

Room temperature strain rate sensitivity in precursor derived HfO₂/Si-C-N(O) ceramic nanocomposites

Cite as: AIP Advances 4, 017129 (2014); <https://doi.org/10.1063/1.4863537>

Submitted: 08 December 2013 • Accepted: 13 January 2014 • Published Online: 23 January 2014

Ravindran Sujith and Ravi Kumar



View Online



Export Citation



CrossMark

ARTICLES YOU MAY BE INTERESTED IN

[Epitaxial growth of \$\gamma\$ -Al₂O₃ on Ti₂AlC\(0001\) by reactive high-power impulse magnetron sputtering](#)

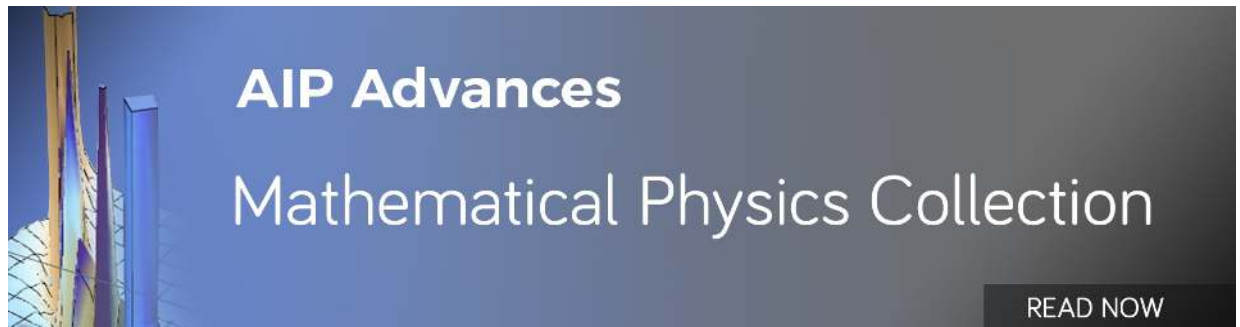
AIP Advances 4, 017138 (2014); <https://doi.org/10.1063/1.4863560>

[Calculation of self-diffusion coefficients in iron](#)

AIP Advances 4, 017128 (2014); <https://doi.org/10.1063/1.4863462>

[Dielectric and microwave attenuation properties of graphene nanoplatelet-epoxy composites](#)

AIP Advances 4, 017139 (2014); <https://doi.org/10.1063/1.4863687>



Room temperature strain rate sensitivity in precursor derived HfO₂/Si-C-N(O) ceramic nanocomposites

Ravindran Sujith and Ravi Kumar^a

Materials Processing Section, Department of Metallurgical & Materials Engineering, Indian Institute of Technology Madras, Chennai-600036, India.

(Received 8 December 2013; accepted 13 January 2014; published online 23 January 2014)

Investigation on the room temperature strain rate sensitivity using depth sensing nanoindentation is carried out on precursor derived HfO₂/Si-C-N(O) ceramic nanocomposite sintered using pulsed electric current sintering. Using constant load method the strain rate sensitivity values are estimated. Lower strain rate sensitivity of $\sim 3.7 \times 10^{-3}$ is observed and the limited strain rate sensitivity of these ceramic nanocomposites is explained in terms of cluster model. It is concluded that presence of amorphous Si-C-N(O) clusters are responsible for the limited flowability in these ceramics. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4863537>]

Specific polymer derived ceramics (PDCs) exhibit excellent thermo-mechanical properties and significant oxidation and creep resistance.¹⁻³ Henceforth, these materials have been considered for various structural and functional applications in small scale appliances such as in micro-electro-mechanical-systems (MEMS) and in printed sub-100 nm structures.⁴⁻⁶ Therefore an understanding of the deformation mechanism at very small length scales is important. Recently, depth sensing nanoindentation technique is being used as an effective technique for the understanding of elasto-plastic behavior of PDCs at small length scales.⁷⁻⁹ Upon indentation these polymer derived ceramic (PDC) materials were observed to undergo plastic deformation owing to the large hydrostatic pressure under the indenter tip.¹⁰

During constant load holding segment a change in the indentation depth is commonly observed in most of the material systems, which is referred to as the indentation creep at room temperature. The effect of this indentation creep is to reduce the hardness value due to the increase in displacement occurring at the maximum load. Among the several methods^{11,12} suggested for the measurement of indentation creep, the model developed by Mayo *et al.*^{13,14} commonly known as constant load (CL) method, is extensively used for the understanding of indentation creep and estimation of the strain rate sensitivity. The advantage of this method is that the strain rate sensitivity can be determined from a single indentation.¹⁵ Besides a few studies on the plastic deformation of PDCs, the effect of time dependent deformation on PDCs are limited. For instance, investigation on the creep response of Si-C-N PDCs was reported by Janakiraman *et al.*¹⁶ Hence, for a comprehensive understanding of the influence of indentation creep, a detailed study was carried out by determining strain rate sensitivity in HfO₂/Si-C-N(O) ceramic nanocomposites.

The present study focuses on the determination of room temperature strain rate sensitivity of precursor derived ceramics by using a depth sensing nanoindentation technique. For this purpose HfO₂/Si-C-N(O) ceramic nanocomposites pulsed electric current sintered at two different temperatures (1400 and 1500 °C) were considered. The time dependent deformation mechanism is understood from the constant load holding segment and the values are compared with Si-O-C

^aCorresponding author, Tel: +91-44-22574757, Fax: +91-44-22574777, E-mail: nvrk@iitm.ac.in

ceramic also produced through the same route. The cluster model proposed by Ohkawara *et al.*¹⁷ was used to explain the difference in the estimated values with other PDCs.

HfO₂/Si-C-N(O) ceramic nanocomposites were synthesized by the thermolysis of hafnium alkoxide modified polysilazane at 1300 °C respectively for 2 h in Ar atmosphere. For comparison silicon oxycarbide ceramics were also synthesized and for this polyhydridomethylsiloxane was used as the starting precursor. Polyhydridomethylsiloxane, and hafnium n-butoxide were purchased from Sigma Aldrich, India whereas, polysilazane was purchased from Clariant, Germany. The detailed synthesis procedures of each of these materials were discussed elsewhere.^{18–20} The thermolysed ceramics were ground and sieved to fine powders of particle size less than 125 μm. Henceforth, the powder particles were sintered and pellets of ~ 20 mm diameter and ~ 4 mm thickness were produced using a pulsed electric current sintering machine (Sumitomo Coal Mining Co. Ltd, Japan). The sintering parameters were reported in Ref. 21. The pulsed electric current sintered Si-O-C at 1400 and 1500 °C will be hereafter referred to as SiOC1400 and SiOC1500 respectively, whereas Si-Hf-C-N(O) at 1400 and 1500 °C will be referred to as SiHfCNO1400 and SiHfCNO1500 respectively.

Nanoindentation studies were carried out using a Hysitron Triboindenter (USA) with a load and displacement resolution of 0.1 μN and 0.2 nm respectively at room temperature. A standard Berkovich indenter was used and the area function calibration was achieved by performing 25 indentations on fused silica supplied by the instrument manufacturer. Accordingly, the area function of the indenter used is given by Eq. (1)

$$A = 24.50h_c^2 - 1.0108e^5h_c + 1.1062e^7h_c^{1/2} - 1.3482e^8h_c^{1/4} + 3.7233e^8h_c^{1/8} - 2.5182e^8h_c^{1/16} \quad (1)$$

where, h_c is the maximum contact depth. Five indentations were taken at a constant load of 10 mN and the average values of strain rate sensitivity were reported for each of these ceramics. The loading and unloading rates were kept constant at 10 mN/s and a holding time of 10 s was maintained throughout.^{11,22}

Time dependent deformation of HfO₂/Si-C-N(O) ceramic nanocomposites ceramics were determined by monitoring the depth change as a function of holding time. The creep displacements (h) as a function of holding time (t) at a maximum load of 10 mN are exemplified in Fig. 1 and were deduced by taking the difference between incremental displacement occurring during the load holding time and initial displacement at the beginning of holding time. The starting points of holding time and displacement were aligned to zero to facilitate comparison between the values. From Fig. 2 it can be inferred that the rate of increase of creep displacement was higher initially (stage I) and finally a steady state was reached (stage II). Moreover, Si-O-C ceramics showed higher creep displacement in contrast to HfO₂/Si-C-N(O) ceramic nanocomposites. Since these ceramics were obtained by the solid state thermolysis of the polymeric precursor often an open structure is resulted. Though the reasons for the room temperature creep displacement are not very clear, the presence of open structure could be one of the possibility.

From the creep displacement, the room temperature strain rate sensitivity (m) was determined for these PDCs using the general flow equation modified for indentation deformation (Eq. (2)).

$$\frac{d\varepsilon}{dt} = kH^s \quad (2)$$

where, $d\varepsilon/dt$ is the strain rate, H is the hardness and s is the stress exponent. Eq. (2) was obtained by considering H in place of σ (uniaxial flow stress) in the general flow equation. Such an approximation is possible since as per Tabor's law,²³ $H \equiv 3\sigma$ and hence H and σ can be assumed to be linearly correlated. Henceforth, strain rate sensitivity was determined as per the expression, $s = 1/m$.

For the determination of $d\varepsilon/dt$, the $h-t$ plot was fitted as per Eq. (3).^{11,24}

$$\varepsilon = h_{t0} + at + bt^c \quad (3)$$

where, h_{t0} is the initial displacement at $t = 0$ s and a , b , c are the fitting constants. Upon fitting correlation coefficients of ~0.98 was obtained. Subsequently, $d\varepsilon/dt$ was determined as per Eq. (4)

$$\frac{d\varepsilon}{dt} = \frac{1}{h} \frac{dh}{dt} \quad (4)$$

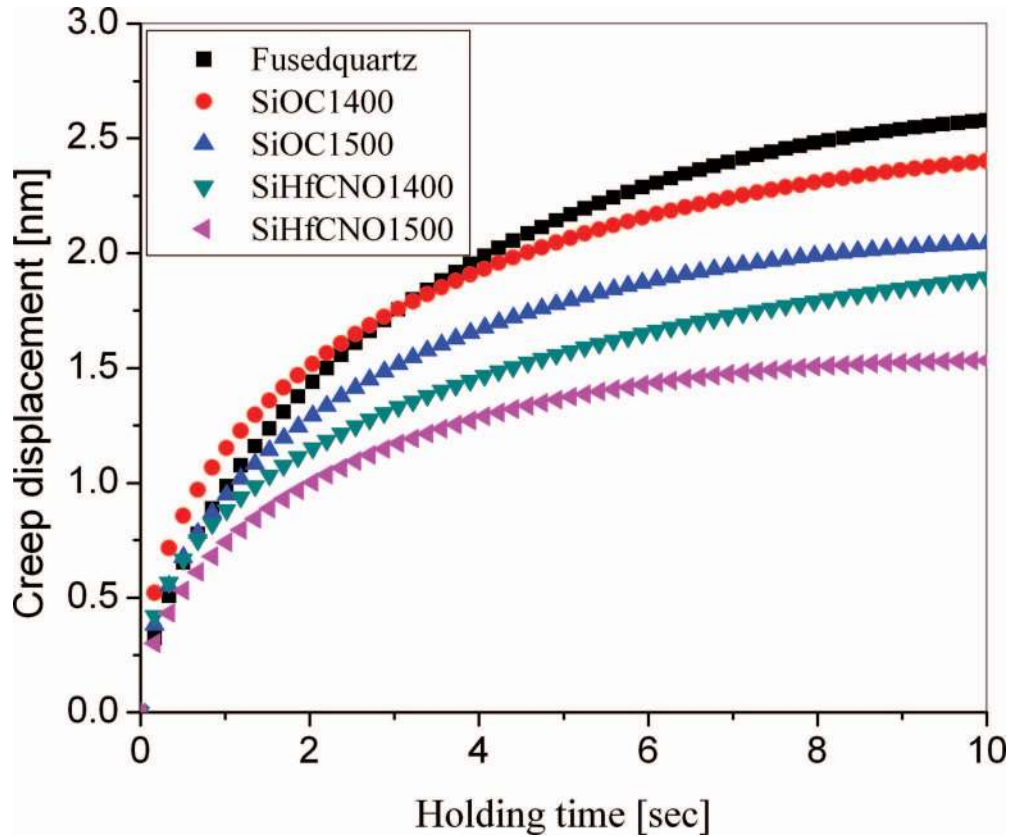


FIG. 1. Representative fitted creep displacements with load holding time for the Si-O-C and HfO₂/Si-C-N(O) ceramics.

where, h is the displacement during the constant load period. Fig. 2 shows the variation in creep rate with holding time for these PDCs. In all the cases, for the initial periods of load holding time the strain rates were found to be higher which tend to asymptotically reach a steady state of $d\epsilon/dt < 0.003/s$. For the determination of strain rate sensitivity the procedure as suggested in Ref. 11 was adopted. The new contact depths with increase in holding time were determined as per Eq. (5)²⁵

$$(h_c)_{t_{hold}=t} = (h_{max})_{t_{hold}=t} \left[\frac{(h_c)_{t_{hold}=0}}{(h_{max})_{t_{hold}=0}} \right] \quad (5)$$

From the contact depths, the new contact areas were calculated using Eq. (1). Accordingly the hardness during the holding time was calculated as $H = P_{max}/A_c$, where A_c is the new contact areas. The variation in strain rate with hardness is plotted as a double logarithmic plot (Figs. 3(a)–3(d)) and from the instantaneous slope derived from the linear portion of this plot (stage 2) the steady state stress exponent was determined as per Eq. (2). Finally, the corresponding strain rate sensitivity values were determined.

The room temperature strain rate sensitivity values for these PDCs are provided in Table I and it can be inferred that strain rate sensitivity of HfO₂/Si-C-N(O) ceramics was $\sim 3.7 \times 10^{-3}$. However, for Si-O-C ceramics the strain rate sensitivity at comparable loads were observed to be marginally lower ($m = 5.4 \times 10^{-3}$). Janakiraman *et al.* have done a similar study on SiCN PDCs produced by cast route and the strain rate sensitivity values were observed to range between $\sim 2 \times 10^{-3}$ and 8×10^{-3} . The lowest was observed for amorphous SiCN ceramic and the value progressively increased with phase separation. Conversely, in contrast to these PDCs strain rate sensitivity of fused quartz ($\sim 31 \times 10^{-3}$)²⁶ and soda lime glass were reported to be much higher ($\geq 20 \times 10^{-3}$).²⁷ This difference could be attributed to the presence of stiffer Si-C bonds for both the ceramics. However,

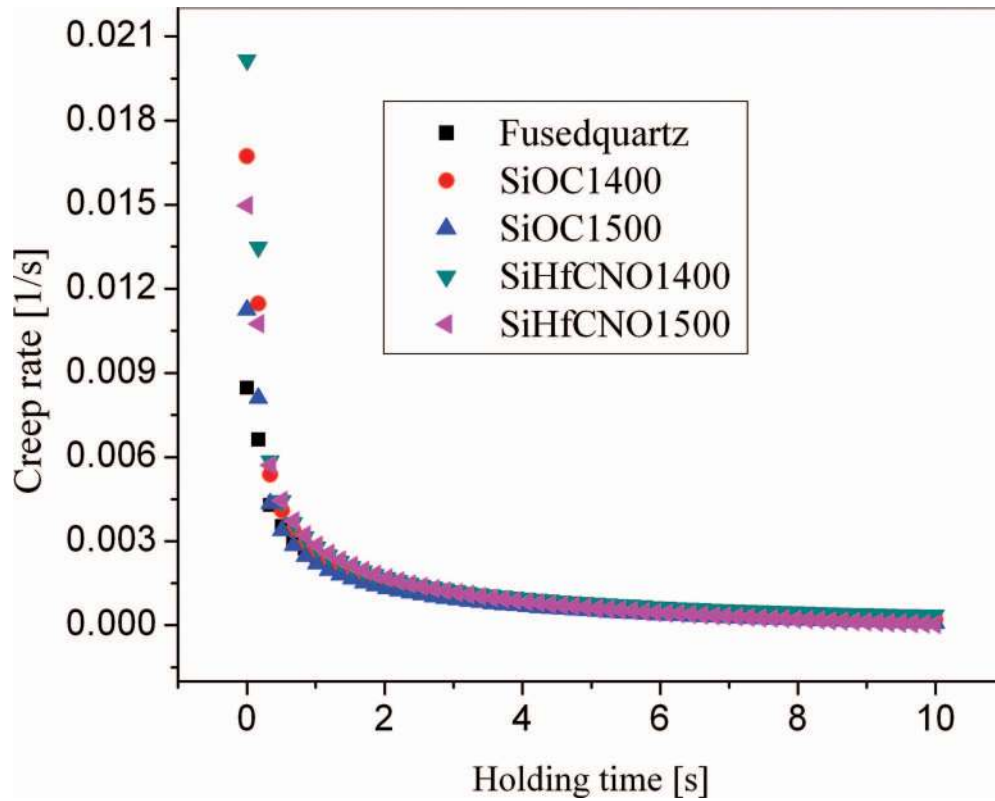


FIG. 2. Evolution of creep rate with holding time for Si-O-C and HfO₂/Si-C-N(O) ceramics.

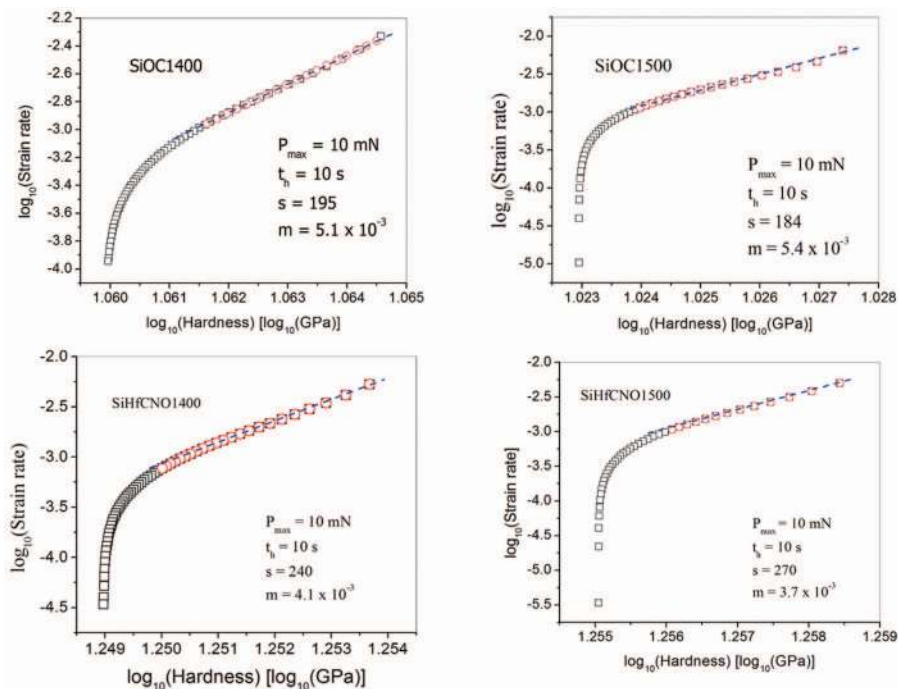
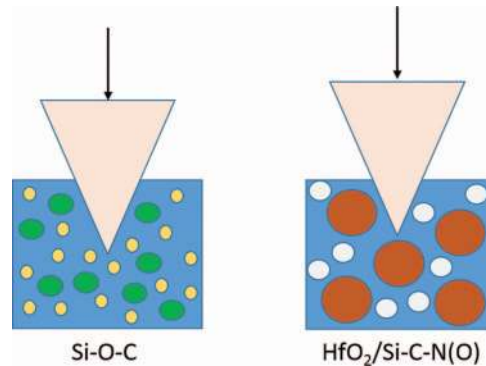


FIG. 3. Double logarithmic plot showing the variation in creep rate with hardness for Si-O-C and HfO₂/Si-C-N(O) ceramics.

TABLE I. Room temperature strain rate sensitivity of PDCs produced by pulsed electric current sintering technique.

Material system	SiOC1400	SiOC1500	SiHfCNO1400	SiHfCNO1500
Strain rate sensitivity (m)	0.0051	0.0054	0.0041	0.0037

FIG. 4. Schematic showing the effect of difference in the type of clusters of Si-O-C and HfO₂/Si-C-N(O) on the flowability.

close correlation in the flowability behavior was observed with that of amorphous hydrogenated carbonitride films.¹⁷

The flow behaviour of these materials can be understood in terms of the cluster model proposed by Ohkawara *et al.*¹⁷ The cluster model was initially proposed for hydrogenated SiC ceramics wherein successive dehydrogenation from the initial structure will result in a material with large collection of clusters. As the number density of the clusters increases, the flowability also improves because of the increase in the freedom of the movement of these clusters. The structure of HfO₂/Si-C-N(O) ceramic nanocomposites consists of hafnia nanocrystallites of crystallite size ranging between 15 and 20 nm dispersed in an amorphous matrix of Si-C-N(O) matrix. The schematic of the structure of HfO₂/Si-C-N(O) ceramic nanocomposite is shown in Fig. 4 and the X-ray diffractogram of the same is provided in Fig. 3 of Ref. 21. The existence of amorphous matrix of Si-C-N(O) explains the limited flowability observed in HfO₂/Si-C-N(O) ceramic nanocomposites even though the phase separation has occurred. In contrast, Si-O-C ceramics have slightly higher strain rate sensitivity value. In Si-O-C ceramics, the clusters after phase separation are made of Si-C and Si-O of crystallite size ranging between 3 and 5 nm (Please see Fig. 1 of Ref. 20). The presence of these flexible Si-O clusters in contrast to stiffer covalent bonds of Si-C and Si-N in amorphous Si-C-N have resulted in the higher strain rate sensitivity of Si-O-C PDCs. In addition, the reason for the lower strain rate sensitivity of SiHfCNO1500 in comparison to SiHfCNO1400 can be explained in terms of the difference in the type of the clusters of hafnia. SiHfCNO1400 consists of only tetragonal hafnia, whereas SiHfCNO1500 consists of both monoclinic and tetragonal hafnia (Fig. 3 of Ref. 21). While undergoing phase transformation from tetragonal to monoclinic hafnia volume expansion is experienced and this accounts to the limited flowability of SiHfCNO1500.

In summary, indentation creep behaviour was observed in HfO₂/Si-C-N(O) ceramic nanocomposites and the creep displacement was lower for HfO₂/Si-C-N(O) ceramic nanocomposites in contrast to Si-O-C ceramics at similar loads. Using the constant load method, the room temperature strain rate sensitivity values for these PDCs were determined. The cluster model was used to explain the limited strain rate sensitivity observed in HfO₂/Si-C-N(O) nanocomposites. Moreover, the presence of stiffer bonds in the nanocomposite was also considered as the reason for the limited flowability.

¹ R. Riedel, G. Mera, R. Hauser, and A. Klönczynski, *J. Ceram. Soc. Jpn.* **114**, 425–44 (2006).

² P. Colombo, G. Mera, R. Riedel, and G. D. Soraru, *J. Am. Ceram. Soc.* **93**, 1805–37 (2010).

³ K. Terauds, D. B. Marshall, and R. Raj, *J. Am. Ceram. Soc.* **96**, 1278–84 (2013).

⁴ M. Schulz, *Adv. Appl. Ceram.* **108**, 454–60 (2009).

- ⁵ Y. Liu, L.-A. Liew, R. Luo, L. An, M. Dunn, V. M. Bright, J. W. Daily, and R. Raj, *Sens. Act. A* **95**, 143–51 (2002).
- ⁶ B. Duong, P. Gangopadhyay, J. Brent, S. Seraphin, R. O. Loutfy, N. Peyghambarian, and J. Thomas, *Appl. Mater. Interfaces* **5**, 3894–99 (2013).
- ⁷ Y. T. Cheng and C. M. Cheng, *Mater. Sci. Eng. R* **44**, 91–149 (2004).
- ⁸ B. Bhushan and X. Li, *Int. Mater. Rev.* **48**, 125–164 (2003).
- ⁹ J. Alkorta, J. M. Martínez-Esnaola, and J. G. Sevilano, *Acta Mater.* **56**, 884–93 (2008).
- ¹⁰ M. Rodríguez, J. M. Molina-Aldareguía, C. González, and J. LLorca, *Acta Mater.* **60**, 3953–64 (2012).
- ¹¹ M. J. Mayo and W. D. Nix, *Acta Metall.* **36**, 2183–92 (1988).
- ¹² B. N. Lucas and W. C. Oliver, *Metall. Mater. Trans. A* **30**, 601–10 (1999).
- ¹³ M. J. Mayo, R. W. Siegel, A. Narayanasamy, and W. D. Nix, *J. Mater. Res.* **5**, 1073–1082 (1990).
- ¹⁴ M. J. Mayo, R. W. Siegel, Y. X. Liao, and W. D. Nix, *J. Mater. Res.* **7**, 973–979 (1992).
- ¹⁵ D. Peykov, E. Martin, R. R. Chromik, R. Gauvin, and M. Trudeau, *J. Mater. Sci.* (2012).
- ¹⁶ N. Janakiraman, and F. Aldinger, *J. Am. Ceram. Soc.* **93**, 821–9 (2010).
- ¹⁷ Y. Ohkawara, S. Ohshio, T. Suzuki, H. Ito, K. Yatsui, and H. Saitoh, *Jpn. J. Appl. Phys.* **40**, 7007–12 (2001).
- ¹⁸ R. Sujith, A. B. Kousaalya, and R. Kumar, *Ceram. Internl.* **38**, 1227–33 (2012).
- ¹⁹ B. Papendorf, K. Nonnenmacher, E. Ionescu, H. J. Kleebe, and R. Riedel, *Small* **7**, 970–8 (2011).
- ²⁰ R. Sujith, N. Srinivasan, and R. Kumar, *Adv. Eng. Mater.* (2013).
- ²¹ R. Sujith and R. Kumar, *Ceram. Internl.* **39**, 9743–7 (2013).
- ²² T. Chudoba and F. Richter, *Surf. Coat. Technol.* **148**, 191–8 (2001).
- ²³ D. Tabor, *Hardness of metals* (Oxford: Clarendon Press; 1951).
- ²⁴ D. Peykov, E. Martin, R. R. Chromik, R. Gauvin, and M. Trudeau, *J. Mater. Sci.* **47**, 7189–200 (2012).
- ²⁵ D. Ma, C. W. Ong, and T. Zhang, *J. Mater. Res.* **23**, 2106–15 (2008).
- ²⁶ H. Li and A. H. W. Ngan, *J. Mater. Res.* **19**, 513–22 (2004).
- ²⁷ N. M. Keulen, *J. Am. Ceram. Soc.* **76**, 904–12 (1993).