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ABSTRACT

The “nano-indentation continuous stiffness measurement technique” has been employed to analyze the failure dynamics of mesoporous SiO₂ based material (Vycor). The depth dependence of the indentation hardness (H), elastic modulus (E), and elastoplastic parameter (S²/P) shows crackling noise, which has been analyzed to monitor the jerky strain release. The noise is power law distributed with exponents near C24 1.5 over several decades, confirming avalanche criticality. This value is in good agreement with literature results obtained by other techniques and with earthquake statistics.

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The breakdown and collapse behavior of porous structures due to external pressure and deformation is of great importance. Among others, porous materials have been the object of various studies: e.g., for nuclear materials1 and CO₂ capture and storage,2 as models for studying the effects and the mechanisms prior and during earthquakes,3 and the collapse of ultralight materials4 and artificial and natural formations (e.g., mines, buildings, and bones).3–8 A general better understanding of the occurring phenomena helps to increase the precision of forecasting collapse events. During compression (well before the final breakdown) of porous materials, sudden changes of the internal strain field have been found, seen as discontinuities of the stress displacements. They do not occur continuously, but as coupled events in avalanches leading to cracking noise. Under slow loading, many systems generate crackles, e.g., our earth during earthquakes,3,10 a sheet of paper while crumpling,11 ferroic materials under electric and magnetic fields as a result of domain wall movements,12–15 metals and alloys during martensitic phase transitions16,17 and plastic deformation,4,18 and even steel cantilevers as parts of ultrasensitive gravitational wave detectors.19 An effective way to detect such abrupt strain field variations, the “jerks,” is to measure the related acoustic emission (AE) events.20 The underlying physical process is the formation of avalanches, seen as sequences of jerks.20

Nano-indentation has been successfully used as a complementary method to investigate avalanches in metallic glasses and metals.18,21–23 In this study, we extend this approach. We employ the so-called “continuous stiffness measurement (CSM) technique”24–26 to identify avalanches in porous materials during indentation. CSM has been used, e.g., by Greer and Nix27 to investigate size effects in gold. In this technique, a small dynamic oscillation is imposed on the applied force or displacement, and the amplitude and phase of the corresponding signal are measured with a lock-in amplifier. This dynamic measurement differs greatly from the static indentation method in that all parameters are determined as dynamical response functions at a frequency of 100 Hz.

The indentation hardness (H), elastic modulus (E), and elastoplastic parameter (S²/P) are functions of the indentation depth and monitor the collapse behavior (C24 jerks) of the mesoporous synthetic silica (SiO₂) glass “Vycor” (Corning, Inc., New York) during penetration. The maximum likelihood (ML) method28–31 was used to characterize the jerk spectra superposed to H, E, and S²/P.

The sample was a polished plane-parallel plate of Vycor. This material is a nongranular structure composed of a continuous glass skeleton with a porosity (Φ) of 0.4 and an average pore diameter of 7.5 nm.32 The mechanical properties were measured with a Nanomechanics iNano nanoindenter, equipped with a diamond Berkovich indenter tip that operates in a continuous stiffness mode (CSM). Using CSM, the sample stiffness (S) is measured continuously during loading of the indenter.24–26 Fused silica was the reference material for calibration. The instrument software calculated the hardness (H) and the elastic modulus (E) during the loading process according to Oliver and Pharr24 with
\[ H = \frac{P}{A}, \]  
\[ S = \beta \frac{2}{\sqrt{\pi}} E_r \sqrt{A}, \]  
\[ \frac{1}{E_r} = \frac{1}{E_i} + \frac{1 - \nu^2}{E}. \]  

where \( P \) is the imposed load and \( A \) the projected contact area between the indenter and the sample determined from the shape of the indenter and using the Oliver and Pharr method.\(^{25,33} \) The measured contact stiffness \( (S) \) is related to the elastic properties of both the sample and indenter and the contact area through\(^ {34} \):

\[ \frac{P}{S^2} \approx \frac{1}{\pi} \frac{H}{E_r} \]  

\( P/S^2 \) is known to give a good approximation for \( H/E_r \) for materials with a significantly lower modulus than diamond,\(^{13} \) which is the case for Vycor. In this study, we use the inverse parameter \( S^2/P \), the elastoplastic factor.

The maximum likelihood estimation (MLE) method\(^ {28} \) has been used to analyze the jerk spectra\(^ {29-31} \) by:

\[ \varepsilon(x_{\text{min}}) = 1 + n \left[ \sum_{i=1}^{n} \ln \frac{x_i}{x_{\text{min}}} \right]^{-1} , \]

with \( x_i, i = 1, \ldots, n \), being the observed values of \( x \) such that \( x_i \geq x_{\text{min}} \) while \( \varepsilon \) (defined as a positive quantity) is the exponential parameter indicated by a plateau in the results of the analysis. The standard error\(^\text{e} \) is expressed as:

\[ \sigma = \frac{\varepsilon(x_{\text{min}}) - 1}{\sqrt{n}} + O \left( \frac{1}{n} \right). \]

From nano-indentation measurements, we obtained an average elastic modulus for Vycor of \( \approx 17.2 \pm 0.4 \) GPa in excellent agreement with manufacturer specifications (2.5 \times 10^6 psi) and with literature data.\(^ {26} \) Our value is also close to that calculated from Resonant Ultrasound spectroscopy (15.8 GPa) by Koppensteiner et al.\(^ {32} \) We measured an average indentation hardness of \( \approx 1.57 \pm 0.04 \) GPa and an elastoplastic parameter of \( \approx 249.9 \pm 9 \) GPa. \( E \) is directly related to interatomic bonding and \( H \) denotes the resistance to plastic deformation, while the directly measurable \( S^2/P \) is connected to both via Eq. (4). These mechanical parameters depending on the internal structure have been used to monitor the ongoing volume collapse of Vycor caused by the penetration of the indenter tip.

The depth evolution of \( H, E, \) and \( S^2/P \) is shown in Fig. 1. The jerk spectra were constructed as the square of the first derivative of the primary depth dependences. No smoothing of the original data was used. The jerks are hence a measure for the energy change \( (\delta H)^2, (\delta E)^2 \), and \( S^2/P \) with the related squares of their derivatives (jerk-spectra). The total number of recorded signals is \( N = 22552 \).
and \((\delta S^2/P)^2\), per unit depth change. Deng et al.\(^3\) have already simulated such behavior where sudden drops in hardness are indeed not smooth curves but contain jerks and subjerks during the drop. The method of identifying jerks as the squares of the slopes includes these effects and is hence more reliable than the registration of simple drop spectra. The review of Hardiman et al.\(^3\) provides further details. Yield points were observed in GaAs and Fe-3 wt. %Si single crystals when surfaces were indented.\(^4\) The closeness of our results to the energy exponents in mean field theory (1.33–1.6) is relevant to identify the physical origin of the jerk spectra. Similarly, Budrikis et al.\(^4\) have explored indentation in a theoretical model and concluded that the size distribution of avalanches follows a much smaller exponent of 1.29 which can be estimated to relate to an energy exponent well below the mean field limit. A full analysis of the atomic mechanisms and thereby the exact identification of the power law exponents, namely, “energy” or “size,” is intended for future molecular dynamics simulation. The effect of the squaring of the slopes has already been simulated.\(^5\) It was shown that the statistical analysis is not significantly influenced, while the statistics of the dataset is much improved for the squared datasets (see the supplementary material).

Figure 2 depicts the ML analysis of six indents. The depth evolution of \((dH/d\text{Depth})^2\), \((dE/d\text{Depth})^2\), and \((d(S^2/P)/d\text{Depth})^2\) indicates flat plateaus over around 3 decades that define an exponent around 1.5. This exponent is in good agreement with previous measurements using a Dynamical Mechanical Analyzer (DMA)\(^3,3\) which provide a similar energy exponent from fitting of the power law distributions and a slightly higher value of \(\varepsilon \approx 1.7\) from MLE. Our value is close to that from AE spectroscopy (1.39).\(^5,4\) In comparison with mean field theory, our experimental exponent lies between the limits 1.33 and 1.667 for fast and force integrated jerks, respectively.\(^5,4\) From the point of view of earthquake statistics,\(^4\) our exponent is in excellent agreement with that suggested by Kagan.\(^5\) The histograms of the probability distribution function (PDF) of the binned jerks are shown as log-log plots (see insets in Fig. 2).

In summary, we showed that the nano-indentation in Vycor using continuous stiffness measurements is suitable to detect avalanches in porous materials. The mechanical properties (i.e., indentation hardness, elastic modulus, and elastoplastic parameter) as a function of depth are sensitive parameters to monitor the chain reactions of collapsing pores during indentation. \(E\) directly mirrors the breaking of bonds and provides the best defined plateau. Using the maximum likelihood method, we obtain an exponent \(\sim 1.5\) that is in good agreement with literature data for energy exponents in Vycor. We found mean-field behavior in good approximation. In addition, our measurements provide further evidence for the strong similarity between the failure of porous Vycor and earthquake statistics. If it criticality represents the “interface” between ordered and disordered states,\(^4\) nano-indentation CSM is an excellent technique (related to its small scale) to drive a system to several critical points without provoking a complete breakdown of the material.

See the supplementary material for the exemplary effect of the squaring of the slopes.

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REFERENCES


