

Loading Rate Effect on Nanoscale Plasticity in MgO Doped Alumina

Payel Maiti and Jiten Ghosh

XRD & SEM Units, Materials Characterization and Instrumentation Division, CSIR-
Central Glass and Ceramic Research Institute, Kolkata-700032, India
Email: jiten@cgcricri.res.in

Anoop Kumar Mukhopadhyay

Department of Physics
Manipal University Jaipur, Jaipur 303007, Rajasthan, India.
Email:anoopkumar.mukhopadhyay@jaipur.manipal.edu

(Received December 09, 2020)

Abstract: Here we report for the very first time the effect of loading rate on nanoscale plasticity in 1-5 wt.% MgO doped Alumina (MA) ceramics. All samples are characterized by X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and Nanoindentation (NI) techniques. The experimentally measured load versus depth plots confirm the profuse signature of nanoscale plasticity through ‘micro-pop-in’s. The results show both critical load and critical depth are sensitive functions of the loading rates and the amount of sintering aids. Further, the nanoscale hardness is also found to be strongly affected by the loading rates. The occurrence of nanoscale plasticity or micro-pop-in is explained by the generated maximum shear stress inside the nanoindentation cavity.

Keywords: nanoindentation, plasticity, nanohardness, young’s modulus, shear stress.

1. Introduction

Alumina is one of the most important structural and functional ceramic material¹⁻⁵. Nanoindentation has now emerged as the most versatile technique to study its mechanical properties at microstructural length scale. For instance, nanoindentation technique has been used to study 3D printed alumina ceramics for scaffold application¹, meso-porous alumina for bio-

prosthesis application², thin alumina coatings for nuclear application³, alumina based composite coating for biomedical application⁴ and for experimental verification of modelling related to mechanical integrity of brittle solids at the nanoscale⁵. The present author and co-workers have applied nanoindentation technique to polycrystalline alumina⁶, single crystal alumina^{7,8} as well as alumina-based nanocomposites⁹⁻¹¹. Despite such a wealth of literature¹⁻¹¹, however, there is no study reported yet globally on the effect of loading rate variation on the nanoscale plasticity of magnesia doped pressureless sintered alumina ceramics. Thus, the objective of the present work is to study this aspect.

2. Materials and Methods

All details of the materials synthesis and characterization techniques have been reported already by us elsewhere⁶⁻¹¹ and hence will not be repeated here for the sake of brevity. Nominally speaking (1, 3 and 5 wt.%) magnesia doped alumina ceramics were prepared by pressureless sintering at 1600°C for 2h in air. These are termed as MA 1, MA 3 and MA 5, in correspondence. Measured by the Archimedes' principle the samples had relative densities of about 96%, 96.6% and 97.3% of theoretical density (3.958 g.cc⁻¹). The samples were characterized by XRD (X'PertPro MPD, Panalytical, The Netherlands), FESEM (Supra VP35, Carl Zeiss, Germany) and Nanoindentation (Fischerscope H100-XYp, Fischer, Switzerland) techniques. In the nanoindentation experiments, the load was kept fixed at 1000 mN but both the loading time and the unloading time were varied in the range of 1 to 1000 s to produce loading rates (dL/dt) in the range of 1 to 1000 mN.s⁻¹. However, for any given experiment the unloading time from the maximum load was kept the same as the loading time to that maximum load. All the nanoindentation experiments were conducted on mirror polished sample discs of MA 1, MA 3 and MA 5 ceramics at room temperature. The load (L)-versus depth (d) plots resulting from the nanoindentation experiments were utilized to evaluate the experimental nanohardness (H_{Ex}) and Young's modulus (Y_{Ex}) values of these samples following the well-known Oliver-Pharr model¹². Further details are already reported by us elsewhere⁶⁻¹¹. The maximum shear stress (σ_{sm}) active just underneath the nanoindenter was estimated by the following equation (1.1) as^{12,13}

$$(1.1) \quad \sigma_{sm} = 0.45 \left(\frac{16L_c Y_r^2}{9\pi^3 r^2} \right)^{\frac{1}{3}},$$

Here, L_c denotes the critical load at which the nanoscale plasticity events happen. In addition, Y_r represents the reduced Young's¹². Further, r is the radius of the nanoindenter tip (~ 150 nm).

3. Results and Discussions

3.1 Phases and Microstructure Analysis: The XRD pattern of MA1, MA3 and MA5 samples are shown in Fig. 1(a). Inset of Fig. 1(a) represents the microstructure of MA 5 ceramics. From Fig. 1(a) it is found that there is presence of both spinel and corundum alumina phases.

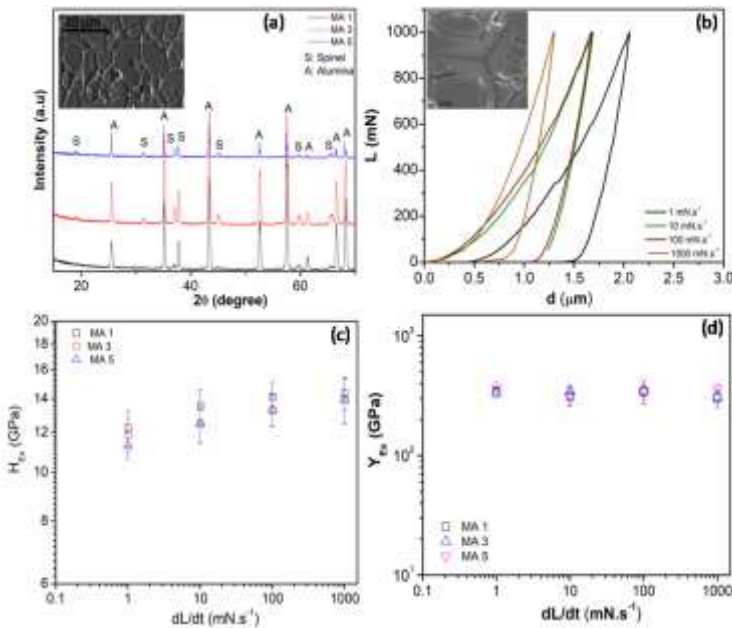


Figure 1. (a) XRD patterns of MA 1, MA 3 and MA 5 ceramics. Inset represents the thermally etched FESEM image of MA 5 discs. (b) Typical load (L)-depth (d) plots of MA 1 ceramics at different loading rates (1 - 1000 mN.s^{-1}). FESEM image of nanoindenter is clearly shown in the inset. Variations of (c) nanohardness (d) Young's modulus with the loading rates (dL/dt) for MA 1, MA 3 and MA 5 ceramics.

3.2 Loading Rate Influence on Micro-pop-in Events: The L - d plots of MA1, ceramics conducted at 4 different loading rates (1 , 10 , 100 and 1000 mN.s^{-1}) are shown in Fig. 1(b). Similar load vs depth (L - d) plots were obtained for the samples MA3 and MA 5 but are not shown here for the sake of brevity. The FESEM image of nanoindenter is presented in inset of Fig. 1(b). The occurrence of serrations showing distinct transition from elastic to plastic deformation at all loading rates (Fig. 1b) suggests the

existence of micro-pop-in during nanoindentation. Similar serration events were also noted to be present in the (L-d) plots of the MA3 and MA5 ceramics but are not included here for the sake of brevity only.

The existence of these micro-pop-in events provide evidence that nanoscale plastic events are happening here. Similar observations are also reported for alumina, alumina-based nanoceramic composites and metallic glass samples⁶⁻¹³. Further, as can be seen from Fig. 1(c), with the increase in loading rate from ~ 1 to 1000 mN.s^{-1} , the nanohardness (H_{Ex}) values increase to 14.17, 13.98 and 13.92 GPa from the values of 12.26, 11.88 and 11.33 GPa for MA1, MA3 and MA5 ceramics, respectively. These experimental results are in well agreement with the data reported in literature¹⁴. Thus, with the increase in loading rate from ~ 1 to 1000 mN.s^{-1} , the improvement of H_{Ex} value for MA 1, MA 3 and MA 5 ceramics is found to be $\sim 16\%$, 18% and 23% , respectively.

These increases are quite significant considering that these are inherently brittle polycrystalline ceramics. However, the Young's moduli (Y_{Ex}) values of the MA1, MA3 and MA5 ceramics show no significant changes with the variations in loading rates (Fig. 1(d)). The average magnitude of Y_{Ex} (i.e., 350-370 GPa) corroborates well with literature data¹⁴⁻¹⁶.

An appropriate part of the (L-d) plot of the MA1 ceramics is shown in exploded view in Fig. 2(a) as a typical illustrative example. As shown in Fig. 2(a), the presence of micro-pop-in is clearly observed at loading rate (1000 mN.s^{-1}) for MA1 ceramics. The identification of first critical load (L_{c_j}) and the corresponding critical depth (d_{c_j}) for the j^{th} nanoscale plasticity event are illustrated in the inset of Fig. 2(a). Actually the critical load refers to the ultra-small load at which nanoscale plasticity or micro-pop-in events just initiate and the corresponding depth of penetration is known as critical depth. In other words, (L_{c_j}) represents intrinsic contact deformation resistance against initiation of the j^{th} nanoscale plasticity event. It means that at least the applied load in the nanoindentation experiment must be greater than or equal to (L_{c_j}) at or beyond which the micro-pop-in events takes place on the surface of the mirror polished MA1 disc sample. Its magnitude will of course vary from material to material. Here we only present the variation of micro-pop-in parameters for MA 1 ceramics. The same parameters for the MA3 and MA 5 ceramics are not shown here for the sake of brevity. The typical illustrative examples of

difference between two critical load (ΔL_{cj}) and corresponding difference between two critical depth (Δd_{cj}) for two consecutive (i.e., the j^{th} and the $j+1^{\text{th}}$) nanoscale plasticity events to occur in the MA1 ceramics are depicted in Fig. 2(b). Similar observations are also reported by us and by others in the case of alumina ceramics, alumina based nanoceramic composites and metallic glass samples⁶⁻¹³.

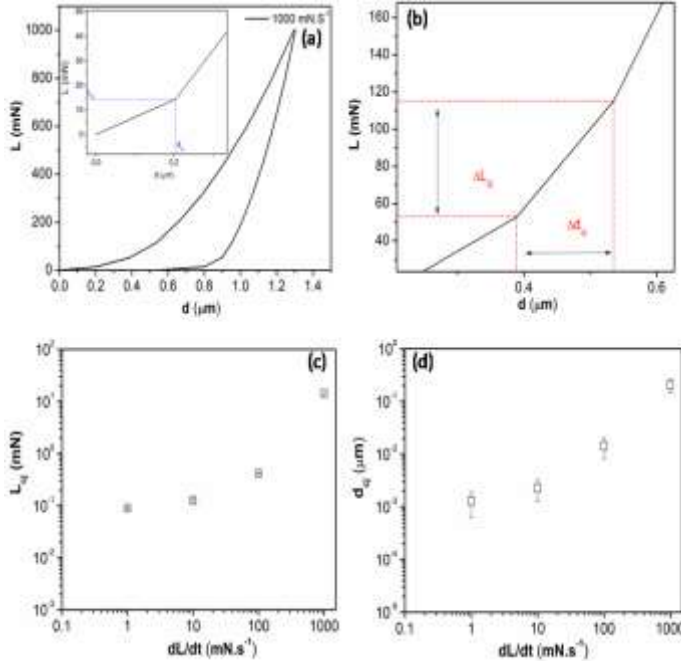


Figure 2. (a) The typical $L-d$ plot at loading rate 1000 mN.s^{-1} for the MA 1 ceramics. The inset shows the occurrences of (L_{cj}) and (d_{cj}) (b) Exploded view of typical $P-h$ plot showing micro pop-in events, at loading rate 1000 mN.s^{-1} for MA 1 ceramics. Variations of (c) L_{cj} and (d) corresponding (d_{cj}) on (dL / dt) for the MA 1 ceramics.

3.2.1 Micro-pop-in Related Parameters: The variations of micro-pop-in related parameters i.e. L_{cj} , d_{cj} , ΔL_{cj} , Δd_{cj} as a function of loading rate are respectively shown in Fig. 2(c, d) and Fig. 3(a, b) for the MA1 ceramics. It is found that all these parameters (i.e., L_{cj} , d_{cj} , ΔL_{cj} , Δd_{cj}) enhance with the loading rates. As L_{cj} enhances with the loading rate that means MA ceramics have intrinsic ability to increase their own resistance against

contact induced deformation at the nanoscale range. In other words it has the interesting ability to adjust to the change in energy transfer rate from the loading train and accordingly also enhance its own intrinsic resistance against contact induced deformation at the nanoscale.

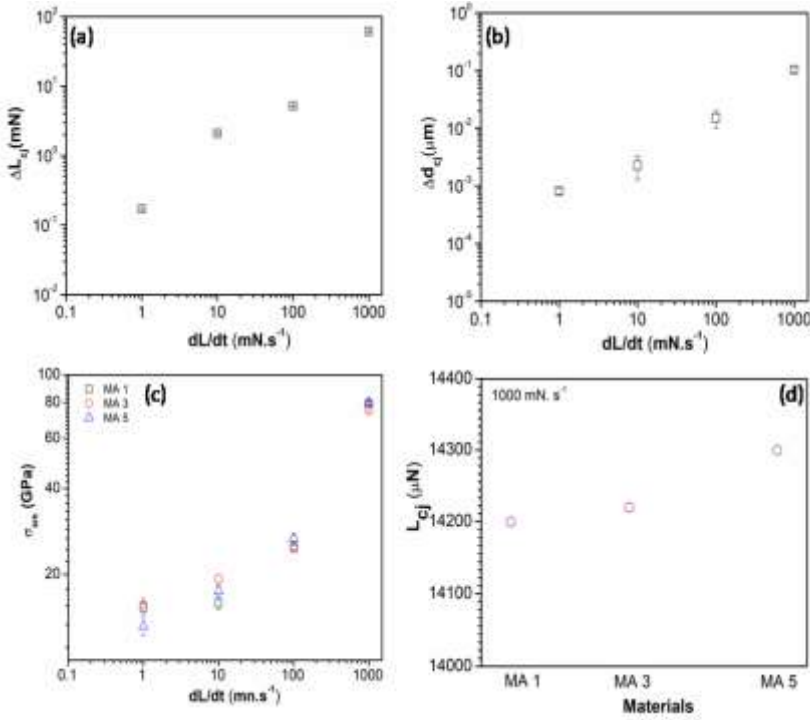


Figure 3. Variations of (a) ΔL_{cj} and (b) Δd_{cj} on (dL/dt) for the MA 1 ceramics (c) Variations of σ_{sm} on loading rates for MA 1, MA 3 and MA 5 ceramics. (d) The variations of critical load (L_{cj}) with the amount of MgO as a sintering aid in alumina ceramics for the applied loading rate of 1000 mN.s⁻¹.

3.3 The Role of Shear Stress in Micro-pop-in: From the loading rate dependent micro-pop-in parameters in MA ceramics, the magnitudes of σ_{sm} (~15-80 GPa for MA1 (Fig. 3c), 15-75 GPa for MA3 (Fig. 3c) and 13-75 GPa for MA5 ceramics (Fig. 3c)) are found to be much higher than the corresponding theoretical shear strength of MA ceramics ($\sigma_{theo\ MA}$) of ~ 2.82, 2.96 and 3.11 GPa, respectively. $\sigma_{theo\ MA}$ is evaluated through the usage of the rule of mixtures where $\sigma_{theo\ Al_2O_3}$ and $\sigma_{theo\ MgO}$ are assumed as ~2.75¹⁷ and 10 GPa¹⁸, respectively. Therefore, as σ_{sm} is » $\sigma_{theo\ MA}$ for all the MA ceramics, so probability of more dislocation nucleation inside the nanoindentation cavity is very much enhanced. These considerations

suggest that shear stress induced highly localized deformation is connected to the genesis of micro-pop-in events and hence, nanoscale plasticity events in the MA1, MA 3 and MA5 ceramics^{6,7,8,13}.

3.4 The Role of Sintering Aid: The critical loads (L_{cj}) required to initiate nanoscale plasticity events in the MA1, MA3 and MA5 ceramics also increase with the increase in the magnitude of loading rate, Fig. 3(c). This information conveys that all these MgO doped alumina ceramics can enhance their nanoscale contact deformation resistance as the rate of externally supplied energy is enhanced.

Further, for a particular loading rate of e.g., 1000 mN.s^{-1} , the magnitude of critical loads (L_{cj}), required to initiate nanoscale plasticity events, increases with the increase in the amount of the sintering aid. It may be recalled in this connection that the amount of MgO sintering aid is varied from 1wt.% in MA1 to 3 wt.% in MA3 to 5 wt.% in MA5 ceramics (Fig. 3d). Similar experimental data were also recorded for lower loading rates. However, the variations of L_{cj} with sintering aid at low loading rates are not shown here for the sake of brevity. It reveals that the trend of enhancement of L_{cj} with the increase in sintering aid is valid in the whole experimental regime of applied loading rate. It is quite likely that MgO sintering aid may go into solid solution during the sintering process forming the spinel phase, Fig. 1(a). Thus, there would be more of the spinel phase formation as the amount of MgO used as sintering aid is enhanced. The more is the amount of spinel phase the higher is the amount of lattice strain as the crystallite size goes down from about 130 nm in the MA1 to about 80 nm in the MA 5 ceramics¹⁹.

4. Conclusions

The major conclusions of the present research are:

- (i) The present work achieves the very first systematic study of the roles of MgO as sintering aid and nanoscale plasticity i.e., micro-pop-in in pressureless sintered alumina ceramics i.e., the MA ceramics (e.g., MA1, MA3 and MA5 sintered with respectively 1, 3 and 5 wt.% of MgO used as sintering aid).
- (ii) The nanohardness (H_{Ex}) of MA ceramics shows an increasing trend with the loading rate .
- (iii) The maximum shear stress plays a significant role in micro-pop-in in loading rate ($1\text{-}1000 \text{ mN.s}^{-1}$) controlled nanoindentation experiments

of the MA ceramics.

- (iv) Intrinsic contact deformation resistance increases with the amount of sintering aids in MA ceramics.

Acknowledgements: All authors are grateful to the Director, CSIR-Central Glass and Ceramic Research Institute, Kolkata 700032, India for his kind permission to publish this paper. Author AKM thanks Manipal University Jaipur for continued support. Finally, Ms. Payel Maiti acknowledge DST INSPIRE fellowship scheme of DST, GOI for financial support (Grant no. DST/INSPIRE Fellowship/2016/IF160102).

References

1. H. Li, Y. Liu, Y. Liu, Q. Zeng, K. Hu, Z. Lu and J. Liang, Effect of Debinding Temperature under an Argon Atmosphere on the Microstructure and Properties of 3D-Printed Alumina Ceramics, *Mater. Charact.*, **168** (2020), 110548.
2. M. Moula, S. Meille, V. L. Corre and J. Chevalier, Mechanical Characterization of Meso-Porous Alumina by Micro- and Nanoindentation, *Mater. Today Commun.*, **25** (2020), 101315.
3. A. Zaborowska, Ł. Kurpaska, E. Wyszowska, M. Clozel, M. Vanazzi, F. Di Fonzo, M. Turek, I. Jóźwik, A. Kosiński and J. Jagielski, Influence of Ion Irradiation on the Nanomechanical Properties of Thin Alumina Coatings Deposited on 316L SS By PLD, *Surf. Coat. Technol.*, **386** (2020), 125491.
4. R. Barkallah, R. Taktak, N. Guermazi, K. Elleuch and J. bouaziz, Mechanical Properties and Wear Behaviour of Alumina/Tricalcium Phosphate/Titania Ceramics as Coating for Orthopedic Implant, *Eng. Fract. Mech.*, (2020), <https://doi.org/10.1016/j.engfractmech.2020.107399>.
5. J. Gong, B. Deng, H. Qiu and D. Jiang, Description of the Nanoindentation Unloading Curves with a Universal Function: Theoretical Consideration and Applications to Brittle Materials, *Mater. Chem. Phys.*, **251** (2020), 123165.
6. M. Bhattacharya, R. Chakraborty, A. Dey, A. K. Mandal and A. K. Mukhopadhyay, New Observations in Micro-pop-in Issues in Nanoindentation of Coarse Grain Alumina, *Ceram. Int.*, **39** (2013), 999-1009.
7. M. Bhattacharya, A. Dey and A. K. Mukhopadhyay, Self-Adjusting Unique Nanoscale Contact Resistance of a Single Alumina Grain, *Mater. Res. Express*, **3** (2016), 045017-34.
8. M. Bhattacharya, A. Dey and A. K. Mukhopadhyay, Influence of Loading Rate on Nanohardness of Sapphire, *Ceram. Int.*, **42** (2016), 13378-13386.
9. P. Maiti, M. Bhattacharya, P. S. Das, J. Ghosh and A. K. Mukhopadhyay, A Critical Note on Nanoscale Plasticity in 20 ZTA Ceramics, *Ceram. Int.*, **45** (2019), 25034-25043.

10. P. Maiti, A. Eqbal, M. Bhattacharya, P. S. Das, J. Ghosh and A. K. Mukhopadhyay, Micro pop-in Issues in Nanoindentation Behaviour of 10 ZTA Ceramics, *Ceram. Int.*, **45** (2019), 8204-8215.
11. P. Maiti, J. Ghosh and A. K. Mukhopadhyay, New Observations and Critical Assessments of Incipient Plasticity Events and Indentation Size Effect in Nanoindentation of Ceramic Nanocomposites, *Ceram. Int.*, **46** (2020), 3144-3165.
12. W. C. Oliver and G. M. Pharr, Measurement of Hardness and Elastic Modulus by Instrumented Indentation: Advances in Understanding and Refinements to Methodology, *J. Mater. Res.*, **19** (2004), 3-20.
13. C. E. Packard and C. A. Schuh, Initiation of Shear Bands Near a Stress Concentration in Metallic Glass, *Acta Mater.*, **55** (2007), 5348-5358.
14. A. Krell and S. Scha'dlich, Nanoindentation Hardness of Submicrometer Alumina Ceramics, *Mater. Sci. Eng.*, **A 307** (2001), 172-181
15. A. D. Norton, S. Falco, N. Young, J. Severs and R. I. Todd, Microcantilever Investigation of Fracture Toughness and Subcriticalcrack Growth on the Scale of the Microstructure in Al_2O_3 , *J. Euro. Ceram. Soc.*, **35** (2015), 4521-4533.
16. P. C. Twigg, F. L. Riley and S. G. Roberts, Nanoindentation Investigation of Micro-Fracture Wear Mechanisms in Polycrystalline Alumina, *J. Mater. Sci.*, **37** (2002), 845-853.
17. T. F. Page, W. C. Oliver and C. J. McHargue, The Deformation Behavior of Ceramic Crystals Subjected to Very Low Load (Nano) Indentations, *J. Mater. Res.*, **7** (1992), 450-473.
18. T. S. Duffy, R. J. Hemley and H. K. Mao, Equation of State and Shear Strength at Multimegabar Pressures: Magnesium Oxide to 227 Gpa, *Phys. Rev. Lett.*, **74** (1995), 1371-1374.
19. P. Maiti, J. Ghosh and A. K. Mukhopadhyay, Modelling of Nanoindentation Behaviour in Mgo Doped Alumina, *Ceram. Int.*, (2020), <https://doi.org/10.1016/j.ceramint.2020.12.033>.