a higher reactivity to water and acids than TbO_x. Thereby the formation of PrO_2 is more rapid than that of TbO_2.

The first important problem is now to determine the mechanism of the selective dissolution under US irradia-

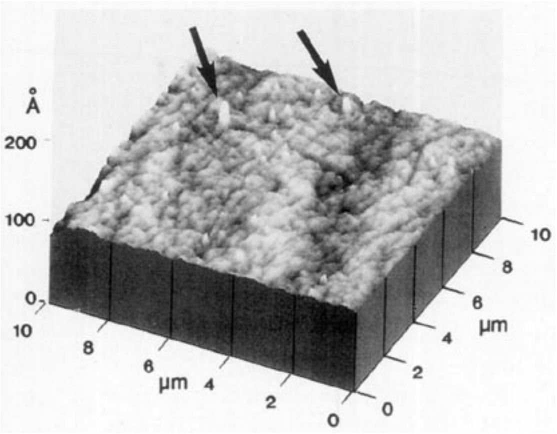

FIG. 12. AFM image of the abraded glass with the PrO_2 sonicated powder. The arrows indicate the deceptive appearance of humps which look like stalagmites (due to the drawing scale).

tions. Among the various kinds of phenomena which occur during such a treatment, two seem to be more effective. The first one is linked to the different mechanical effects provided from cavitation. These can either fragment the crystallites or increase the concentration of dislocations, defects, and pits inside the grains. Larger specific surfaces are then displayed to the preferential acetic acid attacks. The second process is linked to a chemical effect. It has been shown (3, 4) that water and acetic acid are decomposed by US to yield H_2, O_2, H_2O_2, HO_2, H^+, OH^-, and e^- (aq$^-$); and succinic acid, H_2O_2, OH^-, and H_2 species respectively. Therefore secondary oxidation and reduction reactions can occur during sonication (1, 33). Kang and Eyring (30, 32) have shown that the transport of oxygen (as O^- and O^{2-} ions), electrons, OH^-, H^+, and other anionic species in the reaction zone induces an oxidation–reduction reaction. These species diffuse along dislocations, pits, grain boundaries, . . . , and these areas' dissolution of the oxide is complete. For instance, the oxygen diffuses along defects, effectively transporting R^{3+} ions to the reaction sites for dissolution, making it possible to oxidize the RO_x compounds (30). Therefore, the destructive force of US greatly increases the number of sites of solvent attacks. The two mechanisms (mechanical and chemical effects) should act together and strongly accelerate the leaching reaction. But it is difficult to determine which one is playing the leading part. Finally the obvious result which is obtained is a large decrease in the grain size. The problem of aggregation or deaggregation (11) of powders by means of US depends on the experimental conditions. The occurrence of the two opposite phenomena could be governed by the different parameters listed in the sonochemistry section. Thus, the behavior of the particles inside the liquid depends strongly on these factors. For a frequency of 20 KHz the liquids are generally firmly stirred, and the particles are always on the move, inducing numerous collisions. In the case of metallic grains, it has been observed that head-on collisions induced agglomerates, while glancing collisions smoothed the surface (6). In the first case the grains are joined to each other in that they are melted together after impact. In our case, SEM photographs (Figs. 7a, 9c, and 10) taken with broadly scattered powders show that the particle shape is often close to be parallelilipipedic. The RO_x compounds are known to be refractories, and the particles have not fused. Thus, few agglomerates are observed. One can conclude that the initial tough crystallites have been strongly smashed into fragments whatever the collision mode.

A second result must be discussed. Indeed, it has been observed that as the bath temperature increases the beginning of the leaching of Pr_6O_{11} takes shorter times. Such a result is comparable to that of Brauer and Pfeiffer (27) who report that they could produce PrO_2 from Pr_7O_{12} by boiling it in water for 3 hr (the final product is then rich in $Pr(OH)_3$), whereas the formation of PrO_2 at ambient conditions by the way of a 5% acetic acid solution takes place after 8 days. It seems that the bath temperature is an important parameter for improving conditions for leaching. In the case of Pr_6O_{11} the chemical reaction is enhanced for a bath temperature above 333 K. One must note that this is different from numerous organic syntheses for which maximum yields and minimum sonication periods occur at low temperatures (between 265 and 280 K).

CONCLUSION

US irradiations of liquid/solid mixtures induce numerous complex phenomena which are ruled by different parameters. The greater part of them are still not clearly explained. These phenomena which occur either together or independently from each other do not accurately explain the whole of the chemical reactions. Nevertheless, one can assert that some inorganic materials are very sensitive to US irradiations. For instance, compared to classical chemistry, the formation of pure PrO_2 and TbO_2 can be carried out within sonication periods of 7 to 15 hr, instead of several days or weeks. Another interesting result is that US treatments produce a submicrometer grain size distribution. To obtain further information on the interaction between US and selective dissolution, other oxides characterized by a fluctuant oxidation state ought to be studied. Such experiments are now in progress. Another set of experiments will also be carried out by means of higher frequency (between 30 and 100 kHz) and higher powder US in order to obtain better yields and finer particles.

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