

Deformation – Entropy Metrics in Si-C-N Hard Coats

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Research Article

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Abstract

Distorted indented geometries are representations of dissipation of localized locked-in stress on the hard coating surface. The distortions in most occasions manifest themselves in different ways in the load-depth (P-h) plots of nanoindentation like Pop-ins, pop-outs and linear unloads. Fracture Mechanical principles applied to those sections provide quantitative fracture parameters like Fracture toughness. As energy is involved in the dissipation, an alternative approach to harness the mechanism involved in the asymmetrical distortions of the indented zones in **Si-C-N** coatings was established. Novel concepts like entropy mediated energy dissipation, stress localization, non linear stress redistribution and a transition occurring from a stable energy accommodation to instability driven delamination were explored on the basis of some new parameters like entropy dissipation coefficient (S_d), stress gradient (Λs), nonlinear instability function (Φ_n), deformation, and strain accommodating parameter (Γ_p) which could provide a more accountable explanation on the distortion occurring in the indent shape than conventional thin film fracture mechanics.

1. Introduction

Hard nanocomposite coatings provide protection through their heterogeneous morphology involving nanocrystalline and amorphous phases. They are mostly based on Ti-, B-, Si, Al- and C- containing systems. Apart from high hardness, the coatings also have high toughness, low friction, thermal stability are used in versatile applications like cutting tools, biomedical implants, automobile sector, aerospace and even microelectronic and MEMS applications [1].

Polymer derived Silicon Carbon Nitride (Si-C-N) coatings have high thermal stability, chemical inertness, oxidation reaction and ability to sustain harsh mechanical stimulus. SiCN in the form of coatings find applications in MEMS base devices in unfavorable climatic conditions. Due to their heterogeneous morphology comprising of amorphous, nanocrystalline and clustered crystallite regimes, a collective influence causing redistribution of the indentation induced stress [2].

Hardness, fracture toughness (K_{IC}), crack propagation and interfacial delamination have been addressed previously for Si-C-N coatings. A deeper insight takes into consideration the stress distribution, localized shear transport, dissipative strain evolution, and hydrostatic confinement [3–6]. Conventional fracture mechanics is therefore not sufficient to explain the asymmetry arising in the indented zones and an alternate perspective of entropy assisted deformation evolution, where indentation is considered to be the non linear redistribution of energies through competing pathways involving localized plasticity, instability nucleation, shear localization and metastable stress confinement [7]. The pop-in events during the indentation process were linked to localized energy dissipation and dislocation mediated plasticity, dislocation nucleation, their multiplication and migration analogous to the localized energy bursts [8]

The distorted indentation geometries are therefore as topological manifestation of dissipative stress evolution. To quantify this behaviour, a new set of thermodynamic (entropy) based descriptors were

introduced and validated.

2. Materials and Methods

Ti-B-Si-C(N) and Si-C-N coatings were deposited on Si substrates by magnetron sputtering (HINDHIVAC, Bangalore) using a sintered SiC and TiB₂ target and nitrogen/Argon gas. The chamber was first evacuated using diffusion pump to a pressure of 10^{-6} mbar. The 2 inch diameter SiC and TiB₂ target acts as the cathode to which initially Ar gas introduced to cause ad-atoms getting ejected out from the surface ; and the N₂ gas in different proportions to cause reactive sputtering forming the TiBSiC and SiCN coating on pre-positioned Si(100) substrates in the line of sight. The coatings were found to have hardness between **12–22 GPa** with varied deposition conditions forming different contrasts of hard phases viz TiB₂, CN_x, SiC, SiN_x, CN_x and even Diamond like nanocomposites(**DLN**) forming useful for many engineering applications [3–6, 9].

Although nanoindentation is the preferred choice for the mechanical characterization of thin films, the hard operating conditions depend on the testing of the coatings under higher loads, for Si-C-N and Ti-B-Si-C coatings is a pragmatic alternative to nanoindentation as it reveals qualitative and quantitative aspects to the cases where external stimulus gets applied at macro/microscopic scale. The workflow presented here is micro indentation by Vickers indenter backed by hydrostatic stress evolution, strain gradient assisted deformation and localized instability arised in the proximity of the indented region. Three dimensional finite element analysis is used to study the indentation process.

3. Results

3.1 Nanoindentation

The nanoindentation profiles showing a maximum load of 0.65 mN (P_{max}) required to achieve a depth of 50 nm (h_{max}) can be seen in the loading portion of the P h plot (Fig. 1a) Using the empirical relation of hardness, i.e $H = P_{max} / \text{Contact area (Ac)}$ and perfect Berkovich geometry ($Ac = 24.5 h^2$), the Hardness came out as close to 11 GPa. The contact depth (h_c) was taken as being equal to the maximum depth (h_{max}). The Oliver and Pharr method, however takes into consideration the elastic recovery as well and hence the contact depth is calculated as $h_c = h_{max} - \epsilon P_{max} / S$, where S is the unloading stiffness which can be estimated from the plot as being equal to 0.039 mN/nm and ϵ (≈ 0.75) is a constant based on the indenter geometry. The contact depth therefore reduces from 50 nm to 41 nm making the hardness about 15.GPa (Fig. 1b) The reduced modulus ($E_r = \sqrt{\pi/2} \beta. S / \sqrt{Ac}$ where $\beta = 1.034$ for Berkovich indenter), modulus of diamond ($E_i = 1140$ GPa), its Poisson ratio ($\nu_i = 0.07$) as well as that of the sample material SiCN ($\nu = 0.25$) were used to determine its elastic modulus ($E \approx 170$ GPa) (Fig. 1b) [10] as per the relation $1/E_r = (1 - \nu^2)/E + (1 - \nu_i^2)/ E_i$. [11, 12] (Table 1)

Table 1
Nanoindentation and Mechanical Properties

Parameter	Symbol	Value	Unit
Maximum load (nanoindentation)	$P_{\max}$	0.65	mN
Maximum depth	$h_{\max}$	50	nm
Contact area (Berkovich)	A_c	$24.5 h^2$	-
Hardness (ideal, $h_c = h_{\max}$)	H	~ 11	GPa
Unloading stiffness	S	0.039	mN/nm
Indenter constant	ϵ	≈ 0.75	-
Contact depth (Oliver & Pharr)	h_c	41	nm
Hardness (Oliver & Pharr)	H	$\sim 15.5 (= 15)$	GPa
Berkovich correction factor	β	1.034	-
Diamond modulus	E_i	1140	GPa
Diamond Poisson ratio	ν_i	0.07	-
Si-C-N Poisson ratio	ν	0.25	-
Elastic modulus (Si-C-N)	E	~ 170	GPa
H/E ratio	H/E	0.09	-
Modulus saturation depth	-	~ 20	nm
Coating hardness range (deposition)	H	12–22	GPa

The H/E ratio is the elastic strain ($\epsilon_{\text{elastic}}$) limit lie how much the material can get strained before failing and there is usually lower in case of brittle ceramics compared to metals. Talking of wear especially when protective coatings like DLC, nitrides, HEAs and nanocomposite like in this case of Si-C-N, the H/E corresponds to resistance being imposed on sliding loads and an increased value suggests better resistance to plastic deformation, improved scratch resistance, lower frictional damage and better tribological performance.

The ability to redistribute stress elastically near contact is also determined by the H/E ratio and it can be said the crack initiation, shear localization gets suppressed if the ratio increases and catastrophic indentation failure can be avoided. The typical H/E values range between 0.03–0.06 for brittle ceramics 0.06–0.10 for nitrides and 0.1–0.15 for DLC coatings. A value of 0.09 obtained in this case of Si-C-N shows the nanocomposite nature where multiple phases act in a synergistic manner creating improved coating durability.

The modulus got saturated around 20 nm while the hardness showed an increasing trend. As E is mainly associated with bond stiffness and not on indentation depth. The E value attains saturation around 20 nm as elastic responses are likely to get stabilized earlier. The hardness however followed an opposite trend. Hardness being a depth dependent property undergoes stiffening which can occur in an amorphous – near amorphous (nanocrystalline) morphology typical in Si-C-N coatings.

The unloading portion is non-ideal with an extended linear region mild asymmetry caused by localized shear accommodation. The increasing Hardness due to densification as discussed above can lead to constrained flow zones causing distortions. Although there is no major catastrophic discontinuities present, the large difference between $h_{\max}$ and h_f suggests high elastic recovery, non uniform stress distribution causing a distorted residual indent geometry

3.2 Deformation and topology evolution

Indentation morphologies were found asymmetric in certain cases, with localized uplifted regions, stress channeling zones, shear assisted deformation corridors, and instability nucleation pockets. The deformation morphology in addition to radial cracking showed multiple interacting stress redistribution pathways. At lower loads (< 0.5 kgf) the coatings exhibited stable energy accommodation characterized by smooth pile up and distributed stress diffusion. Increasing the loads beyond 1 kgf, deformation topology evolved towards instability driven edge delamination and mesoscale stress collapse regions. These regions represent transition from distributed energy accommodation towards localized entropy concentration. This forms adiabatic shear leading to temporary viscoelastic reduction and enhanced plasticity

A representative simulated load-depth (**P-h**) plot for Si-C-N coatings under Berkovich nanoindentation showing the loading and unloading branches are given in Fig. 2a. The loading part follows the parabolic Oliver-Pharr relationship $P = Ch^2$ while the unloading part follows a Power Law $P = A(h - h_f)^m$ where $m = 1.35$ as per elastic-plastic contact mechanics of ceramic coatings. The shaded region represents the total energy dissipated which includes both plastic deformation and viscoplastic flow. Upon complete unloading, a residual depth of **$h_f = 120$ nm** can be seen which corresponds to about **85%** elastic recovery. As the maximum penetration depth of 800 nm was achieved for a maximum load of 500mN. This high percentage of elastic strain recovery is common for hard ceramic nanocomposite coatings [13]

In the absence of any pop-in events, the loading curve exhibits smooth continuous displacement with no abrupt strain bursts. This is an idealized response representing an idealized response where deformation is due to distributed dislocation nucleation and diffused shear band propagation. However the actual indentation response involves discontinuities (or pop-ins) which are more likely to occur due to the heterogeneity in the morphology of Si-C-N coatings. Stiffness $S = dP/dh$ derived from the unloading portion is used in estimating the elastic modulus.

Figure 2b illustrates the simulated and experimental pop-In events interpreted as local energy bursts (with Fig. 2c - e showing optical images of indented regions with increasing depth of penetration) and

are basically sudden displacement jumps at a nominally constant load attributed to the cooperative rearrangement of nanocrystalline clusters within the amorphous matrix. The magnitude of the displacement (2–5 nm) can be correlated with the nanocrystallites as observed in the TEM image (Fig. 3). The size distribution of the crystallites gives an average diameter of ~ 7 nm. The nanoscale structural heterogeneity influences the local stress distribution and strain accommodation during the indentation process. The variations in size, spacing and matrix constraint may affect the localization of deformation, the onset of displacement burst and transition from stable energy accommodation to damage initiation.

These above mentioned affects arising out of heterogeneity in crystal growth gets reflected through the set of parameters discussed below. A study of the crystalline nature of the observed features and quantitative correlation with the indentation responses are necessary before assigning specific deformation mechanism to them

3.2 Entropy Dissipation analysis

To quantify non linear deformation evolution, the entropy dissipation coefficient (S_d) was introduced as given in **Eq. 1a** where W_p represents the plastic work, A_c is the projected contact area, T is the temperature, σ_h is the hydrostatic stress and σ_y is the yield stress. Higher values of S_d therefore means enhanced dissipative plastic accommodation and distributed stress relation. Lower values on the other hand account for the generation of concentrated instability and localized stress rampage.

$$S_d = (W_p / A_c T) \ln (1 + \sigma_h / \sigma_y) \quad (1a)$$

$$S_d = \int (\sigma_{ij} \dot{\epsilon}_{ij}^p) / T \cdot dt. \quad (1b)$$

$$S_d = \eta (W_p / V_d T) \quad (1c)$$

S_d in simple terms is the entropy change that occurs with volume change over which the dissipation occurs i.e $\Delta S / \Delta V$ in units of $J / m^3 K$. **In terms of stress tensor σ_{ij} , S_d gets expressed as Eq. 1b** where $\dot{\epsilon}_{ij}^p$ is the plastic strain rate tensor. The S_d values can also be calculated from the pop-ins as per **Eq. 1b** **where** W_p is the plastic work, V_d is the deformed volume ; T the absolute temperature and η represents the fraction of plastic work converted to heat with 0.9 on an average for ceramics at high strain rates. The average plastic work per pop-in as per Fig. 2 was estimated to be around 0.5 pJ. So considering the deformed volume as a sphere of 360 nm radius, S_d was calculated to be $7.7 \times 10^3 J/m^3 K$ for 300 K. To make a comparison, The S_d values reported for silicate glass was reported $2 \times 10^3 J/m^3 K$ $1 \times 10^4 J/m^3 K$ for amorphous silicon and $5 \times 10^3 J/m^3 K$ for high entropy alloys (HEA) [14]

To navigate further, one can also represent the localized stress gradient (Λ_s) the ratio of the equivalent stress gradient ($\nabla \sigma_{eq}$) and average equivalent stress (σ_{avg}). (**Eq. 2a**)

$$\Lambda_s = |\nabla \sigma_{eq}| / \sigma_{avg}. \quad (2a)$$

An increase in Λ_s was therefore the indication of stronger localization of the deformation pathways and instability confinement. To proceed further, the nonlinear instability function (Φ_n) being represented by plastic strain rate ($\dot{\epsilon}_{pl}$), critical strain threshold (ϵ_c) as in eq, m being the non linearity coefficient is the indicator of rapid instability propagation and edge delamination when exceeding unity.

$$\Phi_n = \int (\dot{\epsilon}_{pl} / \epsilon_c)^m dt \quad (3)$$

The deformation topology coefficient ($D_d = A_s / A_t$) and strain accommodation parameters ($\Gamma_p = U_p / U_t$) where A_s is the shear deformed area, A_t is the total deformed area, U_p is the plastic energy absorbed and U_t is the total energy are significant. (Table 2)

Table 2
Simulated P- h and energy parameters

Parameter	Symbol	Value	Unit
Max penetration depth (sim.)	h max	800	nm
Max load (sim.)	P max	500	mN
Residual depth	hr	120	nm
Elastic recovery	-	~ 85	%
Unloading power-law exponent	m	1.35	-
Pop-in displacement magnitude	-	2–5	nm
Average crystallite diameter (TEM)	-	~ 7 (median 6.9)	nm
Plastic work per pop-in	W_p	~ 0.5	pJ
Deformed volume radius (sphere)	-	360	nm
Temperature	T	300	K
Plastic work to heat fraction	η	0.9	-

3.3 Distortion and delamination

Distorted indented geometries reflect how the plastic work gets dissipated. High values of S_d in these cases was from the distributed plastic accommodation, smoother pile up

and distortion while lower S_d values cam from concentrated instability sharp distortions and edge delamination. The distortion zones correspond to steep local stress gradients. An increase in Λ_s indicate stronger confinement of stress channels causing delamination and distorted indentation shapes Delamination occurs when the stress can no longer be redistributed and $\varphi_n > 1$ causing edge cracking and collapsed zone. The indent made at 1000 nm shows a stable pile up and limited pile up associated with moderate Γ_p . For indents made at higher depths of 1500 nm, more shear corridors are formed,

asymmetric distortion and uplifted edges with large D_d values. Higher depth indents at 2000 nm has $\phi_n > 1$ and $E_a = 0.4$ where instability propagation dominates. (Table 3)

Table 3
Entropy and Instability Metrics

Parameter	Symbol	Value	Unit
Entropy dissipation coefficient (SiCN)	S_d	7.7×10^3	J/m ³ K
S_d silicate glass (ref.)	S_d	2×10^3	J/m ³ K
S_d amorphous Si (ref.)	S_d	1×10^4	J/m ³ K
S_d HEA (ref.)	S_d	5×10^3	J/m ³ K
Entropy accommodation index	E_a	0.4	-
Nonlinear instability threshold	Φ_n	1 (delamination)	-
E_a at 2000 nm indent	E_a	0.4	-

3.4 Finite Element Analysis

The boundary conditions used in the Finite Element model are shown in Fig. 4(a). Total 38360 linear hexahedral elements of type C3D8R is used for the analysis. Elastic-plastic finite element analysis is performed using ABAQUS 6.13. Young's modulus E , Poisson's ratio, and Yield stress versus plastic strain required for the FEA are obtained from Nano Indentation test. The material is considered to be Isotropic elastic and isotropic hardening plastic material behaviour for the analysis. 3-D finite element modelling is done for quarter specimen. 8-node isoparametric hexahedral elements with 8 Gauss points taken for calculation. Reduced integration is done with full Newtonian non-linear analysis computation for all the specimens. The mesh was refined with an element volume of $0.0002 \times 0.0002 \times 0.0002$ mm³ in the region ahead of Indenter. The element size is kept constant near the crack tip to facilitate the calculation of stress distribution. To induce large strain expected in the Indenter tip, large deformation theory is used.

The Berkovich Indenter is taken as a discrete rigid object and surface to surface contact is established between the indenter and the film. The indenter surface is considered as the Master surface and the film is considered as slave surface. The discretization method used is Node to surface. A reference point is created on the indenter and displacement is provided through it. The displacement is applied in two steps. In the first step a displacement of 480 nm is provided with small initial increment of 0.01. The unloading or elastic recovery is provided in the second step of 430 nm with small initial increment of 0.01.

Figure 4(c) and 5 represent the Hydrostatic stress verses indentation depth from where it can be observed that layer of element directly under the indenter reaches twice the yield stress value at 200 nm and little variation and ultimately increases as indentation depth increases. This result is replicated at

200 nm below the indentation point a so it is not kept on the figure. But from 400 nm from the indenter the element did not reach the threshold value of 2000 MPa and as we move further away from the indenter tip the value is lower than the threshold value. Figure 4(d) reveals that Shear stress σ_{xy} did not reach the optimum yield stress value as $\tau_y = 2/3 \sigma_y$ and $\tau_{frac} = 2(2/3) \sigma_y$. (Table 4)

Table 4
Load – dependent deformation regimes

Indent depth (nm)	Regime	Observation
100	Stable energy accommodation	Smooth pile-up, distributed stress diffusion
500	Instability-driven	Edge delamination, mesoscale stress collapse
1000	Stable pile-up	Limited pile-up, moderate Γ_p
1500	Shear corridor formation	Asymmetric distortion, uplifted edges, large D_d
2000	Instability-dominated	$\varphi_n > 1$, $E_a = 0.4$, edge cracking

3.5 Gradient Assisted Viscoplasticity

The deformation caused by indentation can be modelled using gradient assisted viscoplasticity. The flow stress (σ_{flow}) can be represented as **Eq. 4** showing the gradient effect where σ_o is the intrinsic flow stress, ρ_d is the dislocation density, l_g is the material length scale parameter and ϵ_p is the plastic strain

$$\sigma_{flow} = \sigma_o + k \sqrt{\rho_d} + l_g^2 \nabla^2 \epsilon_p \quad (4)$$

The gradient term significantly influenced the deformation stability beneath the indentation region by creating metastable deformation pockets which evolved due to localized stress evolution. Interestingly the pockets were connected by dissipative shear path ways. The hydrostatic compressive stress beneath the indenter promoted stress confinement and delayed instability. However, the regions adjacent to free surfaces experienced tensile redistribution leading to localized instability bursts. The deformation morphology can therefore be claimed as to be a function of stress confinement and entropy driven instability propagation. (Table 5)

Table 5
FEM and Gradient Plasticity parameters

Parameter	Value	Unit
Element type	C3D8R (linear hexahedral)	-
Total elements	38,360	-
Mesh element volume (refined)	$0.0002 \times 0.0002 \times 0.0002$	mm ³
Loading displacement (Step 1)	480	nm
Unloading displacement (Step 2)	430	nm
Initial increment	0.01	-
Yield-stress threshold reached	2000 ($2\sigma_y$) at 200 nm depth	MPa
Gradient length scale. L_g	(material parameter, Eq. 4)	-

3.6 Nanostructural heterogeneity

The nanoindentation $P-h$ plots showed multiple pop-in events which were In fact entropy release events occurring due to structural rearrangements at the atomic level during the indentation process. Having a nanocomposite structure, where the amorphous phase being softer caused instability whereas the near amorphous or nanocrystalline phases caused a redistribution of stress by deflecting any crack generated. Although the distribution of the nanocrystallites was mostly amorphous There were some regions where clustering of the nanocrystallites took place which could absorb stress and ease out the instability.

The deformation morphology therefore was the result of a mixed effect of stress gradients and nanocrystalline heterogeneity. An entropy accommodating index (E_a) can be formulated as $E_a = (f_c + f_n) / f_a$ where f_a , f_c and f_n corresponding to the amorphous, crystalline and nano-crystalline fractions. The values close to unity represented balanced deformation accommodation and enhanced instability resistance. From the TEM image of SiCN films (Fig. 3), a dense dispersion of nanocrystallites on a predominantly amorphous matrix can be observed. A small fraction of the total area also showed formation of larger crystallites following clustering. The estimated accommodation index E_a was about **0.4** suggesting the fact that although partial hindrance to crack growth was present in the SiCN coatings, having a higher f_a , makes the deformation accommodation still in the unbalanced state and therefore the toughness enhancement is moderate rather than optimal. However chances of strain localization in the amorphous matrix itself still persists. (Table 6)

Table 6
Comparative Benchmark values

Material	Property	Value
Brittle ceramics	H/E range	0.03–0.06
Nitrides	H/E range	0.06–0.10
DLC coatings	H/E range	0.1- 0.15
Si-C-N (this work)	H/E	0.09
Liner unloading		

The observed heterogeneous structure can however cause tip blunting, nano-crack shielding energy dissipation through interfacial deformation and can suppress catastrophic shear band run away. In purely amorphous materials like metallic glass, the deformation gets concentrated into very narrow regions called shear bands where the strain localizes rapidly and the material can fail catastrophically with very little plastic deformation. The numerous nanocrystalline-amorphous interfaces as observed in the morphology act as barriers to shear band propagation and the mechanical energy gets dissipated through interfacial sliding, localized atomic rearrangement, and shear band deflection leading to comparatively better deformation stability [15–18] The interaction between the heterogeneity and localized shear deformation also reduces strain localization and delay crack propagation through enhanced plastic accommodation near the interfaces [19, 20]. Similar studies featuring heterogeneous multilayer coatings have also been reported where shear band, deformation twins and amorphization have been shown to behave like competing deformation pathways [21]

3.7 Entropy based distortion and delamination

The indentation induced distortion and delamination in Si-C-N and Ti-B-Si-C (N) coatings can hence be represented or rationalized through the entropy based descriptors introduced above. The entropy dissipation coefficient, S_d with a value $7.7 \times 10^3 \text{ J/m}^3\text{K}$ indicates accommodation of localized plastic deformation. A decrease in S_d will account for distortion in the indentation geometry and instabilities in localized pockets. The stress gradient Λ_s rises sharply at the uplifted edges, channeling the stress into confined pathways promoting asymmetric distortion The no-linear instability function $\Phi_n > 1$ is the signature of a dominant propagation of instability. Leading to edge delamination as observed in Fig. 2d, e. In the same notion, reduced strain accommodation (Γ_p), elevated deformation topology coefficient (D_d) signify poor energy diffusion and enhanced shear corridor formation, both of which act as precursor to delamination. The entropy accommodation index E_a , having a value **0.4** reflects unbalanced nanostructural heterogeneity, explaining why distortion persists with moderate delamination. These findings align with prior reports on entropy mediated instability in ceramics and high entropy alloys [22, 23], as well as shear band controlled deformation in metallic glasses [24, 25]

4. Discussions

4.1 Hardness- Modulus Synergy

The Oliver and Pharr correction which involved change of the contact depth h_c to 41 nm from 50 nm created an increase in hardness from 11 to 15.5 GPa showing elastic recovery to be significant even in hard coatings. The $H/E = 0.09$ places SiCN in the nitride to DLC transition zone, consistent with its nanocomposite (nanocrystalline growth on amorphous matrix)morphology which serves as a synergistic multiphase- structure that suppresses crack initiation and shear localization better than single phase hard but brittle ceramic coatings.

4.2 Depth-dependent hardening and modulus saturation

The modulus (E) being a bond-stiffness controlled elastic response stabilizes early and hence saturated at a depth of penetration, $h \sim 20$ nm. The hardness (H) however kept on increasing with h indicating densification driven stiffening in the near-amorphous/ nanocrystalline morphology. This phenomenon of decoupling reflects the strain gradient effects.

4.3 High elastic recovery ($\sim 85\%$) with non-ideal unloading

The extended linear unloading region and large $h_{\max} - h_r$ difference indicates localized shear accommodation and non-uniform stress distribution, producing distorted residual indent.

4.4 Entropy dissipation coefficient (S_d)

The entropy dissipation coefficient (S_d) was found to be 7.7×10^3 J/ m³ K which falls between the S_d values of silicate glass ($\sim 2 \times 10^3$) and amorphous Si ($\sim 1 \times 10^4$) and above high entropy alloys, HEA ($\sim 5 \times 10^3$). These values points out to the fact that Si-C-N nanocomposite coatings accommodates plastic deformation through distributive pathways rather than concentrated instabilities as found for lower S_d values which ultimately leads to edge delamination.

4.5 Nanostructural heterogeneity

The accommodation index was well below unity for a predominantly amorphous Si-C-N matrix which brings a trivial case of crack tip shielding and shear band deflection but with moderate enhancement of toughness. The 7 nm average crystallite size and 2–5 nm pop-in displacements correspond to a cooperative ,rearrangement of the nanocrystalline clusters even if the strain localization in the amorphous matrix remains a persistent risk.

4.6 Load -dependent transitions

A clear progression from distributed energy accommodation to shear corridor formation to $\Phi_n > 1$ instability / delamination validating the non-linear instability function as a predictive descriptor. The stress at this point can no longer be distributed and the edge cracking dominates.

4.7 FEM Corroboration

Hydrostatic stress reaching $2\sigma_y$ (2000 MPa) directly beneath the indenter at 200 nm decaying beyond ~ 400 nm, confirms stress confinement, shear stress σ_{xy} staying below yield explains why deformation proceeds via distributed plasticity rather than shear induced fracture. The gradient- assisted viscoplasticity term $Lg^2 \nabla^2 \epsilon_p$ rationalizes metastable deformation pockets connected by dissipative shear pathways.

5. Conclusions

The present work establishes a nonlinear entropy based framework for interpreting indentation induced deformations in Si-C-N coatings The main outcomes are

- The indentation based deformations evolved through competing dissipative pathways rather than pure brittle crack propagation.
- Distorted deformation zones were due to localized stress distribution and entropy concentration.
- Entropy dissipation coefficient (S_d), stress gradient (Λ_s), and nonlinear instability function (Φ_n)
- Gradient-assisted viscoplasticity explained metastable stress confinement and localization beneath the indenter.
- Nanoindentation pop-ins represented localized entropy bursts associated with nanostructural rearrangements.
- Nanostructural heterogeneity promoted simultaneous stress accommodation and instability suppression.
- The non linear energy distribution was established as an alternative way to interpret the indentation induced deformation.

Overall, the entropy based descriptors (S_d , Λ_s , Φ_n , D_d , Γ_p , E_a) provide a more complete explanation of asymmetric indentation distortion than conventional

thin film fracture mechanics. The toughness was found to ve governed by competing dissipative pathways : nanocrystalline stress redistribution vs amorphous matrix stress localization.

Declarations

CONFLICT OF INTEREST

The author declares no conflict of interest

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Figures

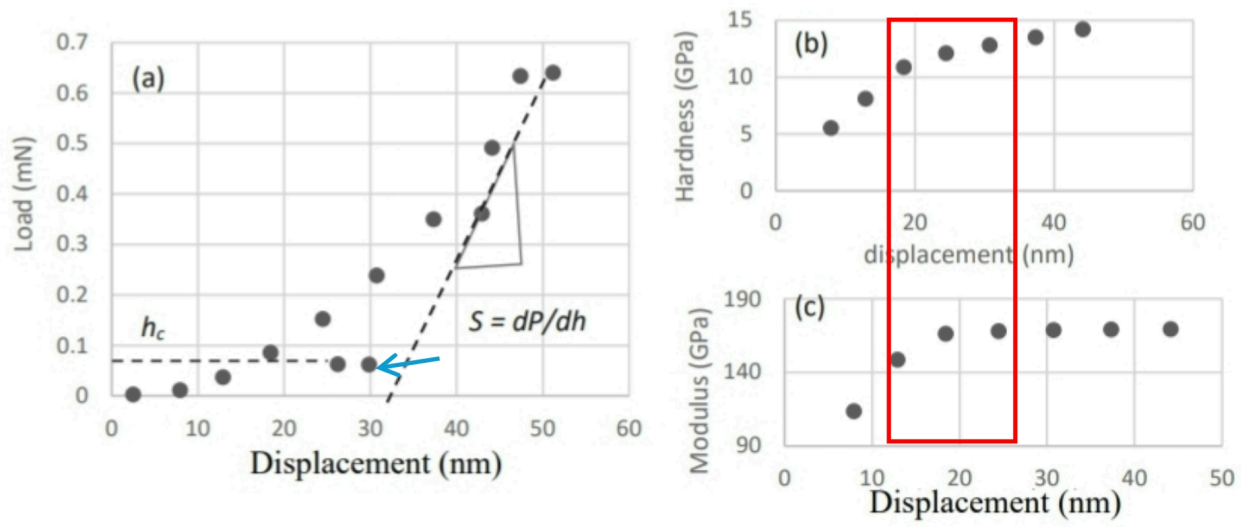
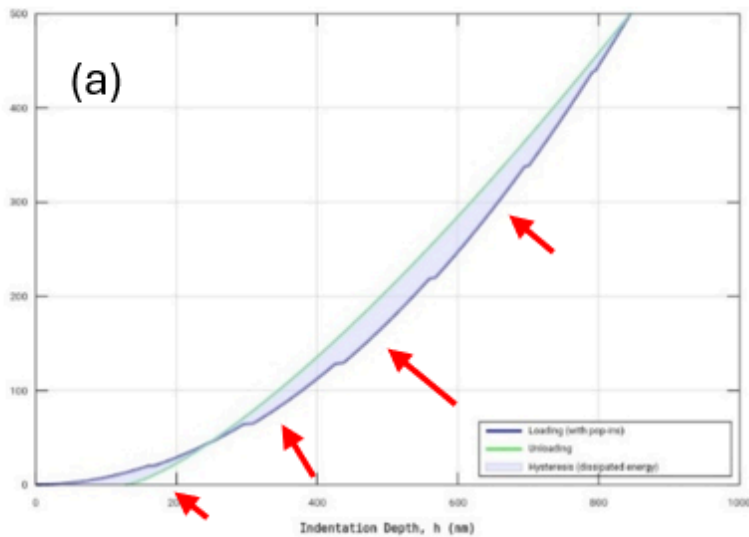


Figure 1

Nanoindentation a) load depth (P-h) plot (b) Hardness ($H \approx 15$ GPa) and (c) elastic modulus ($E \approx 170$ GPa) Reproduced under CC BY Licence **[10]**



(c)

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(b)

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Figure 2

(a) Simulated nanoindentation pop-ins as entropy bursts and b) experimental nanoindentation P- h plots of TiBSiCN coatings showing pop-ins as entropy bursts under nanoindentation on Ti-B-Si-C and optical images of indented regions for indentation performed at (c) 1000 nm (d) 1500 nm and 2000nm [3]

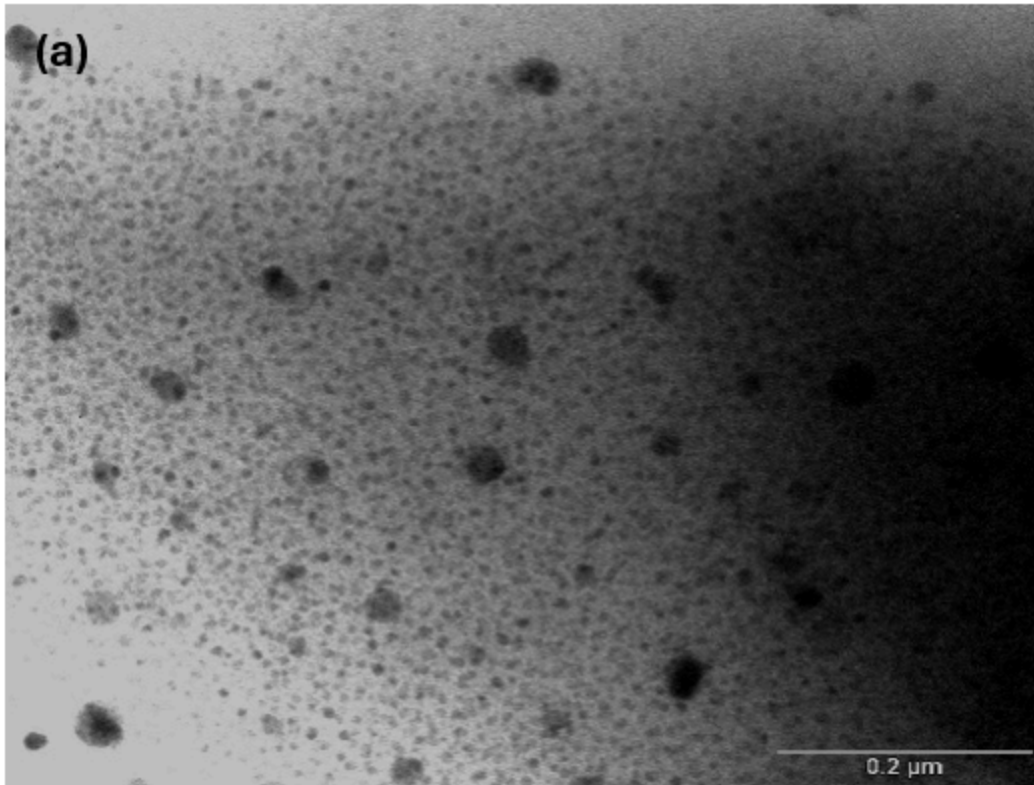
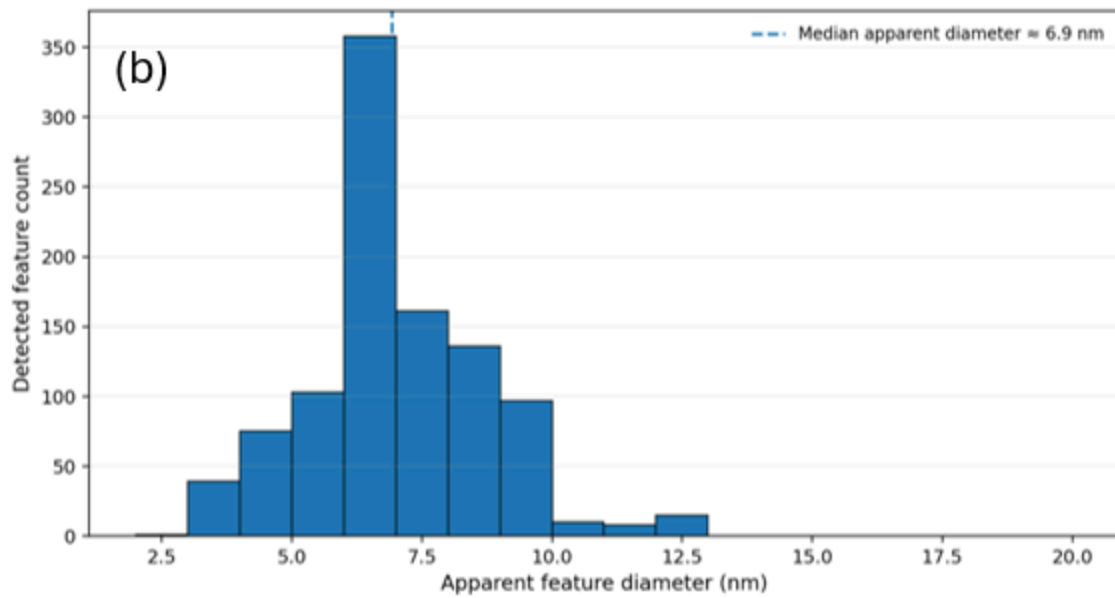


Figure 3

(a) Heterogeneous growth morphology in RF magnetron sputtered SiCN coating [9]

(b) The size distribution of the crystallites **(AI generated)**

(a)
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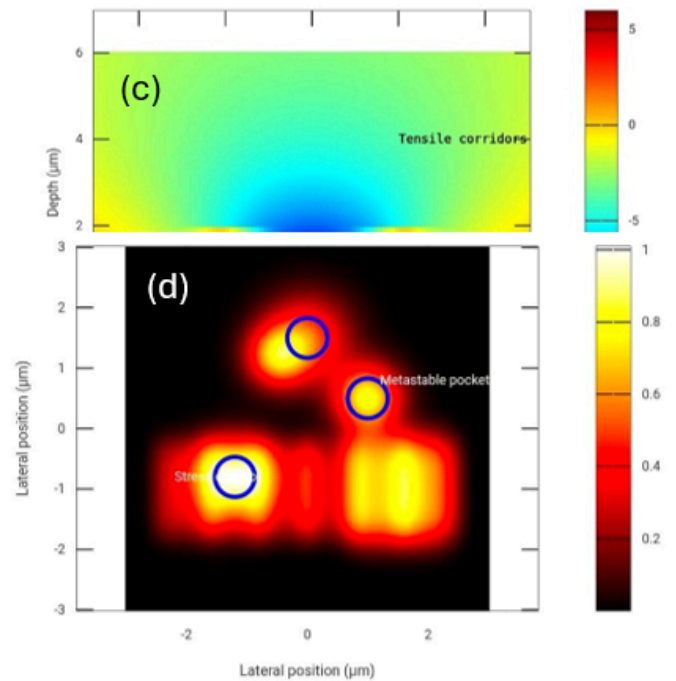


Figure 4
 (a) Quarter Model Along with Boundary Conditions (b) Shear stress σ_{xy} distribution at maximum indentation of 480 nm [3] (c) Hydrostatic Stress distribution (AI) (d) Stress corridors metastable deformation pockets(AI)

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Figure 5
 Hydrostatic stress verses Indentation [3]

Supplementary Files

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