



Graded Materials for Resistance to Contact Deformation and Damage

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The mechanical response of materials with spatial gradients in composition and structure is of considerable interest in disciplines as diverse as tribology, geology, optoelectronics, biomechanics, fracture mechanics, and nanotechnology. The damage and failure resistance of surfaces to normal and sliding contact or impact can be changed substantially through such gradients. This review assesses the current understanding of the resistance of graded materials to contact deformation and damage, and outlines future research directions and possible applications for graded materials.

The composition, structure, and mechanical properties of a material may vary, continuously or in discrete steps, with depth beneath a free surface. Gradations in microstructure and/or porosity are commonly seen in biological structures such as bamboo, plant stems, and bone, where the strongest elements are located in regions that experience the highest stresses (1, 2). Gradual changes in the elastic properties of sands, soils, and rocks beneath Earth's surface influence the settlement and stability of structural foundations, plate tectonics, and the ease of drilling into the ground (3, 4). In engineered materials, gradations in composition occur unintentionally, for example, as a consequence of lattice and grain boundary diffusion, oxidation, and clustering of atomic species or reinforcement particles. In many cases, such gradations may not even be desirable. Learning from nature, materials scientists increasingly aim to engineer graded materials that are more damage-resistant than their conventional homogeneous counterparts. This is particularly important at surfaces or at interfaces between dissimilar materials, where contact failure commonly occurs. With established methods currently available to synthesize and process materials, gradations in composition, structure, and properties could be engineered over a wide range of length scales ranging from nanometers to meters.

Motivation for the Use of Graded Materials

It has long been recognized that gradients in surface composition can improve the mechanical performance of a material [e.g., (1, 2)]. Early examples of the use of synthetic materials with graded properties can be

traced back to the blades of Japanese steel swords using a graded transition from a softer and tougher core to a hardened edge (5). Carburizing and nitriding treatments are commonly given to steel surfaces to impart hardness, and fatigue and wear resistance in transmission gear teeth. However, theoretical understanding of such phenomena has not received much attention.

Graded transitions in composition, either continuous or in fine, discrete steps, across an interface between two dissimilar materials (such as a metal and a ceramic), can be used to redistribute thermal stresses (6, 7), thereby limiting the stresses at critical locations and thus suppressing the onset of permanent (plastic) deformation, damage, or cracking (8, 9). Graded transitions can also reduce stress concentrations at the intersection between an interface and a free surface (10, 11). Similarly, the local driving force for crack growth across an interface can be increased or reduced by altering the gradients in elastic and plastic properties across the interface (12, 13). Smooth transitions in composition across an interface also improve interfacial bonding between dissimilar materials (2), thereby facilitating the deposition of much thicker surface coatings (typically more than 1 mm thick) than is feasible with sharp interfaces. In some applications, such as diesel-engine piston heads, thicker coatings impart better protection against thermal degradation. Thin films with graded composition play an important role in heteroepitaxial multilayers used in semiconductor devices. The graded films are deposited between a substrate and a quantum well to control the density and kinetics of threading dislocations. They protect the quantum wells and light-emitting diodes with specific optoelectronic properties from the deleterious effects of these dislocations, which are introduced at interfaces as a result of lattice mismatch and thermal expansion mismatch strains during layer deposition (14).

In the late 1980s and early 1990s, interest

in graded materials primarily focused on controlling thermal stresses in structures exposed to very high temperatures (~ 2000 K) in components used in aerospace applications and solid-oxide fuel cells, and in energy conversion systems using thermoelectric or thermionic materials (15). The use of graded layers and interfaces in materials exposed to high temperatures for long periods of time, however, is complicated because of diffusion. Research has therefore increasingly focused on lower temperature applications of graded materials on the basis of their resistance to contact damage. This research direction was also motivated by advances in techniques for controlled indentation and by a growing need to develop damage-resistant surfaces and coatings—for example, in magnetic storage media, nano- and microelectromechanical systems, barrier coatings for structural components, dental implants, articulating surfaces in hip and knee prostheses, and penetration-resistant materials for armor plates and bullet-proof vests (16).

Contact Resistance of Graded Surfaces

The indentation of a surface with a sharp or blunt probe (indenter) provides basic and quantitative information that typifies the resistance of the surface to normal contact. If the spatial variation of the mechanical property with depth beneath the indented surface is well defined and known a priori, analysis of the indentation load versus indenter penetration depth into the surface can also provide valuable information about the contact-damage resistance of the surface.

Theories of normal elastic contact. Over the past several decades, the geomechanics community has studied the evolution of stresses and displacements, under a point load, in elastically graded substrates (3, 4, 17–22). In these studies, the Young's modulus, E , was varied as a function of depth beneath the indented surface, z , according to the power-law function $E = E_0 z^k$, where E_0 is the reference Young's modulus at the surface and $0 \leq k < 1$ ($k = 0$ for a homogeneous material). Such variations in elastic modulus are typically seen in sandy soils and consolidated clay deposits. These studies did not provide general solutions of the variation of indentation load (P) with the depth of penetration (h) of the indenter into the surface for common indenter geometries (such as a sphere, cone, cylinder, or a pyramid) or with

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the contact radius, a , of the indenter with the substrate, which are needed for direct experimental validation of such theories.

A general theory for frictionless normal indentation of elastically graded materials by point loads and axisymmetric indenters was recently developed (23) for two general variations in Young's modulus with respect to depth: the power-law variation, $E = E_0 z^k$, and an exponential variation, $E = E_0 e^{\alpha z}$ (where $1/\alpha$ signifies a length scale associated with the gradient in modulus beneath the surface when $\alpha \neq 0$), for any specific value of Poisson ratio, ν (the ratio of the negative of the lateral strain to the axial strain in a uniaxial tension test), which was taken to be spatially invariant. Explicit analytical expressions were derived to relate the indentation load, P , to the penetration depth, h , or the contact radius, a , for different indenter geometries. Computer simulations of the simultaneous variation of the Poisson ratio, ν , with depth revealed that the effect of varying ν was substantially smaller than that of varying E .

Predictions of resistance to normal elastic contact. Consider an elastically graded material with constant ν that is subjected to indentation by a rigid sphere of radius R (Fig. 1A). Let the Young's modulus increase or decrease exponentially, or remain constant as a function z (Fig. 1B). A homogeneous elastic material exhibits an indentation response for which P scales with $h^{1.5}$ (Fig. 1C). If E increases beneath the indented surface, the indentation response is stiffer; the stiffness of the response reaches a vertical asymptote as the limit of the exponential increase in elastic modulus is reached. If $\alpha < 0$, the elastically softer material beneath the indented surface promotes a compliant response compared with a homogeneous solid; the indentation load-carrying capacity vanishes in the asymptotic limit as E decreases exponentially beneath the surface.

Theory (23) also predicts that when the modulus increases (or decreases) monotonically with depth, peak values of local tensile stresses, which result in the nucleation of damage at the surface, are spread further into the interior (or moved closer to the surface) compared with a homogeneous material. This is because the underlying material has a higher (or lower) E than the surface and can thus sustain a greater (or lower) stress.

Experimental evidence. Experimental verification of the effect of a continuous elastic gradation on indentation cracking resistance requires a composite microstructure with at least two different constituent phases of different elastic moduli, whose relative concentrations are gradually changed beneath the surface. Synthesis of such a system at elevated temperatures and subsequent cooling to room temperature would introduce large ther-

mal residual stresses, thereby complicating interpretations of such experiments. This problem can be circumvented by synthesizing a "clean" model system in which the constituent phases have the same coefficient of thermal expansion (CTE) and Poisson ratio (ν), but markedly different Young's moduli.

Such a graded elastic system has been produced by infiltrating an oxynitride glass into a fine-grained α - Si_3N_4 matrix (24). The α - Si_3N_4 matrix, consisting of 93.7% of the bulk Si_3N_4 , contained elongated grains, 0.5 μm in diameter and 2 μm in length, in a glass matrix. The infiltrated oxynitride glass, hereafter referred to as SiAlYON, had a chemical composition close to that of the glass matrix in the bulk Si_3N_4 . Infiltration of SiAlYON at 1500°C for 2 hours produced a continuously graded elastic composite, with ~ 30 volume % glass at the surface gradually decreasing to 0% about 0.5 mm beneath the surface (Fig. 2A). The elastic modulus of α - Si_3N_4 is 320 GPa and that of SiAlYON glass is ~ 110 GPa; $\nu \approx 0.22$ for both materials. The CTE of α - Si_3N_4 is essentially the same as that of the infiltrated glass, and therefore no long-range internal stresses develop in the graded composite. However, because the modulus α - Si_3N_4 is three times that of glass, a change in glass composition from 30% at the surface to 0% 0.5 mm beneath the surface resulted in a corresponding smooth variation of elastic modulus from about 225 GPa at the surface to about 315 GPa over the same depth (Fig. 2B).

In a cross section perpendicular to the indented free surface of the homogeneous α - Si_3N_4 ceramic (Fig. 2C), classic Hertzian cone cracks are seen after spherical indentation to a maximum load of 3 kN with a WC-Co indenter with a radius of 4.76 mm. These cracks form at the contact perimeter where the maximum tensile stresses develop. Homogeneous SiAlYON glass, and a nitride/glass composite of uniform composition equal to the surface composition of the graded material, develop similar cone cracks under spherical indentation. Despite the lower strength and lower toughness of the glass at the surface, the graded nitride-glass composite could sustain an indentation load as high as that in homogeneous α - Si_3N_4 without forming any cone cracks (Fig. 2D), solely as a consequence of the reduction in maximum tensile stress at the contact surface due to grading. Similar beneficial effects of modulus gradations have been demonstrated in a fine-grained aluminum oxide infiltrated with aluminosilicate glass (25).

Resistance of graded materials to sliding-contact damage. Experiments of frictional sliding of spheres on elastically graded surfaces also point to the beneficial effects of modulus gradations. Frictional sliding by a steel sphere on an alumina-glass graded composite (with CTE-matched alumina and glass

phases), with a power-law increase in modulus beneath the sliding surface, showed that a graded material with a 40 vol. % soft glass phase at the surface could sustain as high a load as the homogeneous alumina without developing any "herringbone" cracks (26). These circular cracks develop around the contact perimeter under the influence of the maximum principal tensile stress (27, 28). The graded composite could sustain a normal load more than twice that carried by the monolithic glass before herringbone cracks developed in the glass. Despite its low strength and low toughness at the contact

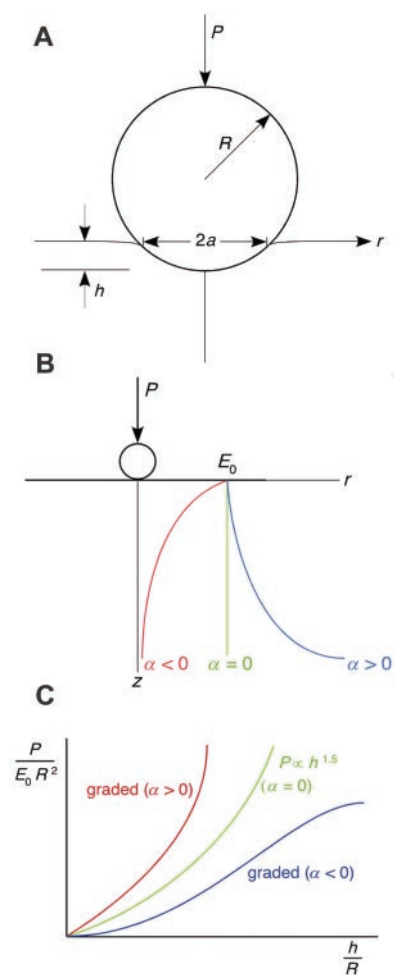


Fig. 1. Indentation response of an elastically graded surface. (A) Details of the contact region underneath the spherical indenter subjected to a load P . (B) Schematic illustration of an exponential increase ($\alpha > 0$) or decrease ($\alpha < 0$) in Young's modulus as a function of depth z beneath the indented surface; $E = E_0 e^{\alpha z}$, where E_0 is Young's modulus at the surface and $\alpha = 0$ represents an elastically homogeneous material. (C) Schematic illustration of the variation of normalized indentation load as a function of normalized depth of penetration for the homogeneous and graded surfaces. For the graded surfaces, the variation of P with the penetration depth h is a complex function of the surface and indenter properties, the indenter radius, and the gradient in elastic modulus α (23).

response is a function of the gradient in strength, m , indenter shape and tip geometry, and strength (Fig. 4C). If σ_y decreases with depth, the material rapidly loses its capability to sustain the indentation load, and the indenter sinks into the substrate. If σ_y increases beneath the indented surface, the indentation stiffness is higher compared with that of a plastically homogeneous material.

A comprehensive theoretical framework for the interpretation of blunt and sharp indentation of plastically graded metals with different strain-hardening characteristics is presently unavailable. The extent to which changes in the P - h response arising from plasticity gradients at the surface translate

into contact-damage suppression and wear resistance remains to be established through systematic experiments. Such studies should also assess the complex interactions among contact loads, contact geometry, property gradients, the mechanics of contact fracture and fatigue at surfaces, and the evolution of wear damage in different environments.

Issues of length scale. Analyses of homogeneous, isotropic materials by contact mechanics require consideration of different length scales. For continuum analyses to be valid, mechanical length scales, such as the contact radius a or the depth of penetration h (which are influenced by the shape and size of the indenter), should be large compared with the characteristic structural size scale such as grain size. In graded systems (for example, Fig. 2), the zone of influence of the contact loads beneath the indented surface should be sufficiently large to capture significant variations in elastic and plastic properties. In geological systems, this size scale could be hundreds of meters (as in the case of drilling to lay the foundation for a tall structure), whereas for nanostructured coatings it could be as small as a few nanometers. The yield strength of metallic films scales with the square root of the dislocation density, and therefore gradients in dislocation density over small distances beneath a surface could also induce plasticity gradients which, in turn, could strongly influence nanoindentation response. Although strain-gradient plasticity theories seek to address such length-scale issues by accounting for higher order effects (32, 33), systematic experiments at different length scales, which would provide estimates of the regions of validity of such theories, are currently unavailable.

Continuum descriptions of *elastic* indentation response are known to be valid to indentation penetration depths as small as a few nanometers (34). However, experiments show (34, 35) that even homogeneous thin films of crystalline metals exhibit discrete jumps in indentation response as a consequence of defect nucleation and motion. In general, gradients in elastic and plastic properties in the vicinity of the surface should be tailored in such a way that the field of indentation produced around the contact region samples the entire length scale over which property gradients occur, so that the full effect of compositional gradation can be realized.

Outstanding Scientific Issues and Challenges

The use of graded materials in contact-critical applications has important implications for a multitude of disciplines. Studies of the effects of compositional, structural, and property gradients on the resistance of surfaces to normal, sliding, rolling, or fretting contact and wear have only recently begun to emerge. This sec-

tion highlights some possible applications, and examines key challenges.

With recent advances in instrumented micro- and nano-indentation (36), depth-sensing indentation is rapidly becoming a research tool to characterize the elastic, plastic, and fracture characteristics of a variety of engineering materials and surfaces at length scales approaching atomic and molecular dimensions. Such interest is also spurred by the rapid miniaturization of features and components in microelectronic devices, magnetic storage media, and nano- and microelectromechanical structures. Examples include electromechanical and biological sensors and actuators, and miniature power devices such as microturbines, motors, and pumps (37, 38).

In many of these applications, graded surfaces provide appealing prospects for controlling surface damage and failure during repeated contact. Progress in materials synthesis—for example, by molecular beam epitaxy, vapor deposition, three-dimensional printing, bulk and surface micromachining, and lithography—now afford the flexibility to fabricate gradients at surfaces with dimensions approaching a few atomic layers to macroscopic size scales (1, 2, 37, 38). However, systematic studies of the effects of compositional gradation on the indentation response and contact-damage resistance and failure of crystalline and amorphous solids and surface coatings have thus far not been conducted. The mechanisms of damage evolution in these situations also have not been examined by characterization techniques such as atomic force or electron microscopy. Further interest in the resistance of graded materials to contact loading stems from their possible use as penetration-resistant surfaces.

Hertzian cone cracks (Fig. 2C) are known to be deleterious to contact resistance and tribological performance at surfaces. The suppression of such cracks through modulus gradients provides one avenue for enhancing the contact-damage resistance without introducing tensile residual stresses in the bulk. Alternative methods, such as tempering, layering, phase-transformation, coating, ion-exchange, differential densification, grinding, and surface heat treatment, promote compressive residual stresses at contact surfaces but also lead to the concomitant generation of tensile residual stresses in the bulk of the material (24, 25), which can promote cracking. On the other hand, the introduction of heterogeneities, such as second-phase particles, to introduce compressive residual stresses at surfaces and thereby suppress contact cracks has the deleterious effect of imparting nonlinearity to the deformation response of the material which, in turn, can lead to an inferior tribological response and fatigue life.

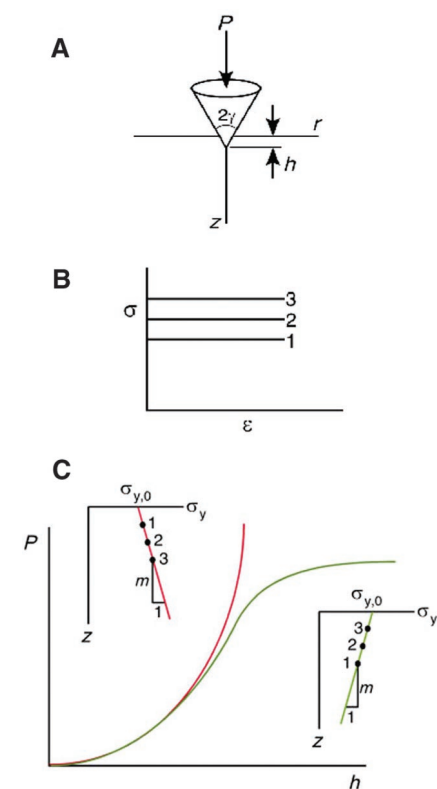


Fig. 4. Conical sharp indentation of a plastically graded surface. (A) Details of contact around the conical indenter. The included tip angle of the conical indenter is 2γ . (B) Stress-stress response, σ , versus ϵ at three different points (1, 2, 3) below the indented surface. (C) The yield strength of this rigid plastic material, σ_y , either increases or decreases linearly with depth below the surface z (as indicated by the red or green straight line, respectively). The yield strength value is $\sigma_{y,0}$ at the surface, and the slope of the σ_y versus z plot is m . For a plastically homogeneous surface indented by a conical indenter, P scales with h^2 . However, for the graded surface, theory (31) indicates that $P = C_1 h^2 + C_2 h^3$, where $C_1 = 11.88\sigma_{y,0}(\tan \gamma)^2$, and $C_2 = Bm\sigma_{y,0}(\tan \gamma)^3$, where $B = 13.86$ for $m > 0$ and $B = 16$ for $m < 0$. A positive (negative) value of m leads to a stiffer (more compliant) indentation response than that for a homogeneous material for which $m = 0$.

It is important to note that the use of a low-strength and low-toughness layer at a contact surface could lead to an increased susceptibility to wear damage and material loss, despite the benefits of suppressing indentation cracks during normal loading and frictional sliding. Several different strategies can be implemented to overcome these limitations. First, methods other than infiltration can be used to develop stepwise gradients in elastic moduli at the surface where the modulus increases from a hard surface layer (such as Si_3N_4) to a graded layer (with Si_3N_4 and SiC phases). Such graded materials have been synthesized by sintering to enhance resistance to both contact damage and wear (24). Second, a thin (less than 1 μm thick) surface layer of a hard, wear-resistant coating, such as a layer of diamond-like carbon, could be deposited on the graded surface. Because such coatings could be deposited with a Young's modulus range of 45 to 250 GP and with significant improvements in wear resistance, elastic moduli gradations could be introduced near the contact surface while maintaining a wear-resistant layer at the top layer of contact. If the elastic field of indentation spreads well into the graded layer, beneficial effects of modulus gradations would be expected with respect to contact-damage suppression and wear resistance.

Wear-resistant, nanocrystalline surface coatings, with grain sizes as small as a few tens of nanometers, can now be synthesized—for example, with thermal spray, electrodeposition, electrophoretic deposition, sputter deposition, and metal-organic chemical vapor deposition (39). Many of these methods can create surface layers in which the grain sizes are graded smoothly from the surface to the bulk, thereby inducing controlled gradients in strength and fracture toughness. Similarly, gradients in porosity can be tailored beneath contact surfaces to improve resistance to contact damage as, for example, in coatings used to protect articulating surfaces in hip and knee prostheses.

Such gradients in pore concentration could also be used to facilitate the growth of bone and tissue in many biomedical applications. In polymeric materials (such as ultrahigh molecular weight polyethylene, which is used, for example, in knee prosthesis), gradients in elastic properties can be induced by the introduction of spatial variations in degree of crystallinity and/or molecular weight.

In summary, recent theoretical and experimental work has established that controlled gradients in mechanical properties offer unprecedented opportunities for the design of surfaces with resistance to contact deformation and damage that cannot be realized in conventional homogeneous materials. With currently available materials synthesis and processing capabilities, engineered gradations in properties, over nanometer to macroscopic length scales, offer appealing prospects for the design of damage-, fracture-, and wear-resistant surfaces in applications as diverse as magnetic storage media, microelectronics, bioimplants for humans, load-bearing engineering structures, protective coatings, and nano- and microelectromechanical systems.

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