

TOWARDS INTERNAL LENGTH GRADIENT CHEMOMECHANICS

E.C. Aifantis

Aristotle University of Thessaloniki, Thessaloniki 54124, Greece,
Michigan Technological University, Houghton MI 49931, USA
Beijing University of Civil Engineering and Architecture, Beijing 100044, China
ITMO University, St. Petersburg 197101, Russia
Togliatti State University, Togliatti 445020, Russia

Received: January 24, 2017

Abstract. This survey on past, current and possible future directions on chemomechanics was written on the occasion of the 55th birthday of Ilya Ovid'ko. The seminal contributions of his and his team on nanomechanics of defects in solids, based on earlier developments of his mentors and the Russian school on dislocation and disclination theory, can serve as a foundation for extending their work to include the synergy of internal stress and a diffusing chemical agent. Such synergy governs, for example, the fabrication (by electrodeposition) and subsequent use (as filters and nanocatalysts) of micro/nano-sized metallic particles and objects exhibiting large spatial gradients and developed surface in the presence of structural disclination defects. One possible way for achieving this extension (by modeling the underlying physico-chemo-mechanical couplings) is outlined in the present paper which is partly based on a 2016 proposal to European Research Council (ERC) and a 2017 MegaGrant project funded by the Government of Russian Federation. In particular, the paper outlines a number of key concepts and ideas that have not been explored in the area of chemomechanics or mechanochemistry, i.e. at the meeting point of mechanics and chemistry. The aim is to cast these ideas into an initial mathematical framework for describing a variety of coupled chemomechanical phenomena occurring in earth and the human body, as well as in novel engineering nanomaterials and modern technological processes such as those employing nanofilters and nanocatalysts. The new viewpoint advanced here is that in order to capture and control chemomechanical instabilities at the nanoscale we need to resort to internal length and time scales associated with the evolution of the underlying local mechanical stress and chemical agent. One convenient way to account for this is through the introduction of second spatial (Laplacian) and time (inertia) derivatives of the pertinent mechanical and chemistry variables in the constitutive equations describing the evolution of the chemomechanical system at hand.

1. INTRODUCTION

Chemomechanics and related instabilities – generated by the cooperative action of mechanical stress or strain and diffusion or chemical reaction – emerge as a central issue in nanotechnology, high energy density storage, and biomedical applications. The

task proposed to undertake herein is the development of a multifaceted continuum chemomechanics framework – in concert with experiments and simulations – utilizing internal lengths/ILs (to account for the effect of micro/nano spatial chemomechanical gradients) and internal times/ITs (to account for the effect of corresponding micro/nano temporal iner-

Corresponding author: E.C. Aifantis, e-mail: mom@mom.gen.auth.gr

tia). Surface/interface morphology may be introduced through a corresponding chemostress energy term to account for nonlocal bulk-surface interactions. Stochasticity can be introduced through internal fluctuation terms to account for the competition between deterministic gradients and random micro/nano structures. When differential equations are not available to describe observed intermittent behavior, and power-laws are not sufficient to fit corresponding statistical measurements, Tsallis nonextensive entropy q -statistics could be used to interpret experimental data and related simulation results. This machinery can also serve to deduce the appropriate form of probability density functions to be used in constructing robust combined gradient-stochastic models. Experiments involving nanoindentation/microtensile and AFM/TEM testing, along with simulations based on cellular automata and defect dynamics, may provide substantial input on the aforementioned developments. Fractional/fractal considerations is another tool which could open new directions of research in this field, by replacing usual spatial time derivatives of integer order with corresponding non-integer derivatives and utilize recent results from fractal and fractional calculus.

Such type of IL/IT chemomechanical couplings in the presence of surfaces/interfaces and stochasticity have not been dealt with so far. Our model equations can be used to describe the phenomenology of seemingly different chemomechanical processes governing the behavior of novel structural materials, energetic materials and brain cells. Chemomechanical damage of sodium-ion battery electrodes, amorphization of boron carbide, and neurodegeneration of brain tissue, may be considered as special case-studies of the proposed framework. In Section 2 we sketch motivation and objectives. In Section 3, we provide the background and related state-of-the-art. In Section 4 we outline the methodology employed and briefly elaborate on novel aspects. In Section 5 we discuss three specific chemomechanics problems as indicative case-studies of the proposed framework. In Section 6, we conclude with a number of suggestions for further interdisciplinary research and a brief discussion on broader impacts. Finally, in the Appendix we sketch the relevance of the proposed gradient chemomechanics framework to describe synergistic effects between internal stress and chemical activity due to a diffusing agent. Such internal stress-chemistry couplings govern, for example, the fabrication of pentagonal small particles (PSPs) based on fcc metals obtained by electrodeposition from

an electrolyte solution. In the range of small sizes (0.1-50 micrometers), such objects exhibit large spatial gradients at the atomic scale due to inhomogeneous distributions of elastic fields, which can be viewed as being accommodated by lattice disclination defects. In the range of larger sizes they are also characterized by inhomogeneous or spatial gradient structures (SGS) due to the generation of an excessive density of such lattice defects, leading to highly defective microcrystals (DMCs). Due to the remarkable multifunctional mechano-physicochemical properties of DMCs (high strength, thermal stability, chemical activity), they are used as membranes/filters and nanocatalysts in modern technology.

2. MOTIVATION AND OBJECTIVES

The modest goal of the article is to outline a strategy and general mathematical framework that can be used for monitoring chemomechanical instabilities and pattern formation in a number of material classes sharing common features and phenomenology. The term *chemomechanics* was coined by the author in 1980 [1] to describe synergistic effects between deformation and diffusion in the presence of chemical species. Related classical problems of intense research activity at that time were hydrogen embrittlement and stress corrosion cracking, where chemical reactions and phase transformations under the action of moderate applied stress generate huge internal strains leading to failure. The term *mechanochemistry* was later used by Gilman in 1996 [2a] to describe the direct effect of stress on chemical reactivity at the molecular level – a phenomenon earlier dealt with by Bridgman in 1935 [2b], even though the first documented mechanochemical reaction is traced back to Theophrastus in 4th century b.c. [2c]. The discipline of *biomechanics* or *mechanobiology* emerged as a result of the need to consider the synergy of mechanics and biology for investigating chemomechanically/mechanochemically-sensitive physiological processes at the tissue and cellular level [3].

Existing studies in the above areas are based either on macroscopic theories or atomistic models, often without sufficient attention to the mesoscale and the collective effects associated with the underlying microstructural or nanostructural configuration. In particular, an enriched continuum chemomechanics framework – where collective micro/nanostructural effects and related instabilities can be accounted for in a robust and unifying manner – is missing. Such a micro/nanostructure in-

spired continuum framework is suggested herein. Attention is placed first on elucidating the role of internal material lengths/times, surfaces/interfaces and stochasticity/randomness, as well as on exploring the role of fractionality/fractality. Then, material instabilities – a term also introduced [4] to study bifurcation and deformation patterning in chemically inactive metals and soils – could be dealt with for specific stress-chemistry environments and configurations. In particular, the chemomechanics of grain boundaries may be addressed as typical example of the proposed framework. Moreover, common aspects of three seemingly different problems – i.e. chemomechanical damage of sodium-ion battery tin anodes; boron carbide amorphization; and neurodegeneration of brain tissue – can be considered as special case-studies.

The general formulation and a number of special results are expected to apply to a variety of problems of advanced structural/energy storage technology and biomedicine. For example, they can be of direct use to the technology of lithium-ion batteries/LIBs [5] with nanostructured electrodes, and on spatially-graded catalysts/SGC [6] with nanostructured surfaces. Diffusion of lithium in LIBs tends to cause colossal volume expansions (>300%) in anodes and phase separation in cathodes leading to chemomechanical damage/cracking and capacity fade. Chemical performance of SGS catalysts depends on the internal stress generated by dislocation/disclination defects during processing and their interaction with the morphology of the developed surface. Due to the limited lithium resources, as opposed to abundance of sodium in the earth crust, sodium-ion batteries/NIBs [7] are now being pursued for which, in contrast to LIBs, mechanics studies are absent and the trend for even larger local volume expansion (>400%) seems to be buffered by nanoporosity development suppressing chemomechanical failure and capacity fade. Similarly, in search of superstrong boron carbide for advanced structural applications under dynamic loads, most recent studies [8] suggest that tuning the nanoscopic cage spaces occurring under the synergistic action of local stress and alloy chemistry, could lead to mitigation of amorphization-induced softening. The same group of authors used a variant of their high-strain-rate apparatus to demonstrate the appearance of cavitation damage in brain tissue at the cellular level, after concussion [9a-b]. Analogous type of brain tissue related cavitation damage may occur during organogenesis [9c] and neurodegeneration after stroke [9d]. There is also evidence of nano/microporosity development asso-

ciated with Alzheimer disease (AD) [9e-f]. It thus appears that by pursuing and formally analyzing analogies in the phenomenology between chemomechanical degradation of novel materials and neurodegeneration of brain tissue may help opening up new directions for interdisciplinary research at the interface of engineering and medicine.

3. BACKGROUND AND STATE-OF-THE-ART

Our previous work on purely mechanical or purely diffusional material instabilities could serve as an initial building block for the proposed framework. In a broad sense, the occurrence of shear bands, dislocation patterns and other structural transformations in purely mechanical problems may be viewed as pattern forming chemical-like instabilities driven by stress. When the stress-dependent activation energy in deforming media reaches a certain threshold, a structural transformation emerges, in analogy to a reaction in chemically active media. This, in fact, was the point of view advanced by the author to treat plastic instabilities [10] which could not be addressed by existing theories. He introduced extra Laplacian terms for the plastic strain and the dislocation densities to describe deformation and structural defect patterning, when homogenous material states become unstable. This enabled to predict widths and spacings of shear bands, model solitary plastic deformation waves, capture plastic size effects, interpret dislocation patterning phenomena, and dispense with mesh-size dependence of finite element calculations in the strain softening regime. Introducing the Laplacian of the elastic strain into classical Hooke's Law [11] resulted to elimination of singularities in dislocation lines and crack tips, and also allowed for capturing elastic size effects.

Internal lengths (ILs) accounting for the heterogeneity of underlying micro/nanostructural configuration, appeared naturally in front of the introduced extra Laplacian terms. Internal times (ITs), in the form of micro/nano inertia, emerged in considering dispersive wave propagation in nanotubes [12a-b] and in acoustic metamaterials [12c]. In the first case, the results were consistent with corresponding molecular dynamics simulations. In the second case, the results were consistent with experiments on second band-gaps for higher frequencies. Concerning ILs/ITs and related couplings in biomechanics or mechanobiology, it is noted that their use is entirely absent from neurodegeneration models even though Murray's seminal work on morphogenesis [13a-d] could be used as a guide. In this connec-

tion, it is pointed out that a mixture-based multiporosity theory for the human placenta [14a] and its specialization to dual porosity/diffusivity [14b-c], along with a stress-assisted diffusion theory [14d] earlier advanced by the author, are still finding recent applications to geophysics [15a], biophysics [15b] and potentially the brain [15c-d].

Following the publication of the aforementioned Laplacian-based gradient models, an extensive research activity emerged world-wide, as described in a number of materials science [16]/mechanics [17] books and comprehensive reviews, as well as in relevant references quoted therein. This activity is still going on today focusing on extensions and open issues of earlier theories on second grade [18] and dislocated [19] continua. In particular, Laplacian-based stress/strain gradient models have most recently been used by Rafii-Tabar [20] and coworkers in an extended review article (Physics Reports, 2016) to describe mechanical characteristics of nanoscopic structures (nanotubes, nanoplates, graphene). Laplacian-based multiphysics gradient models have been used by the author [21] in another extended review article (Advances in Applied Mechanics, 2016) to capture size effects and instabilities across scales and disciplines for various classes of manmade and natural materials. Accordingly, we will focus on Laplacian-based chemomechanical models, as the proposed new ingredients and extensions can be easier accomplished and the implications of the results will be more transparent.

4. METHODS AND NOVEL ASPECTS

4.1. Internal Lengths/Times (ILs/ITs)

A *first novelty* in the proposed methodology is to include internal lengths (ILs) and internal times (ITs) to model the spatiotemporal evolution of micro/nanostructures and their effect on the macroscopic chemomechanical description of the system at hand. In the simplest case, it turns out that the ILs enter as (square) multipliers of the extra Laplacian terms: $\ell_\varepsilon^2 \nabla^2 (\lambda \varepsilon_{mm} \delta_{ij} + 2G \varepsilon_{ij})$ for elasticity; $\ell_p^2 \nabla^2 \gamma$ for plasticity; and $\ell_d^2 \nabla^2 j_i$ for diffusion. These terms provide a direct generalization of classical Hooke's law of elasticity, the von Mises flow rule of classical plasticity and Fick's classical law of diffusion. The quantity ε_{ij} denotes elastic strain (λ, G being elastic moduli), γ denotes the equivalent plastic strain, and j_i the diffusion flux. The newly introduced quantities ($\ell_\varepsilon, \ell_p, \ell_d$) denote respective ILs. The emergence of the Laplacian may be deduced from averaging or

homogenization arguments and can also be generated by adiabatic elimination of internal variables evolving at the micro/nanoscale level, which do not explicitly appear in the final governing differential equations of the system's description. In fact, Laplace's operator is the first non-vanishing term when the spatial integral of an average quantity over an elementary material volume is expanded in a Taylor series in terms of the corresponding local quantity. This observation (first recognized by Maxwell himself for providing a physical meaning for the Laplacian) can also be carried out for fractional derivatives and fractal media, thus resulting to a corresponding straight-forward extension of conventional IL models based on integer derivatives and Euclidean geometry. Moreover, due to an earlier mathematical observation of the author and his coworkers [22], it turns out that solutions of boundary value problems for Laplacian-based theories can be obtained in terms of their classical counterparts by solving an inhomogeneous Helmholtz equation. This is another reason for insisting on our proposed formulation, since Green's functions and related mathematical results are available for the Helmholtz equation for both its conventional and fractional/fractal counterparts.

Similarly to ILs, internal times (ITs) in the form of micro/nano-inertia appear as (square) multipliers of second time derivatives of strain (for deformation) and concentration (for diffusion) problems. While the effect of ILs has been studied separately for deformation [10-12] (dislocations/cracks, shear bands/size effects) and diffusion [14b-e] (polycrystals, spinodal decomposition) problems, the coupling between mechanical and chemical ILs has not been addressed. The same holds for the coupling effects between ILs and ITs that emerge under the simultaneous action of stress and chemical activity. These are generic issues which can be conveniently tested and evaluated in the case-study problems outlined in the sequel. Both ILs and ITs should not be just taken as constants or material coefficients, but rather be viewed as configurational parameters depending on the microstructural/nanostructural arrangement and the size of elementary volume at hand. Estimates for the IL/IT parameters can be obtained through appropriate discrete modeling and simulations, as well as related experiments. This will supplement earlier work on identifying purely mechanical or purely chemical ILs and extend it to include IL/IT chemomechanical couplings and access their effect on suppressing instability and controlling failure.

4.2. Surfaces/Interfaces

A *second novelty* is the consideration of bulk IL/IT-couplings with surface or interfacial energy parameters. This can initially be guided by existing purely mechanical theories on coupling effects between surface morphology [23] and growth [24] with elastic [25] or plastic [26] deformation. The new issue that emerges here is the modeling of higher-order bulk-surface interactions in the presence of a chemical agent. As the size of the representative material element reduces, the surface-to-volume ratio increases and surfaces/interfaces need to be treated on the same footing as the bulk. For example, grain boundary or interfacial yielding/strengthening is documented to evolve separately from the bulk and that the overall material behavior is controlled by the dependence of the interfacial energy on nearby dislocation-segregant interactions. It then follows that interactions between bulk ILs/ITs and internal or external surfaces should be accounted for, along with the emergence of surface/interface ILs (for quasistatic problems) and corresponding ITs (for dynamic problems).

To treat internal or external surfaces on their own merit (not just as an extension of the bulk with boundary conditions), we need to introduce an extra interface/surface energy term $\int_S \Phi dS$ (S denotes surface and Φ is a function depending on the deformation state and atomic defect configuration on S). In the case of elasticity (coherent interfaces), the form of Φ may be deduced in connection with the atomic arrangements at the interface and related adhesion/binding properties of the adjacent materials [27]. In the case of plasticity, the form of Φ may be deduced from physical arguments and microscopic models concerning the structure of the interface (or free surface) and the interaction with arriving dislocations from the grain interior. Different forms of Φ will give rise to different forms of surface/interface stresses that will interact with the bulk stresses to determine the overall material behavior. This, in general, is a quite difficult task requiring a separate multi-investigator effort combining continuum theory and multiscale simulations, along with multiprobe experiments. Thus, a more reasonable plan is to focus first on the case where the interface is a grain boundary with known structure and chemistry and develop our continuum formulation accordingly. For this benchmark problem we can also use discrete dislocation dynamics (DD) simulations and nanoindentation (NI)/transmission electron microscopy (TEM), already available or to be properly designed and carried out in the future.

In this connection, it is noted that existing grain boundary-dislocation interaction metal physics arguments [28] and experimental observations on discontinuous yielding and unusual Hall-Petch behavior due to grain boundary segregation [29] can be directly utilized. A specific expression for the grain boundary (as opposed to bulk) yield stress, that can be considered and further elaborated upon within a chemomechanical setting reads $\sigma_{ys}^{GB} = (\gamma^{GB}/2\ell_p) \coth(d/\ell_p)$. This expression was earlier derived for purely mechanical considerations of gradient plasticity with interfacial energy [26a-b] in the absence of chemical activity: σ_{ys}^{GB} is the grain boundary (GB) yield stress, γ^{GB} stands for the interfacial energy parameter, d denotes the average grain size, and ℓ_p is the internal length of the bulk. By stressing a bicrystal using an *in situ* straining stage, the onset of GB deformation through dislocation emission/dislocation absorption/dislocation transference can be captured. At the same time convergent beam electron diffraction patterns taken at the point of plastic strain initiation may be examined to determine the state of strain. This local determination of strain, at the onset of GB yielding, requires the examination of the Kikuchi line configuration giving strain measurements with a precision of 0.01% and high spatial resolution. By using the elastic moduli of the material, the strain can provide the GB yield stress. Furthermore, the dislocation spacing and the dislocation pile up length in front of the interface can be measured throughout straining, and one (or a combination) of these parameters can be used to estimate ℓ_p . Therefore, the only unknown parameter is γ^{GB} which can be obtained by using the measured $(\sigma_{ys}^{GB}, d, \ell_p)$ values in the above formula. In the presence of a chemical agent, say a grain boundary segregator, the concentration of the segregant will enter in the above expression through the interfacial energy term γ^{GB} or, alternatively, through a grain boundary chemical potential term.

4.3. Stochasticity/Randomness

A *third novelty* is the consideration of the competition between deterministic gradients and random constitutive effects associated with internal stress fluctuations in the presence of a chemical agent. This will lead to the development of Laplacian-based chemomechanical gradient-stochastic models. At small scales both bulk and surface or interface fluctuations have a dominant effect and combined gradient-stochastic models (describing the interplay between deterministic gradients and randomness) are needed to capture the observed behavior; in

particular, size-dependent serrated stress-strain graphs and intermittent plasticity phenomena. Some initial results along this direction have recently been reported by the author and coworkers [30a-b] based on a previous related formulation [30c-d] and adopting empirical Weibull distribution functions. These initial results can be revisited and extended to account for chemomechanical couplings through the development of robust combined gradient-stochastic models that can be developed by employing time-dependent probability distributions derived from stochastic differential equations guided by our earlier [31a-b] and most recent [31c] work based on the formalism of stochastic differential equations.

A convenient way to account for the competition between deterministic gradient and random effects is to introduce an additive stochastic term – of the form $h(\gamma, \rho)g(x)$; $\langle g(x)g'(x) \rangle = \ell_{corr} \delta(x - x')$ with (γ, ρ) denoting strain and concentration of the chemical agent, ℓ_{corr} denoting a correlation length and δ being the usual Dirac delta function – in the gradient expression for the flow stress for chemoplasticity problems. This is not an arbitrary assumption but emerges generically if one aims at a description above the scale of the discrete substructure which defines the correlation length – i.e. within a continuum model. The delta function then appears because the individual volume elements of the continuum theory are effectively uncorrelated. The function $h(\gamma, \rho)$ also covers the limiting case where only the material parameters fluctuate while the evolution is deterministic (e.g. in the case of flow stress fluctuations due to fluctuating grain orientation in the presence of a chemical environment). Gradient deterministic models without incorporating stochastic effects seem to be incapable of describing measured statistical aspects of plastic deformation such as intermittent behavior and multifractality of observed deformation patterns. In this connection, it is noted that fractal dimensions for dislocation patterns have been measured and Hurst exponents for surface roughness have been determined through wavelet analysis [32]. Moreover, power-law exponents for dislocation avalanches and strain bursts recorded during nanoindentation and micro/nanopillar compression tests have been determined through combined gradient-stochastic models [30a-d].

When differential equations cannot be invented to interpret experimental data and simulations, system characterization is left to statistical analyses and related efforts to establish power-laws. In many cases, however, the usual power laws based on Boltzmann-Gibbs (BG) statistics exclude the regime of low intensity - high probability events. Tsallis q -

statistics [33] based on nonextensive thermodynamics remove this difficulty and can be employed here to analyze intermittent chemomechanical response and patterned images obtained experimentally [34]. This information allows the construction of appropriate probability density functions (PDFs) to be used in the aforementioned combined gradient-stochastic models. Tsallis non-additive (nonextensive) entropy reads $S_q = k(1 - \sum_i p_i^q)/(q-1)$ and by letting $q \rightarrow 1$ recovers the familiar BG extensive entropy. Corresponding non-equilibrium q -distribution (q -Gaussian, q -exponential, q -Weibull) functions are obtained, which for $q \rightarrow 1$ reduce to their standard B.G. counterparts.

To further document the need for combined gradient-stochastic models and the formalism of Tsallis q -statistics we recapitulate below a result from [21]. In that work the randomness and associated Tsallis q -statistics characterizing plastic deformation was considered. The coupling between deterministic and random constitutive effects was accounted for through a simple one dimensional linear hardening combined gradient-stochastic model of the form $\sigma = \sigma^{ys} + h\varepsilon - \ell_p^2 (\partial^2 \varepsilon / \partial x^2)$ where σ is the applied stress; ε denotes the plastic strain; h is the hardening modulus; and the yield stress σ^{ys} contains both an average and a fluctuating part given by $\sigma^{ys} = (1 + \zeta) \bar{\sigma}^{ys}$: $\bar{\sigma}^{ys}$ denotes mean value and ζ follows a Weibull distribution fitted to experimental data.

When this model was incorporated into a cellular automaton (CA) grid, it resulted to serrated stress-strain curves and Tsallis-type power-law interpretations of the corresponding statistical events (Fig. 1). Appropriate expressions for the stochastic component of the flow stress can be more fundamentally deduced by employing the formalism of random processes and stochastic differential equations. In this connection, reference is made to a class of Tsallis q -distributions that are used in many non-equilibrium physics problems where the usual power-laws based on Boltzmann-Gibbs (BG) statistics fail to predict observed behavior. An example for Mo micropillar compression is given in Fig. 1a where the experimentally measured distribution of burst sizes s is approximated by Tsallis q -exponential distribution function of the form $P(s) = A[1 + (q-1)Bs]^{1/(1-q)}$: (A, B) are constants and the q -index is a measure of the system's fractality. It seems that a power-law relationship between the internal length ℓ_{corr} and the entropic index q may be established, as preliminary results depicted in Fig. 1c indicate.

Along similar lines, Tsallis q -statistics can be employed to interpret multifractality and transition

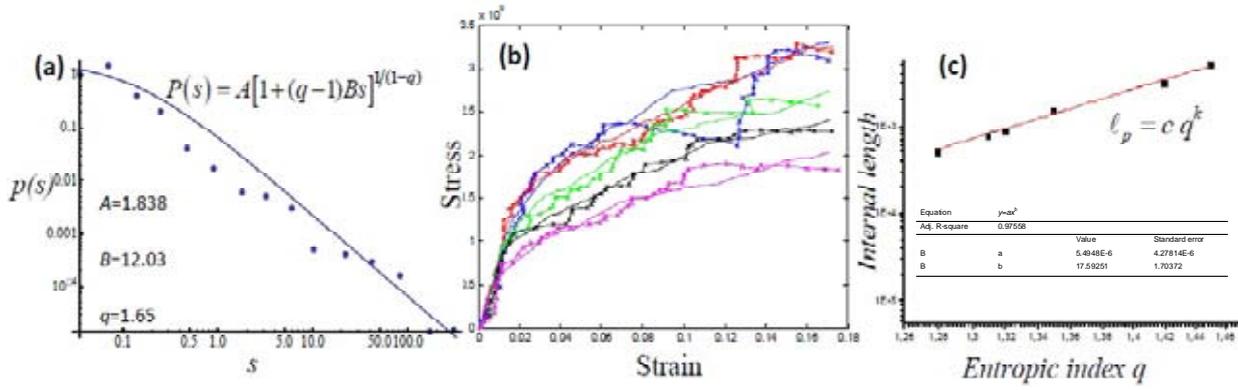


Fig. 1. (a) Fit of strain bursts in Mo micropillar compression by Tsallis q -exponential distribution; (b) Corresponding fits of theoretical predictions to experimental measurements; (c) Semi-log plot of the internal length ℓ_p vs. q ($c=5 \cdot 10^{-6}$ and $k=8.8$).

to chaos of complex deformation patterns as revealed through corresponding microscopy measurements and related micrographs [21]. The needed experimental information on appropriate forms of probability distribution functions (PDFs) for the stochastic component of the flow stress, can be deduced through multiple nanoindentation (NI) tests and statistical analysis of the associated measurements of strain burst events. The PDF of the strain bursts can be related to a corresponding PDF for the flow stress on the assumption that a strain burst of a certain magnitude is the outcome of a number of material points yielding simultaneously. NI measurements at different locations and penetration depths can be conducted to deduce the statistical properties (mean, variance) for the local size-dependent hardness which, in turn, can be directly used (e.g. through the empirical Tabor's rule relating hardness to yield stress, or more sophisticated finite element simulations) to extract information on the form of the stochastic component of the local stress. This requires a sufficiently large number of NI measurements which can be analyzed through standard NI procedures. From these multiple NI measurements we can extract direct information for both the deterministic ILs and the form of the stochastic contribution to the gradient dependent flow stress.

4.4. Fractionality/Fractality

A *final novelty* is the extension of Laplacian-based chemomechanics to include fractional calculus and fractal media considerations. Existing mathematical results for fractional Laplacians and fractal media have already been used for extending our previous gradient elasticity models to include non-inte-

ger derivatives and non-Euclidean geometry [35,21]. This work can guide similar developments for chemomechanics, where the presence and diffusive behavior of a chemical agent is also governed by Laplacians. It is noted that while there is ample evidence that at a certain scale of observation, plastic deformation exhibits a fractal character and some results on fractal dimensions for dislocation clusters and Hurst exponents for surface roughness have already been reported (e.g. in [32] as mentioned earlier), there are no corresponding models predicting or utilizing these findings. An exploratory attempt to consider fractal elastic media with different fractal dimensions for the bulk and the surface can be found in the recent review by the author [21]. The fractal counterpart of the Laplacian term which generalizes the classical Hooke's law of elasticity reads $\ell_F^2 \Delta^{(D,d)}$, where $\Delta^{(D,d)}$ is the fractal Laplacian that takes into account the power-law density of states of the fractal medium under consideration and (D, d) denote (volumetric, surface) fractal dimensions.

5. CASE-STUDIES

In this Section we consider some typical problems of current or emerging scientific technological and socio-economic interest as case-studies of the proposed multiscale chemomechanical framework. We illustrate, in particular, how analogous chemomechanical arguments can be used to address unresolved questions in diverse classes of material behavior ranging from the advanced structural and high energy density storage sectors to biology and medicine. Our multifaceted continuum chemomechanics formulation may provide a comprehensive intellectual platform for considering a variety of apparently

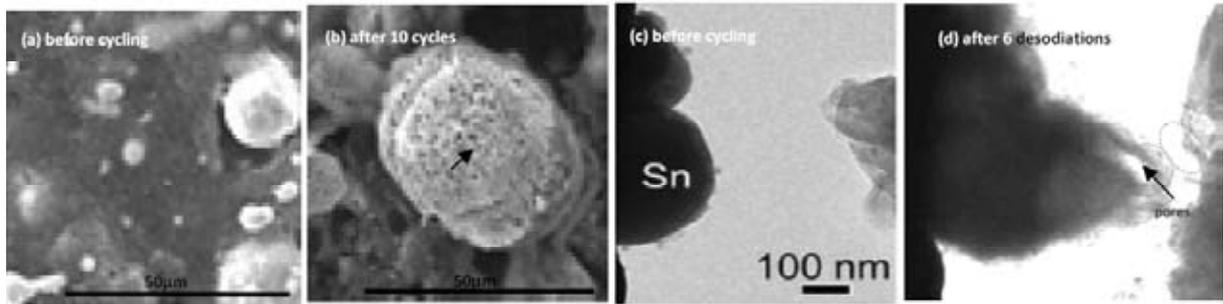


Fig. 2. (a) SEM image of Sn anode prior Na-insertion; (b) SEM image of Sn anode after Na-insertion indicating ‘nanopores’; (c) TEM image of Sn anode before cycling; (d) TEM image of anode after 6 electrochemical cycles.

different chemomechanical processes which, nevertheless, share a similar phenomenology and can be addressed within a common framework. The peculiarities emerging in distinct classes of material behavior can be elaborated upon separately as shown for the specific case-study problems considered below. These case-study problems are concerned with chemomechanical damage of sodium-ion battery tin anodes (Na_xSn); amorphization of boron carbide (B_4C); and neurodegeneration focusing on Alzheimer’s disease (AD). A common feature in these three different problems is the development of (nano/micro) porosity due to external or internal stress which may improve or deteriorate the system’s behavior.

5.1. Na-ion Batteries

Na-ion batteries (NIBs) are being considered as an alternative to Li-ion (LIBs) in applications where miniaturization of the energy source is not required, such as stationary energy storage. Sn is among the most promising anode materials, as it provides a capacity of 847 mAh/g upon the formation of $\text{Na}_{15}\text{Sn}_4$. Similarly to lithiation of Sn, sodiation tends to result in colossal volume expansions (420%), which lead to mechanical degradation and capacity loss [7]. Corresponding theoretical models interpreting damage in Sn-anodes for Na-ion batteries have not been developed, in contrast to the significant work done for understanding fracture in Li-ion cells. In fact, a careful examination of SEM and TEM micrographs [7a-b] indicates the formation of “nanopores” in Sn anodes (Fig. 2) which, however, were not noticed (or not commented upon) by the authors of that work. Pore formation is known as a mechanism by which materials respond to applied stress under mechanical creep conditions. This possibility has not been examined as a potential candi-

date mechanism to accommodate volume change stresses in electrochemical systems. The control of the transition between fracture and pore formation mechanisms could be a transformative concept for improving high capacity electrode lifetime in secondary batteries. It is, therefore, necessary to perform a first systematic comparison of the mechanical effects that Na-ion insertion/de-insertion has on Sn-based anodes, with the corresponding ones that Li-ion intercalation/de-intercalation has on such anodes.

One interesting topic that emerges then for Na-ion anodes is to consider (as for their Li-ion counterparts) the implications of a stress-assisted diffusivity equation with stress-dependent diffusivity. A transport equation for the Na-ion species of concentration ρ can be adopted of the form $\dot{\rho} = (D + N\sigma_h)\nabla^2\rho - M\nabla\sigma_h \cdot \nabla\rho$, where (D, M, N) are phenomenological constants and σ_h is the hydrostatic stress determined by a purely mechanical problem (creep or damage) when certain uncoupling simplifications are assumed.

In a more general treatment, coupled diffusion-creep/damage equations can be derived. Solutions of typical boundary value problems can provide insight on chemomechanical damage and capacity fade in anodes for Na-ion batteries, in analogy to corresponding studies in Li-ion anodes. Existing results and solutions for representative geometry configurations using gradient elasticity/plasticity/damage theories can be extended to include the effect of diffusion and chemistry-induced pore formation and evolution. The new findings can be used for controlling chemomechanical damage, thus reducing capacity fade and optimizing electrode performance during electrochemical cycling.

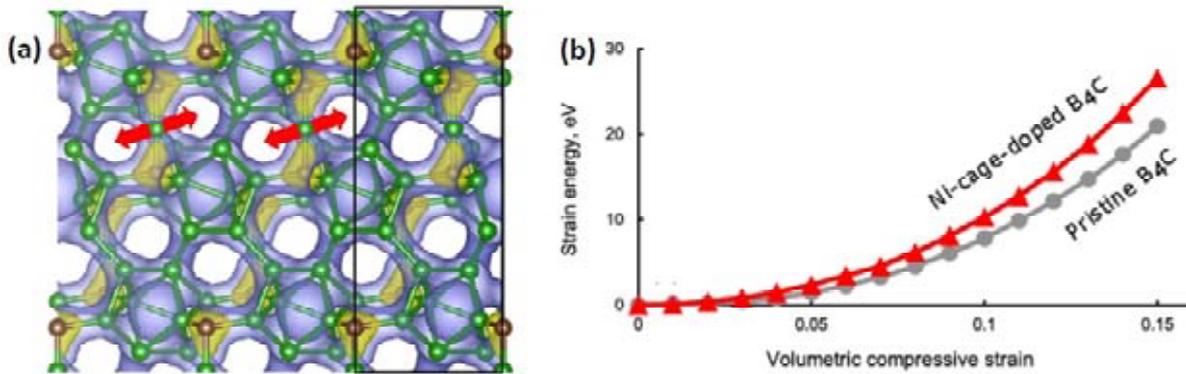


Fig. 3. (a) Electron-density isosurfaces depicted in yellow and blue, respectively, represent high and low levels of spatial distribution of electron density in B_4C crystal structure. White areas are regions with negligible electron density and are hence termed ‘cage spaces’. Arrows depict how the chains are susceptible to bending/buckling into cage-spaces. These empty spaces are continuous and their sizes are sufficient to accommodate additive atoms. Bounding box pertains to one periodic hexagonal unit cell and the view-direction is [100]. (b) Relative performance of pristine boron carbide and cage-space doped with Ni atoms, in a volumetric compression test.

5.2. Boron Carbide

Boron carbide (B_4C) is a unique material with exceptionally high strength and low density. However, it undergoes a deleterious deformation behavior called amorphization, where it loses its crystalline order under high pressures such as those which occur beneath indentation and under impact [8]. Therefore, current efforts focus on understanding the root cause or underlying mechanism responsible for the occurrence of this unique deformation behavior and develop strategies to mitigate the incidence of this mechanism so as to produce ultrastrong boron carbide.

Due to its unique rhombohedral crystal structure, numerous polymorphs can be formed in a fabricated boron carbide depending on the position of the carbon atoms in this crystal structure. Regardless of the polymorphs present in the fabricated material, density functional theory (DFT) calculations have shown that its crystal structure consists of large void spaces, referred to as ‘cage space’ (Fig. 3a), which strongly influence the deformation behavior of the material [8a]. During deformation, the chain atoms can slide (migrate) into these cage spaces, thus causing premature failure of the material. It has also been theorized that filling the void spaces with thermodynamically compatible foreign atoms can prevent this failure mode thus enhancing the strength of B_4C . Fig 3b shows strain energy

as a function of applied strain on undoped and Ni-doped B_4C .

Fig. 4 shows [8a] amorphization bands which can be theoretically treated within our framework, as has already been demonstrated for shear bands in nanopolycrystals and bulk metallic glasses by adopting a pressure-dependent gradient plasticity model. In particular, band widths and spacings, as well as critical local strains required for the emergence of such localized deformation zones, can be evaluated, along with the critical grain size for fully eliminating the incidence of amorphization. This is analogous to suppressing phase separation in our spinodal decomposition chemomechanical example, as discussed in [21]. Now, however, the action of diffusion species is formally replaced by the action of dopant/nanocages complexes. The situation can also be treated in analogy to shear banding and related stability studies for bulk metallic glasses where the governing deformation mechanism is “free volume” evolution [21]. Analogous results can be derived here for B_4C and compared with recent investigations by DeVries et al. [8b] showing that reduction of the grain size from 10 microns to 300 nanometers can significantly reduce the propensity for amorphization. Work in progress employing nanopowders suggests that it is possible to produce materials with different grain sizes as small as 20 nm to evaluate the propensity for amorphization using indentation and TEM investigations along with theoretical stability studies.

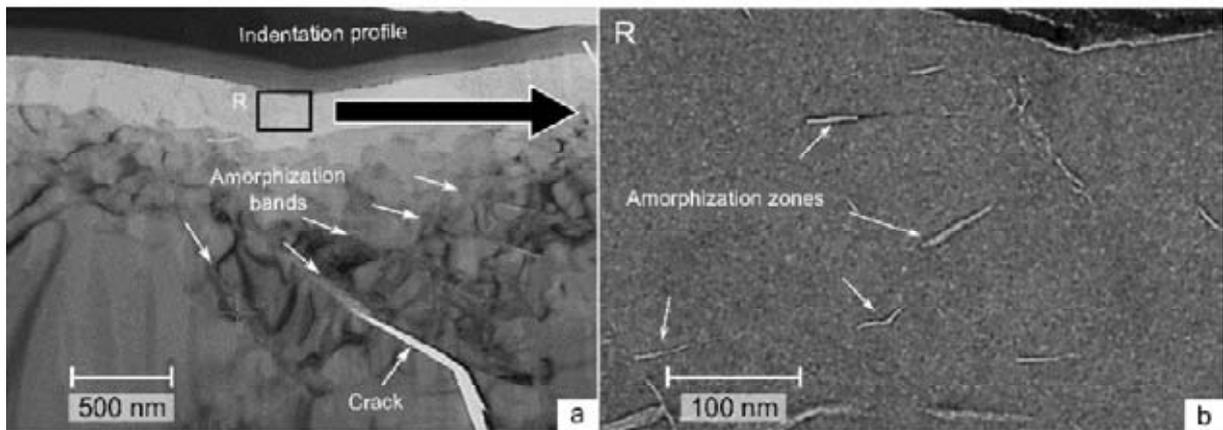


Fig. 4. (a) Transmission electron microscopy (TEM) of region under B_4C indentation revealing amorphization bands and a crack, inset marked 'R', magnified in (b) shows dispersed amorphization zones.

5.3. Brain Tissue

Cavitation damage in human organs and brain tissue has been documented in various instances including traumatic injury, organogenesis, stroke and Alzheimer disease [9]. Typical examples are shown in Fig. 5 below [9c-e]. Recent reviews discuss the role of brain cells, microglia in particular, and their activation during Alzheimer disease (AD) pathogenesis, affecting neurons behavior and the development of amyloid ($A\beta$) plaques, without commenting on possible effects related to porosity development at the cell and tissue levels. Moreover, the importance of mechanical stress effects [36-38] has only very recently been emphasized, but not accounted for in the very limited number of kinetic models [39,40] that have appeared in the literature.

The hypothesis to be examined here is to determine if an evolution equation for a micro/nanoporosity variable can be formulated for neurodegeneration damage in living brain tissue, by mimicking our approach used for micro/nanoporosity damage in non-living materials under the action of mechanical stress. Local mechanical stress has a dual origin: it may either be induced externally due to applied load, or generated internally due to interaction between cells and the much stiffer amyloid fibrils/plaques. In fact, AFM tests and MD simulations [41] for amyloid fibrils determined tensile deformation and fracture properties which were shown to depend on fibril length. In particular, a fracture toughness of $\sim 30 \text{ kcal mol}^{-1} \text{ nm}^{-3}$ for a $\sim 3 \text{ nm}$ long fibril was obtained, comparable to a spider silk crystal of length $\sim 2 \text{ nm}$. The effect of pulling rate was also determined, but it was found to be insignificant for fibrils $> 15 \text{ nm}$. Such nanomechanical size effects are

thought to be important on the physiology of AD, as they can affect mechanical stability and fracture of surrounding tissue and neural cell evolution. They can be interpreted within our gradient elasticity theory, earlier used to model size-dependent tensile and fracture properties of nano-objects.

Independently of the above, another exploratory task that can be pursued here is concerned with the development of stress-assisted reaction-diffusion type models for brain cells and their evolution during AD progress. While a plethora of such models exist for cancer (without usually accounting for local stress and stress gradient effects), they are entirely absent for AD. Our recent work [42] extending the W-A model for mobile and immobile dislocations to consider four types of structural defects (mobile dislocations, immobile dislocations, grain boundary sliding dislocations, and immobile junction disclinations) will be useful here. It is suggested to undertake the task of developing similar types of equations for activated microglia, astroglia, neurons and $A\beta$ peptides. Linear stability analysis can then be used to determine whether or not useful information can be obtained for the emergence of $A\beta$ senile plaques, commonly used as a biomarker for AD progress.

6. DISCUSSION AND BROADER IMPACT

Broadly speaking, *higher-order gradients* in material modeling at various scales of observation can be traced back to the *van der Waals-Maxwell* theory of liquid-vapor interface, the *Ginzburg-Landau* theory of phase transitions, and the *Cahn-Hilliard* theory of

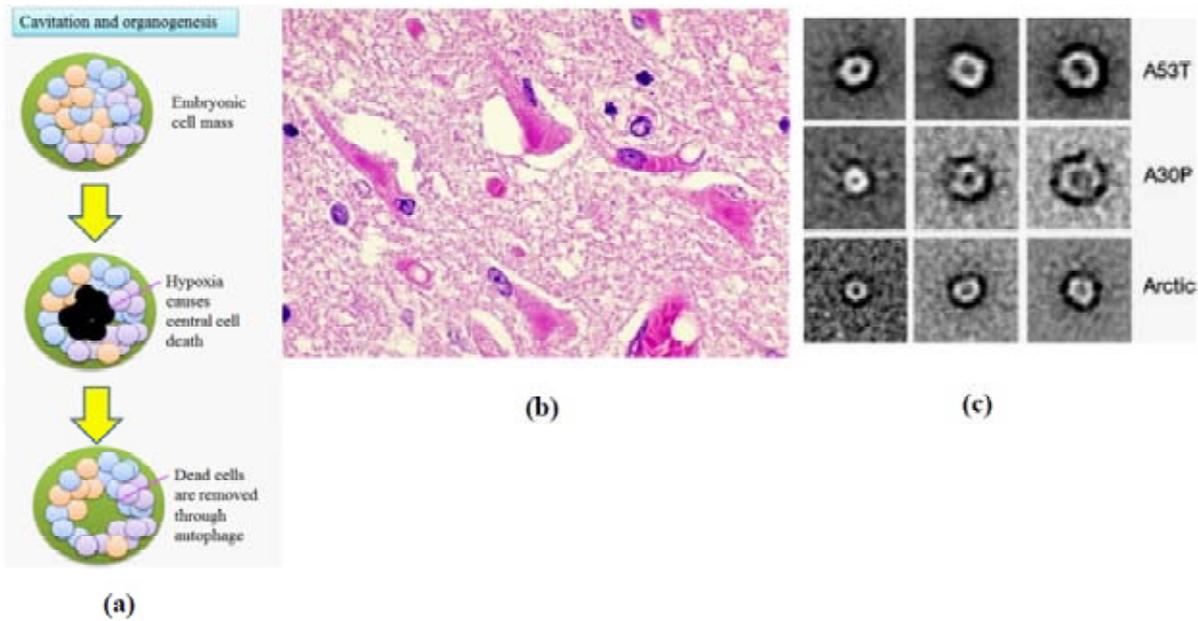


Fig. 5. (a) Cavitation and organogenesis; (b) Porosity development after stroke; (c) Mutations that cause Alzheimer and Parkinson diseases promote the formation of amyloid pores.

spinodal decomposition. More recently, gradients have also been employed in *generalized gradient approximations (GGA)* of *density functional theory* and *phase field theories* [43]. In particular, higher-order gradient theories of remarkable resemblance to the author's initial Laplacian-based models have been used in other fields of engineering science and biology. We refer, in particular, to the *diffusive Johnson-Segalman stress model* for interpreting shear band and pattern formation in complex fluids [44]; the *a-model* for turbulence employing the Laplacian of the symmetric part of the velocity gradient [45]; the *diffusion-reaction model* for crack pattern formation in earth masses [46]; and the "*Go or Grow*" model [47] for cancer. The first two are similar in spirit and form with the author's initial models on gradient plasticity and gradient elasticity. The last two are identical or similar in form with the Walgraef-Aifantis (W-A) model for dislocation patterning. The two families of "aged" and "new born" cracks are shown [46] to obey the W-A equations for "immobile" and "mobile" dislocations. The same holds for the two families of "immotile" and "motile" cells introduced in the cancer model [47]. Last, but not least, reference is made to Chapter 6/Vol. II of Murray's treatise of mathematical biology [48]. His chemomechanical treatment of morphogenesis provided an alternative to Turing's seminal reaction-diffusion model by incorporating the mechanical stress generated during cell crawling within the extracellu-

lar matrix (ECM). His gradient-dependent mechanical equations are of the same form as the author's gradient elasticity model and the cell mobility equations are of the same form as the author's higher-order diffusion theory. It is this analogy between modeling of "nonliving" and "living" materials that has motivated us to suggest brain cell evolution during AD neurodegeneration, as a case-study problem. Our proposed general formulation and anticipated new results should be of interest to the above research areas leading to a multidisciplinary cross-fertilization. Describing and controlling chemomechanical instabilities and associated spatio-temporal pattern formation could lead to **(i)** new protocols for designing engineering materials with exceptional properties, optimize their performance in aggressive environments and prevent malfunctioning and failure; **(ii)** new understanding for geological processes such as snow avalanches, landslides and earthquakes; **(iii)** new tools and biomarkers for monitoring neurodegeneration and progress of AD.

ACKNOWLEDGEMENTS

The support of the Ministry of Education and Science of Russian Federation under Mega Grant Project "*Fabrication and Study of Advanced Multi-Functional Metallic Materials with Extremely High Density of Defects*" (No. 14.Z50.31.0039) to Togliatti

State University is gratefully acknowledged. Particular thanks go to M. Dorogov and M. Gutkin, as well as to Professors A. Vikarchuk and A. Romanov, who provided material and figures for the Appendix that follows after the list of references. The support of Aristotle University to conduct in the Laboratory of Mechanics and Materials earlier research projects on gradient mechanics sponsored by European Community (Marie-Curie, ERC, INTAS, TMR/RTN) and General Secretariat of Research and Technology of Greece was also helpful.

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APPENDIX: SGS ELECTRODEPOSITED MATERIALS AND STRUCTURES

The modest goal of this Appendix is to introduce a specific class of novel technological materials with metastable “far from equilibrium” spatially-inhomogeneous structures (SGS), where internal stress, developed surface, and chemical agent cooperate during fabrication and subsequent use. Fabrication is achieved by electrodeposition and electrocrystallization leading to metallic nanoparticles and distorted microcrystals having five-fold symmetry and containing a high concentration of crystalline structural defects (dislocations, twins

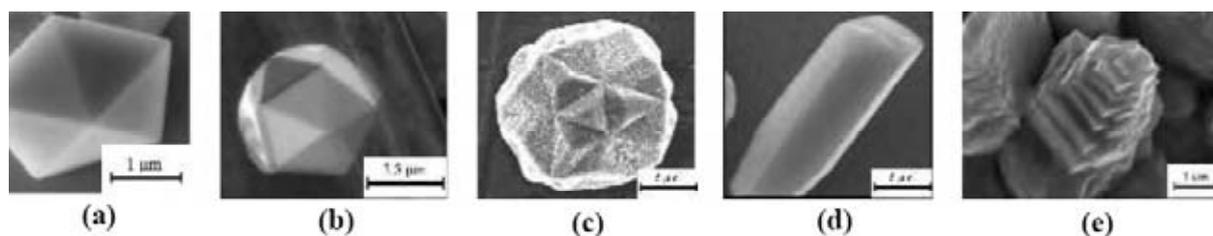


Fig. A1. Copper pentagonal particles and crystals: (a) decahedral small particles (DSPs); (b) icosahedral small particles (ISPs); (c) stellated pentagonal polyhedra (SPP); (d) pentagonal whiskers (PWs); (e) pentagonal pyramids (PPs).

and especially disclinations). In addition to their bulk nanoscopic structural heterogeneity, they also exhibit a nanomorphous developed surface, thus providing a large area for chemical activity. The combination of the cooperative action of internal stress (due, for example, to disclination defects) and chemistry (due, for example, to a chemical agent) makes these SGS material systems ideal for use as filters and nanocatalysts in various areas of petrochemical industries, water purification enterprises, as well as the medical and ecology sectors.

According to their structure and properties, SGS materials may be viewed as “intermediate” between amorphous and crystalline. In Fig. A1 we show representative examples of this class of materials: (a) decahedral small particles (DSPs); (b) icosahedral small particles (ISPs); (c) stellated pentagonal polyhedra (SPP); (d) pentagonal whiskers (PWs); (e) pentagonal pyramids (PPs).

The micro-objects listed above are very promising technologically and have already found various applications in practice [A1-A3]. In particular, DSPs are used as anti-friction additives in motor oils; ISPs are catalysts capable of performing very well in modern fluidized bed reactors; ISPs and SPP form the basis for preparation of “engineered” or developed surfaces with nanowhiskers of copper oxide for photocatalysts working in the visible light range; PWs are efficiently employed for producing cantilevers, microsyringes and composite microwires; PPs can be used to produce effective catalysts intended for destruction of practically all organic and toxic contaminants present in the air and water. Of particular scientific and practical interest are metallic disclinated microcrystals (DMCs) obtained by electrodeposition (Fig. A2), containing disclination type defects (partial disclinations, ragged boundaries, misorientation bands, and twin lamellae) in the initial state, and also possessing energy absorbing fragmented structure, developed surface and unique

mechanical, physical, and chemical properties. Moreover, by compaction or electrodeposition of metallic microparticles with SGS, one can fabricate coating and bulk materials with metastable defect structure and unusual properties (Fig. A3).

Even though the aforementioned new class of SGS materials is very promising with a wide range of applications in modern technology, systematic studies are absent and only a few examples are available, based on rather empirical trial and error procedures. It is noted, in particular, that the proposed gradient chemomechanics platform can provide an effective framework for describing the detailed nonsingular internal stress fields associated with accommodating disclinations in the bulk of SGS objects, by also controlling the development of their enclosing surface. Both internal stress and excess surface are factors directly influencing diffusion and chemical reactions during material processing or component use.

Previous processing/experimental studies of SGS metallic material systems [A4] focus on electrodeposition-based fabrication methods of perfect and defective micro- and nano-sized pentagonal objects (DSPs, ISPs, SPP, PWs and PPs), along with characterization techniques to reveal the features of structure and growth mechanisms. Theoretical modeling of the mechano-physico-chemical properties of SGS objects by expanding our internal length gradient (ILG) mechanics the ILG approach to include chemomechanical couplings as suggested in [21], will enable the establishment of process-structure-properties relationships for SGS materials; with the emphasis, in particular, on the interactions between “bulk” metastable defect patterns and “surface” morphology, as well as on the implementation and application of SGS metallic materials to a variety of technology, energy, and biomedicine sectors, with potential benefits to economy and society.

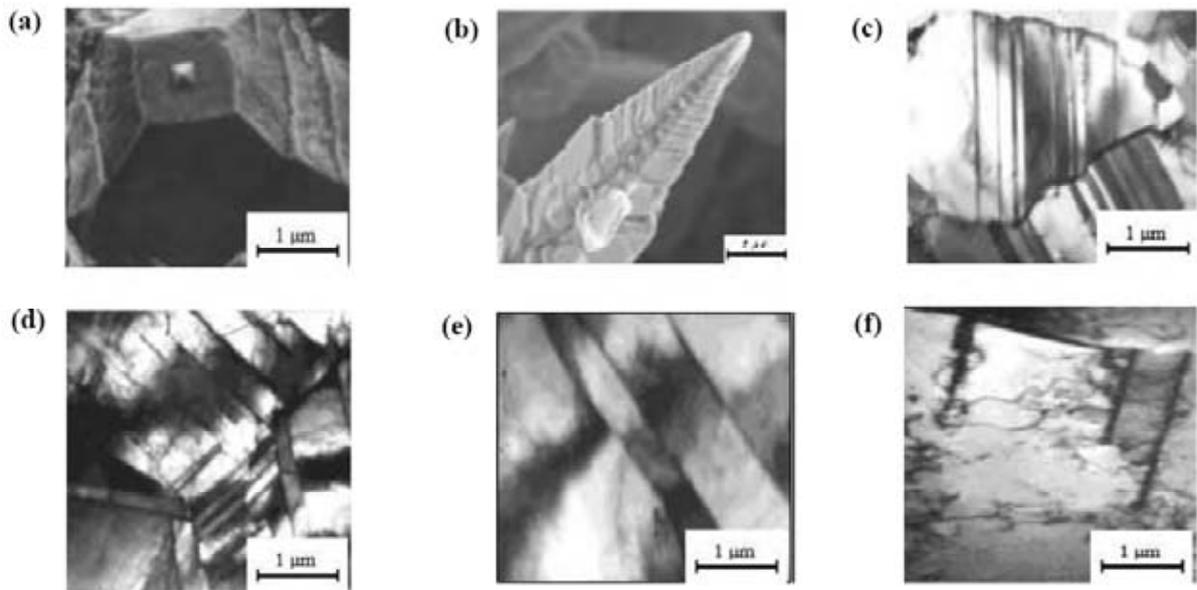


Fig. A2. Crystals with developed surface, defected and fragmented structure: (a)-(d) electrolytic copper; (e)-(f) electrolytic nickel.

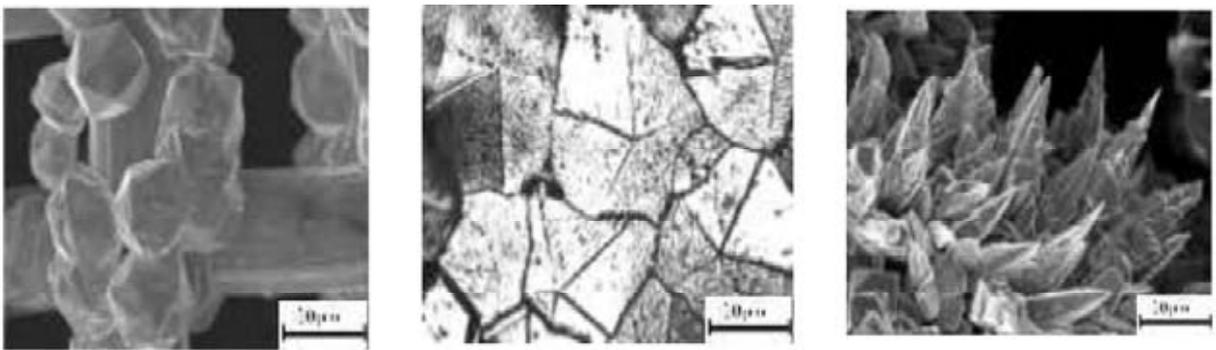


Fig. A3. Layers, coatings and bulk materials based on pentagonal and defect microcrystals.

Figures A4-A5 are extracted from a progress report of this work [A4]. Figure A6 from the same report shows a variety of pentagonal copper crystals obtained by electrodeposition, while Fig. A7 shows the evolution process of obtaining pentagonal crystals from decahedral clusters. This is better illustrated in Fig. A8 for both decahedral and icosahedral clusters, while in Fig. A9, various other objects exhibiting pentagonal symmetry in nature are presented.

We sketch the above possibility directly by outlining the potential implications of gradient elasticity on the stability of an icosahedral (ISP) particle (i.e. a micro/nano particle with pentagonal fivefold symmetry) for which chemical etching has revealed the existence of an internal void developed during electrodeposition usually followed by thermal treat-

ment, as shown in Fig. A10 [A5]. The internal stress field and corresponding elastic energy for this configuration – viewed as a problem of spherical symmetry with external radius R_1 and internal radius R_0 – was calculated in [A5] by using classical elasticity and disclination theory. Moreover, the pressure P_{ISP} on the inner spherical surface was determined as a function of the size of the particle, the elastic constants, the lattice spacing, the surface energy, the assumed disclination strength, and the ratio of the internal to external radii. Mechanical stability preventing fracture is ensured when $P_{ISP} < P_{max}$ where P_{max} denotes the maximum pressure [$P_{max} = 2\sigma(R_1 - R_0)/R_1$; σ is the fracture stress of bulk material] supported by the spherical-like hollow particle before failure. This fracture criterion can be revisited by using in the aforementioned calculation the gra-

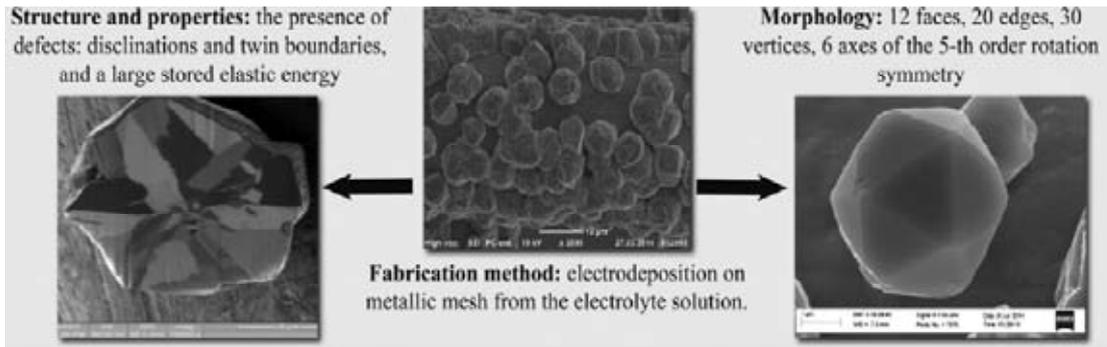


Fig. A4. Metal icosahedral small particles (ISPs) with defects.

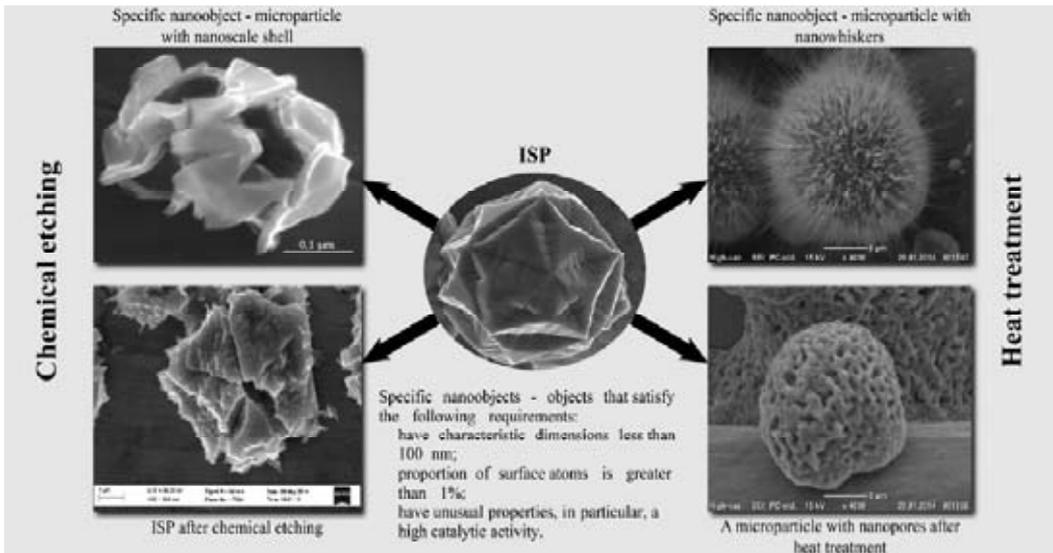


Fig. A5. Preparation of the developed surface of icosahedral small particles.

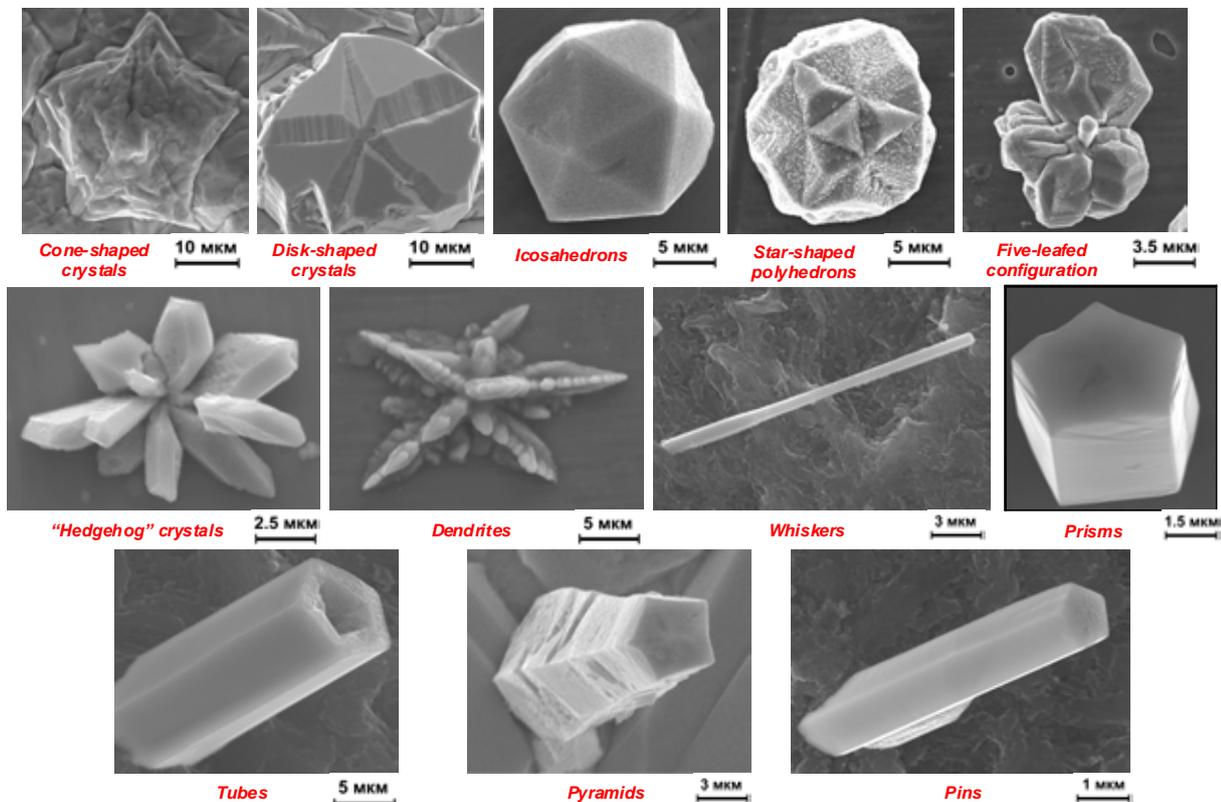


Fig. A6. Different habit planes of electrodeposited pentagonal copper crystals.

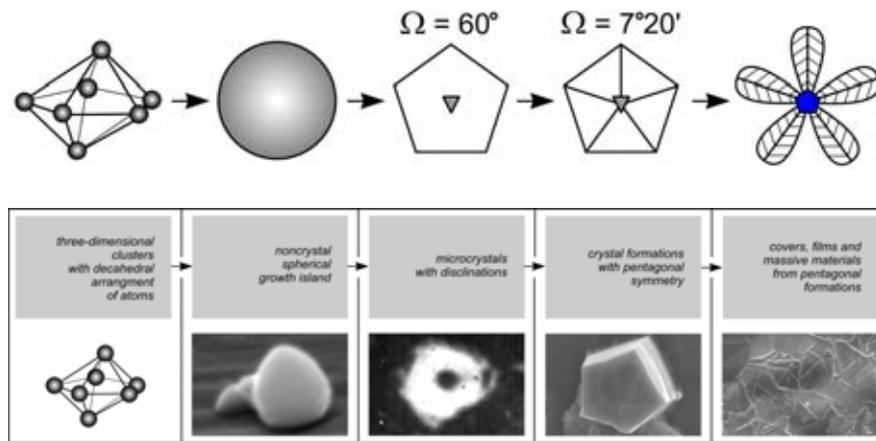


Fig. A7. Evolution scheme and growth model of pentagonal crystals from decahedral clusters.

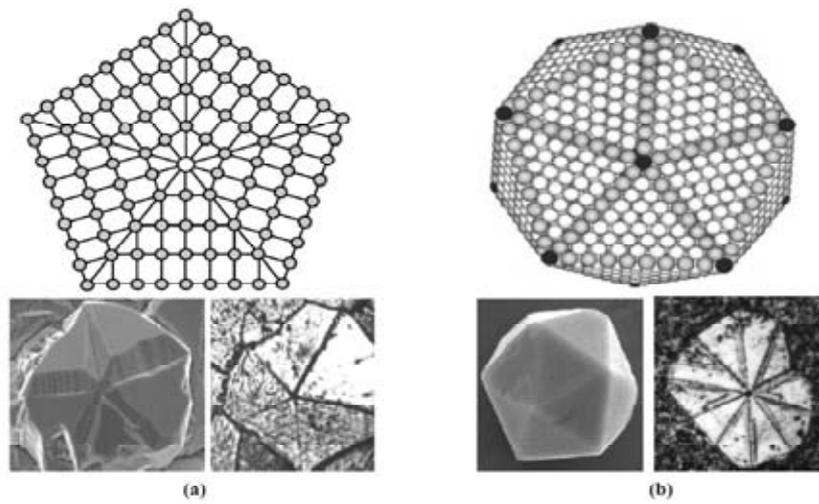


Fig. A8. (a) The result of evolution from decahedral clusters; (b) The result of evolution from icosahedral clusters.



Fig. A9. Pentagonal symmetry in nature.

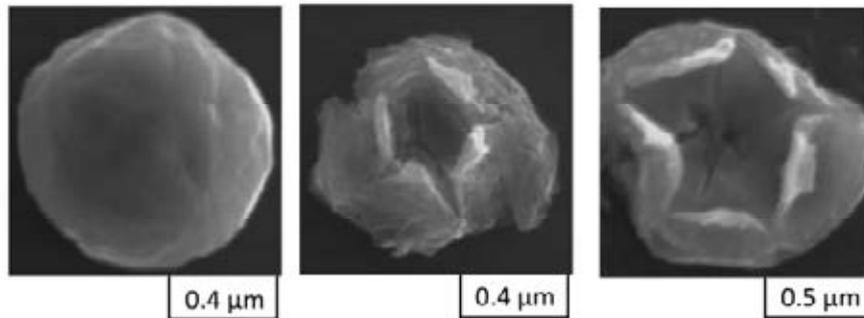


Fig. A10. ISP particle before and after being subjected to chemical etching. The existence of an internal void is revealed.

dient elasticity solution of [A6], giving rise to an alternative fracture criterion depending, in addition, on the ratios of internal length with respect to the particle's radii.

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