Progress in Materials Science 88 (2017) 467–498

Contents lists available at ScienceDirect

Progress in Materials Science

journal homepage: www.elsevier.com/locate/pmatsci

Functional gradients and heterogeneities in biological materials: Design principles, functions, and bioinspired applications

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ARTICLE INFO

Article history:
Received 19 April 2016
Received in revised form 25 October 2016
Accepted 24 April 2017
Available online 25 April 2017

Keywords:
Gradient
Heterogeneity
Biological materials
Bioinspiration
Functionally graded materials

ABSTRACT

Living organisms have ingeniously evolved functional gradients and heterogeneities to create high-performance biological materials from a fairly limited choice of elements and compounds during long-term evolution and selection. The translation of such design motifs into synthetic materials offers a spectrum of feasible pathways towards unprecedented properties and functionalities that are favorable for practical uses in a variety of engineering and medical fields. Here, we review the basic design forms and principles of naturally-occurring gradients in biological materials and discuss the functions and benefits that they confer to organisms. These gradients are fundamentally associated with the variations in local chemical compositions/constituents and structural characteristics involved in the arrangement, distribution, dimensions and orientations of the building units. The associated interfaces in biological materials invariably demonstrate localized gradients and a variety of gradients are generally integrated over multiple length-scales within the same material. The bioinspired design and applications of synthetic functionally graded materials that mimic their natural paradigms are revisited and the emerging processing techniques needed to replicate the biological gradients are described. It is expected that in the future bioinspired gradients and heterogeneities will play an increasingly important role in the development of high-performance materials for more challenging applications.

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http://dx.doi.org/10.1016/j.pmatsci.2017.04.013
0079-6425/

1. Introduction

The advancement in modern technologies continues to impose more stringent requirements for engineering materials with improved mechanical performance; additionally, there is a pressing need for materials to be more energy-efficient and environmentally-friendly. To address this challenge, there is a continual quest to seek new materials with unprecedented combinations of properties and functionalities, such as stiffness, strength, ductility, toughness and formability, with minimal weight and cost. Unfortunately, many of these properties – prime examples are strength and toughness – tend to be mutually exclusive within individual materials [1,2]. Consequently, the development of new structural materials is invariably an exercise in compromise; this is particularly the case for the traditional design and fabrication strategies which primarily result in homogeneous materials with relatively uniform composition and microstructure, despite the fact that many practical applications encompass heterogeneous states of stress, strain and temperature.

A rational solution to this problem is to adapt the local properties of materials to fit their specific requirements, by locating optimized compositions and architectures in appropriate regions, thereby generating multiple advantages within a single material to create improved global properties. For instance, the mechanical performance of structural materials can be intelligently enhanced by designing superior strength and ductility in those regions experiencing the highest levels of stress and strain, respectively [3–5]. In such a scenario, materials can be made to demonstrate site-specific attributes, *e.g.*, composition, architecture and resulting properties, through the inclusion of varying degrees of heterogeneities or gradients. The term “gradient” is employed here in its broad sense to describe the non-uniform nature of materials, frequently near surfaces or internal interfaces, as opposed to a strict homogeneity; it also represents gradual transitions, rather than abrupt changes, between dissimilar nano-/micro-structural features. It has long been recognized that the introduction of spatial gradients can effectively enhance the mechanical and functional performance of materials by, for example, alleviating stress concentrations or singularities, improving interfacial bonding and enabling new functions [3–10]. Indeed, the creation of gradients, or more specifically the development of so-called functionally graded materials (FGMs), offers one promising pathway towards answering the demands for emerging applications of materials.

With respect to such gradients and heterogeneities, Nature provides a rich source of inspiration for the design and fabrication of high-performance synthetic materials and components [5,11–18]. Natural (or biological) materials are generally composites with spatially heterogeneous and tunable properties. These materials have unique characteristics that distinguish them from synthetic ones, which have been referred to as the seven features of the Arzt heptahedron (Fig. 1a) [11,13,16]: (i) self-assembly, (ii) self-healing, (iii) evolutionary and environmental constraints, (iv) importance of hydration, (v) mild synthesis conditions, mostly at temperatures of ~300 K and pressures of ~1 atm, (vi) multi-functionality, and (vii) hierarchy of structure at nano-, micro-, meso- and macro-levels. Despite the vast diversity of biological materials, the building blocks employed by living organisms are limited principally to hard (bio-mineral) and soft (bio-polymer) phases, which invariably display significantly inferior mechanical properties to many synthetic materials. Nevertheless, natural materials, such as seashells, fish scales, bone and teeth, can possess extremely impressive combinations of properties far surpassing those of their constituents; many even outperform their man-made counterparts [11–18]. Such remarkable performance