

Acoustic Emission during Leaching of Pr_6O_{11} in Dilute Acetic Acid

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In the course of the selective dissolution (leaching) of an intermediate praseodymium oxide, Pr_6O_{11} , in contact with a dilute acetic acid solution, it is possible to record an ultrasonic acoustic emission. When the chemical reaction is taking place the solid material loses Pr^{3+} ions to the solution and a residue of PrO_2 remains. Over the course of the experiment (nearly 12 hr) various kinds of signals were recorded. The most important and intense response occurred nearly 8 hr after the beginning of the process. The acoustic emission is tentatively explained in terms of the dissolution of parts of the grains with a high amount of Pr^{3+} ions, and/or discohension or breaking of inclusions. © 1993 Academic Press, Inc.

Introduction

For about 10 years it has been possible to "hear" various types of acoustic signals emanating from solids during internal physical or chemical change. Detection and analysis of those signals, corresponding to an acoustic emission (AE), allow one to obtain information on physical mechanisms connected to deformations and defects throughout a matrix. A classification of different AE (in dB) is reported in Fig. 1. The most important parameters having an effect upon AE are overall: anisotropy, heterogeneity, twins, defects, increasing of the grain size, martensitic transformations, etc. For the latter case, AE generation has been observed for Au-Cd (1, 2), Fe-Ni (3, 4), and Cu-Zn-Al (5, 6) alloys and ZrO_2 (7). It has been also shown that an AE occurs either during crystallization of isotactic polymers (8), or in the course of fracture of sintered alumina (9), or in the case of ferro- and

ferrimagnets (YIG, FeNiBSi) with the creation and/or annihilation of domain walls (10, 11).

In the field of solid state chemistry an AE has been recorded during phase transition in concentrated hydrides of Ta, Nb, and V. It is probably associated to a rearrangement of domain boundaries (from a migrating mechanism) (12, 13). Betteridge *et al.* (14) have shown that AE are generated during many chemical reactions such as copper sulfate with sodium hydrogen carbonate, concentrated sulfuric acid with water and sodium hydroxyde, organic mixtures with large heat of mixing ion-exchange, gel formation, chemiluminescence, etc.

The aim of this paper is to try to demonstrate that during slow leaching (or selective dissolution, or also solvolytic disproportionation) of a mixed-valence compound such as Pr_6O_{11} in dilute acetic acid, an AE can be recorded. A tentative explanation is given in terms of the dissolution of layers rich in Pr^{3+} ions, and/or discohension or breaking of inclusions.

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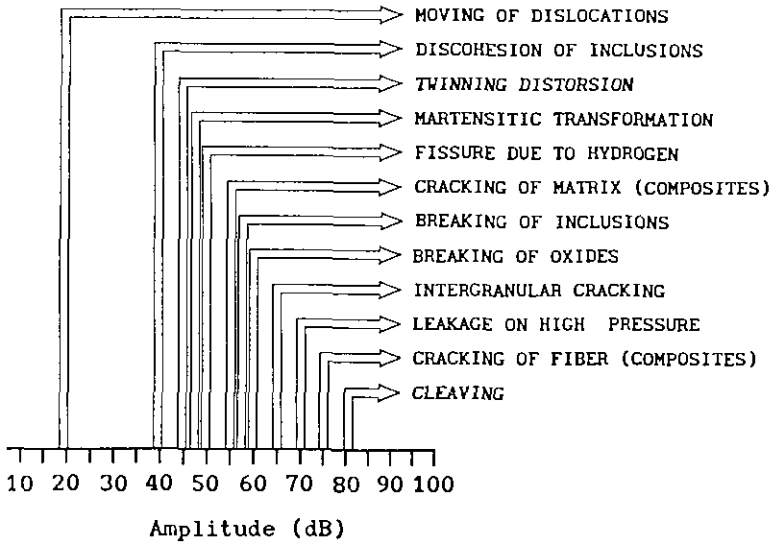


FIG. 1. Classification of the different ultrasonic emissions relative to various sources of noise emission (amplitude in dB). (From J. Roget, Emission Acoustique, Published in "Techniques de l'Ingénieur, Traité Mesures et Contrôles," p. R-3200, 1989).

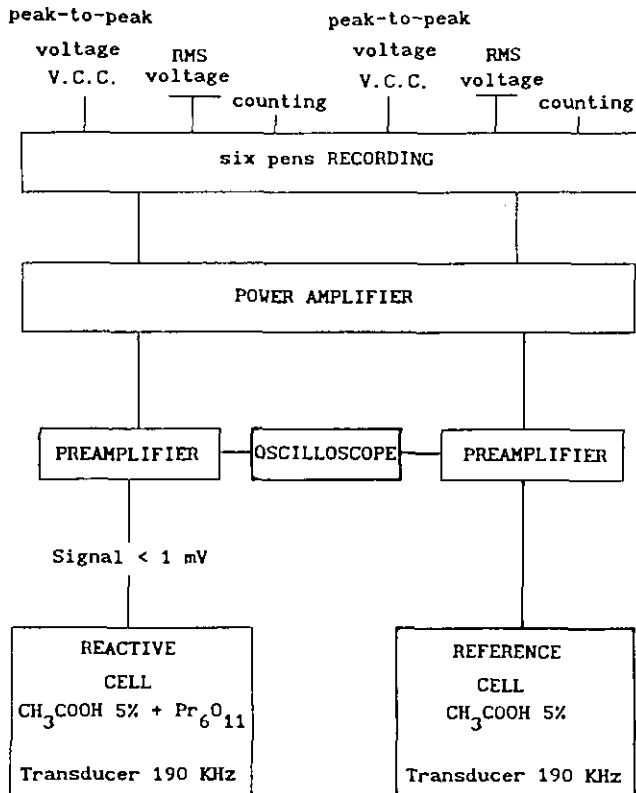


FIG. 2. Scheme of the experimental device.

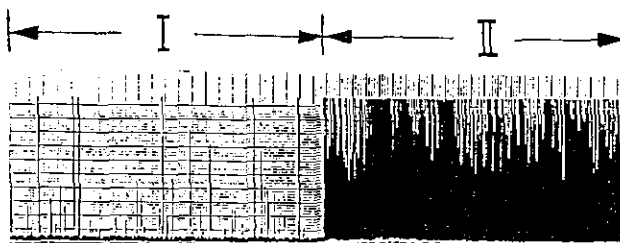


FIG. 3. Spectrum I, AE emanating from bubble bursting and bombardment of CaCO_3 grains on the transducer (V.C.C. mode).

Experimental Procedures

Acoustic Measurements

To record a possible AE two series of experiments have been carried out. Two parallel amplifier channels linked to two transducers (PZT ceramics) with a resonance frequency of about 200 kHz were used. One of the transducers was dipped inside an appropriate test tube (reactive cell) which contained the dilute acetic acid (5% in distilled water) and the Pr_6O_{11} powder. This transducer was maintained 0.5 cm under the liquid surface. The second transducer was set either in air (first experiment) or in an acetic solution (second experiment) as a reference cell. Moreover it was located far from the former (0.5 m) to avoid interference (Fig. 2).

The output signal from the reactive cell is lower than 1 mV. It is amplified by a preamplifier (gain = 40 dB). The output signals (from each cell) are analyzed by means of an oscilloscope. After further amplification, by means of a power amplifier, each

electrical signal leads to the recording of three different types of measures which are defined as follows.

—Alternance: A count every time the output voltage passes beyond the threshold voltage (curve 1).

—VCC (10 V) (voltage crest to crest or peak to peak): it is the maximum voltage (or measurement) of the signal over 0.1 sec (curve 2).

—RMS (root mean square voltage) (curve 3): it depends on the integrated time (as 1 sec) defined by the following formula:

$$V_{\text{RMS}}(t) = \sqrt{\frac{1}{T} \int_0^T [V(\tau)]^2 d\tau}$$

Choice of the Oxide—Treatment of the Solid-Liquid Mixture

(a) It is well known that, among the rare earth elements (R), cerium, praseodymium, and terbium possess a fluctuant valency between 3+ and 4+. Such a particularity leads to the formation of intermediate oxides such

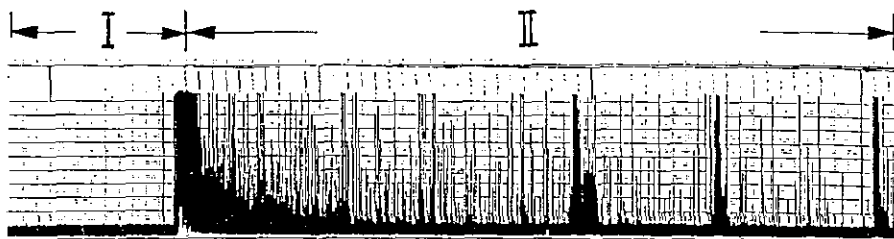
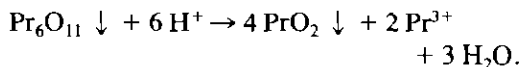
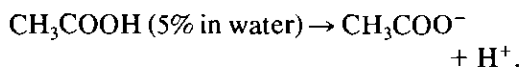


FIG. 4. AE of which the signals decrease in intensity after successive additions of small volumes of acetic acid solution + Pr_6O_{11} (V.C.C. mode).

as RO_x with $1.5 \leq x \leq 2$. Various spectroscopic methods have demonstrated that a RO_x compound is a mixture of R^{3+} and R^{4+} oxides of which the relative weights vary as a function of the x value (15). As demonstrated by Brauer and Pfeiffer (16) and Clifford (17) when a higher oxide, such as Pr_6O_{11} , is exposed to air for a long time, it is disproportionated to PrO_2 and $Pr(OH)_3$. Kang and Eyring (18, 19) have shown that the formation of PrO_2 and TbO_2 can be carried out from Pr_7O_{12} and $Tb_7O_{12} + Tb_{11}O_{20}$ powders. The former are dipped in 5% acetic acid solution stirred for 8 days, the latter immersed in hydrochloric acid and glacial acetic acid at boiling temperature for 5 to 40 min. When a Pr_6O_{11} powder is dipped into a dilute acetic acid a leaching process occurs with the dissolution of the trivalent metal ions into solution. Then, the solution takes on a characteristic green color due to the Pr^{3+} ions. The following chemical reaction occurs:

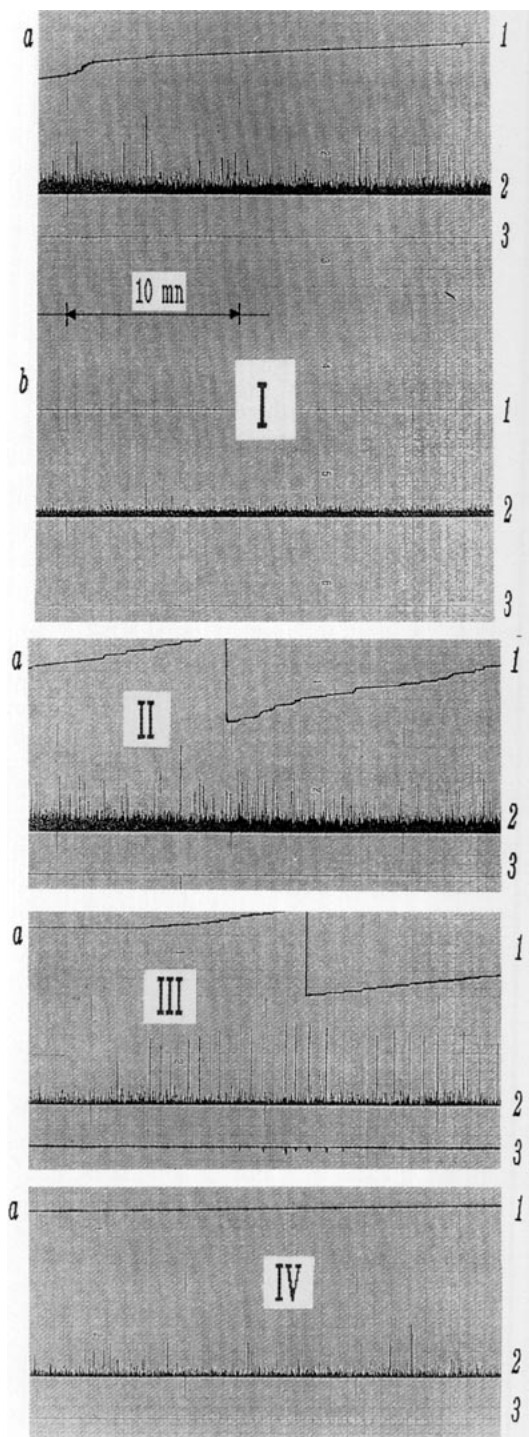


Generally the reaction is fully achieved after two or three days. The H^+ ions result from the partial dissociation of the dilute acetic acid:



(b) To avoid to the maximum the formation of bubbles (therefore ruling out interferences during recording when bubbles burst) the distilled water-acetic acid solution (total volume 0.04 liters) and the Pr_6O_{11} black powder (4 g) have been degassed. The acetic acid solution was quickly submitted (2 min) to ultrasound and then strongly stirred at ambient temperature. Last, before mixing, liquid and solid, were separately put in sealed tubes maintained under vacuum ($\sim 4 \times 10^{-4}$ Pa).

Moreover, during the experiments, which are displayed over about a 12-hr interval, small amounts of CH_3COOH were added to the solution during the first 7 hr. This was



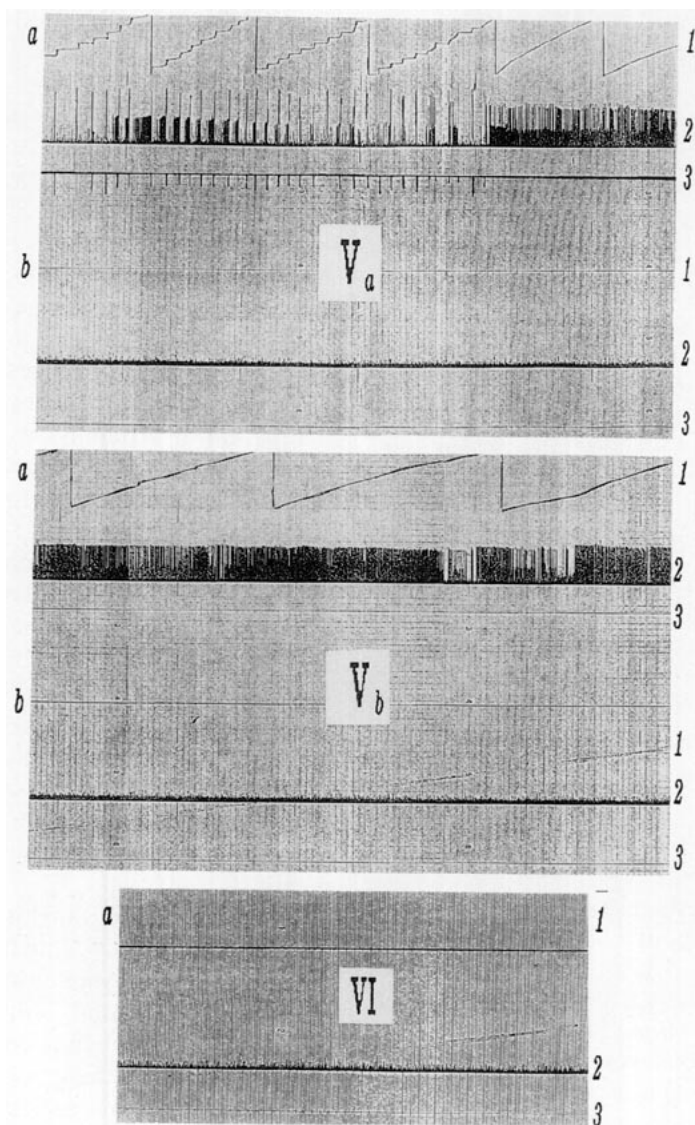


FIG. 5. Different stages of the recorded emissions during Pr_6O_{11} leaching. I. The beginning of the experiments when scattered intense signals are recorded after mixing and stirring (15 min). II. 3.50 hr after mixing: numerous intense signals are recorded. III. 6 hr after mixing: a pseudo-periodic emission appears. IV. During the next 1.50 hr the activity decreases. V. 7.50 hr after mixing: very intense activity is observed and recorded. a. First stage (25 min), characterized by a pseudo-periodic strong RMS signal (left part of the curve) and a scaled step alternance response. The beginning of the second stage characterized by a nearly continuous emission can be observed on the right side. b. Second stage (~ 2 hr) showing a near continuous emission. VI. 10 hr after the mixing the signals become flat.

done in order to avoid the loss of the acid by slow evaporation.

Results

Examples of AE due to Bubbles, Turbulences, and Grain Bombardment

The recordings were carried out according to the VCC mode, by use of a standard transducer dipped in the liquids. The first example is the mixing of CaCO_3 first with H_2O (I) and second with $\text{H}_2\text{O} + \text{CH}_3\text{COOH}$ (II). On spectrum I (Fig. 3) it appears that the AE is due either to bubbles bursting and/or to the bombardment of CaCO_3 grains on the transducer itself. The second example (Fig. 4) shows how the addition of small volumes of acetic acid to the $\text{H}_2\text{O} + \text{Pr}_6\text{O}_{11}$ mixture allowing signals with decreasing intensity to be recorded. As no bubbles were observed in the liquid, the AE at that point is possibly due to turbulent phenomena connected to the mixing of the two liquids.

AE from a Pr_6O_{11} Powder Dipped in a Dilute Acetic Acid Solution

The different stages of the reaction were recorded over about 12 hours. They are reported as Figs. 5.I to 5.VI, respectively, and provide results from the second set of experiments involving PrO_x in which the recording conditions were more refined. The first step (Fig. 5.I) was obtained in the early stage of the experiment. After stirring for homogenization (15 min), some scattered intense signals are observed. One can notice that the background is not negligible. Thirty minutes after the beginning of the experiment the liquid solution takes on a very slight green color. Then, 3.50 hr later, many signals are then recorded (mean intensity of 30/40 dB), and the background is still not negligible (Fig. 5.II). Then during the next 2.5 hr the solution remained at rest. At this point it was quickly stirred (10 sec) again for homogenization. This led to the recording of pseudo-periodic signals (mean intensity of about 40/50 dB) and a weak RMS

response (frequency <500 kHz) (Fig. 5.III). Then over 1.50 hours the activity decreased (Fig. 5.IV).

A more important stage of the reaction started 7.50 hr after the beginning of the experiment: two separate periods were observed. The first one (Fig. 5.V.a) is characterized by a near pseudo-periodic VCC signal (40/50 dB in intensity), RMS signals (characterized by a response extended along more than 1 sec), and near regular scaled steps of the alternance response (due to large impulses beyond the background). This period of instability was recorded for an interval of 25 min (left part of Fig. 5.V.a). Then, a near continuous emission was recorded for about 2 hr [Figs. 5.V.a (right part) and 5.V.b]. The signal intensity is close to 35/45 dB. One can note that RMS and alternance responses remained flat all during that time. Lastly, the activity stopped abruptly and the recording became flat (Fig. 5.VI). At this moment, the reaction seemed to be complete, and the liquid had taken on a more pronounced green color.

Remarks. (a) During the entire experiment no signal was recorded by the reference cell.

(b) One must admit that it was difficult to record good spectra. Indeed, the greater part of the signals were close to those of the electronic background. Moreover, different kinds of external phenomena could display various effects on the emission.

(c) During another series of experiments a phenomenon similar to that reported on Figures 5.V.a and V.b had already been observed. Unfortunately, the contrast of the recorded graph is too badly defined to permit a good reproduction.

Discussion

Crystallographic Data

X-ray diffraction patterns reveal that the fcc parameter of the initial Pr_6O_{11} powder was about $a = 0.547$ nm, when the one of the final products was $a = 0.539$ nm; i.e.,

characteristic of the PrO₂ fluorite structure (18, 20).

Hypothesis on the AE

In order tentatively to explain the various signals recorded all along the experiment, the following hypothesis about the disproportionation of Pr₆O₁₁ has been proposed. The weaker signals (recorded over 7.50 hr) might be connected to the beginning of the Pr³⁺ ion dissolution. For instance, the preferred attack could occur either at the surface of the crystallites, or near dislocations, defects, and grain boundaries. High resolution electron microscopic images performed by Kang and Eyring (18) exhibit clearly that the leaching of small particles occurs overall along dislocations or involves a surface process. The final PrO₂ particles exhibit long and narrow holes and crevices throughout the matrix. The intense AE might be linked to the collapse of predominantly Pr⁴⁺ atomic planes, due to the sudden dissolution of layers more rich in Pr³⁺ ions. This mechanism can be compared to the behavior of a building of which intermediate floors collapse. The recorded AE (intensity emission of about 35/45 dB) could be compared with the one of discohension or breaking of inclusions (40 to 55 dB) in solid materials (Fig. 1).

However, caution is advisable in trying an interpretation of the whole of the recorded signals. First, because the spectra are often only the apparent spectra. It is possible that reflections occur on the walls of the test-tubes and also possibly on the transducer itself. Second, the signals are very complex, and it is not easy to read them: so, as shown in Fig. 5.V.a, it is clear that at least different types of signals are recorded. Third, the various kinds of attack of the particles by acetic acid cannot be differentiated from one another.

Conclusion

It is difficult to interpret the records of AE activity during chemical reactions.

However, as claimed by Betteridge *et al.* (13) it is known that acoustic energy, from chemical reactions, is associated with thermal changes. It is suggested here that this occurs during Pr₆O₁₁ leaching in acetic acid solution.

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