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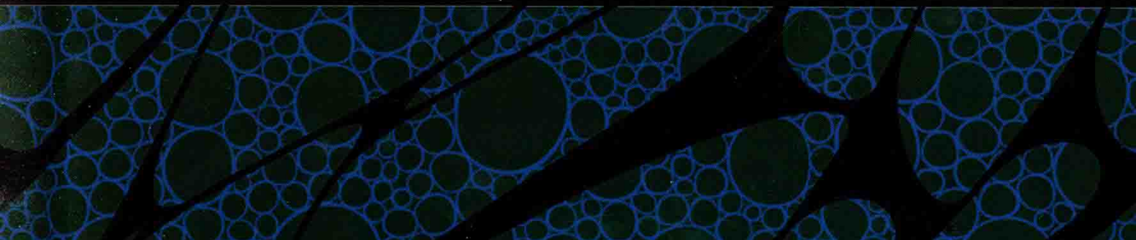

Voids in Materials

From Unavoidable Defects to Designed Cellular Materials

VOIDS IN MATERIALS

From Unavoidable Defects to Designed Cellular Materials

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VOIDS IN MATERIALS

PREFACE

The title of this book, *Voids in materials: From unavoidable defects to designed cellular materials* says everything. All materials have voids at some scale. Sometimes the voids are ignored, sometimes they are taken into account, and other times they are the focal point of the research. In this book, however, we take due notice of all of these occurrences of voids, whether designed or unavoidable defects, we define these voids (or empty spaces in materials), categorize them, characterize them, and describe the effect they have on material properties.

After an introductory chapter, we devote a chapter each on intrinsic voids in crystalline materials (such as metals and ceramics) and in polymers. We explain the differences between ideal and real materials as rooted in the voids and defects. We discuss the origins, diffusion, and coalescence of voids/defects and the relation to phenomena such as creep, physical aging, diffusion, glass transition temperature, thermal expansion, how material properties change with size, distribution, and amount of voids, and the implications that voids have on product design. This is followed by a chapter on intentional voids in materials. Oftentimes, the methods and the vocabulary related to foams are material-specific. Similar methods can be called by different names when working with a metal or ceramic. We point out the commonalities in the way the voids are introduced in different materials, highlight the similarities, and point out the different terms used to describe them. In addition to a chapter on intentional voids in bulk materials, we devote a chapter on the introduction of voids into dispersed phases such as particles and fibers. Structures such as nanotubes, hollow and porous spheres, membranes, and nonspherical particles are technologically important in fields as diverse as catalysis, biomaterials, ablation, composite materials, and pharmaceuticals/medicine. A chapter is devoted to cellular materials or foams, wherein we highlight the commonalities in material properties of voids in polymers, metals, and ceramics. Finally broad applications of such cellular materials are described along with techniques used to characterize voids.

Throughout the book we have taken the approach of highlighting the physics and chemistry of the subject matter under consideration while minimizing the mathematical part. Extensive use is made of line drawings and micrographs to bring home to the reader the importance of voids as unavoidable structural defects as well as voids being an element of design to obtain the desired properties in a material. The intended audience for this book are students, researchers, practicing engineers in the fields of materials science and engineering, physics, chemistry, and mechanical engineering.

Finally, we would like to acknowledge our colleagues without whose help we would not have been able to do this project. Gary M. Gladysz would like to thank A. Boccaccini, K. Carlisle, W. Congdon, L. Dai, S. Emets, N. Godfrey, M. Koopman, M. Lewis, J. Lula, U. Mann, G. McEachen, D. Mendoza, B. Perry, W. Ricci, S. Rutherford, C. Sandoval, and V. Shabde. Krishan K. Chawla would like to thank A. Boccaccini, N. Chawla, K. Carlisle, M. Koopman, M. Lewis, and A. Mortensen. Thanks are due to Kanika Chawla and A. Woodman for help with the figures.

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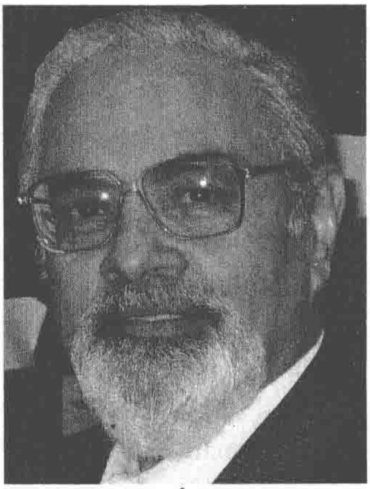
GMG would like to dedicate this to his parents, Edward and Kathy, thank you, and his wife and daughters April, Amelia, and Claire for the constant encouragement!

KKC would like to dedicate this to his wife, Nivi, for always being there!

ABOUT THE AUTHORS

Dr. Gladysz is an owner/partner at Empyreus Solutions, LLC, Seattle WA, USA, where he consults and leads university and government technical interactions. He received his PhD from the New Mexico Institute of Mining & Technology where he participated in the NATO Collaborative Program with the German Aerospace Institute (DLR). Since receiving his PhD, he has led research efforts in university, government, and industrial settings. He has extensive research experience designing and characterizing fibrous composite materials, ceramic composites, polymers, composite foams, and thin films. As a technical staff member at Los Alamos National Laboratory (LANL), he was technical lead for rigid composites and thermoset materials. In 2005 he was awarded the LANL Distinguished Performance Group Award for his work leading materials development on the Reliable Replacement Warhead Feasibility Project. He has served on funding review boards for LANL, National Science Foundation, ACS, and the Lindbergh Foundation. He has been guest editor on four issues of leading materials science journals, including *Journal of Materials Science* and *Materials Science & Engineering*: Dr. Gladysz has organized five international conferences/ symposia on syntactic foams and composite materials. He started and currently chairs the ECI international conference series on Syntactic & Composites Foams: Dr. Gladysz currently lives near Boston, Massachusetts, USA.



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CHAPTER 1

Introduction

1.1 OVERVIEW

So why write a book just on voids as the topic? The answer is simple and twofold—first, the juxtaposition of "empty space" adjacent to solid material seemed, to us, an interesting dichotomy. Second, depending on your perspective or desired outcome, voids can limit or enhance the performance of materials. Is your target a consolidated material or a foam? If your target is a foam, how do material properties change with the type and amount of voids; open cell versus closed cell, the mean size, size distribution, volume fraction of voids, etc.? If your target is a consolidated material, some important questions might be how do properties change with the volume percent, location, geometry, and size of voids? Another interesting question is how do those voids, on the subnanometer and nanometer scale, which are typically not characterized by foam researchers, play into the final properties.

Voids are also very important to understand from a practical engineering standpoint. Even in the most highly engineered densified materials, defects, such as voids, will limit the design of real structures. So along with the theoretical exploration of voids in materials, this book will give examples of these real-world applications so the reader becomes aware of their prevalence in structures all around them.

This book explores such dichotomies; solid versus empty and desired versus undesired aspects of voids and materials. Furthermore, this book sheds light on a "middle ground" of the smart use of voids to help in the optimization of part performance. By middle ground we mean a neutral look at the impact voids have on material/parts and use of voids as a design parameter for optimizing performance in multifunctional materials. There is much published work available on foams (Gibson and Ashby, 1997; Shutov, 2004). Even more numerous are those that provide a passing mention of voids when they are incidental/unwanted during the fabrication of nominally dense materials. This book, however, is not just about foams or residual porosity in materials, important though these contributions are; instead it focuses on the *void* itself. The fact is that all materials have voids; i.e., they are pervasive in all materials at some length scale. So in addition to voids in foams, this book brings in information from a number of different fields of

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study such as material science and engineering, physics and chemistry of materials, and mechanics of materials. This book treats all of these "different" types of voids equally and highlights their commonalities in all aspects; from processing, formation, and characterization to the resulting material properties.

For the purpose of this book, a void has two essential properties, it must be (1) a volume measured in cube of some unit of length and (2) occupied by a vacuum or gas (i.e., solid/liquid materials are absent). In general, there is no size or shape requirement on a void; so they range form subnanometers to millimeters, sometimes even larger, in equivalent diameter. We should make it clear that voids in a liquid and gaseous medium will not be covered in this book. We devote the rest of this chapter to a general discussion on voids.

1.2 DESCRIPTIONS

1.2.1 Intrinsic and Intentional Voids

Intrinsic voids appear in materials because of inherent structure, natural processes, processing limitations, and/or aging in service environments. At some length scale all real materials have intrinsic voids. At the atomic level, if we examine the Bohr atomic model, we see that most of the volume occupied by an atom is empty space. We will not be going into details of the Bohr model in this book but it is important to mention as an introduction. A general chemistry text is sufficient to review the general structure of atoms.

When voids are thought of as defects, they are viewed as having a detrimental effect on material properties. However, some defects can be beneficial and are essential to specific material behavior, such as color centers and semiconducting properties. The intrinsic voids generally range from 10^{-15} to 10^{-3} m; examples include atomic vacancies, free volume, lattice holes, and process induced porosity.

Intentional voids are incorporated by design into a solid material. Such materials are usually, but not always, referred to as foams. This is especially true when the voids are on a micrometer scale. In the early twenty first century, technology has evolved to an extent that we can control voids in the nanometer range. Materials with intentional voids can be classified in many ways. Some important examples are *single-phase foams*, *composite* and *syntactic foams* (Gladysz and Chawla, 2002). There are many ways to introduce an intentional void into a material, therefore the method of

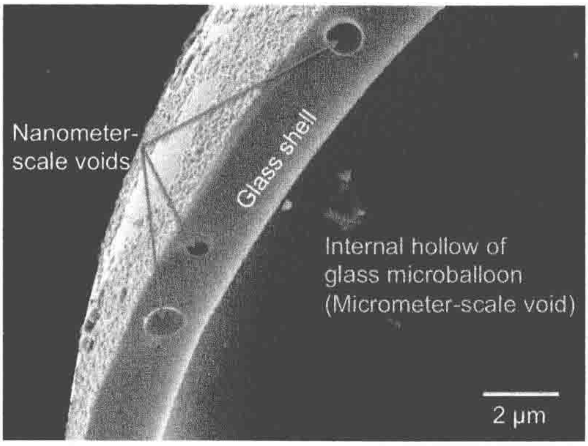

Figure 1.1 ***A hollow glass sphere illustrating nanometer scale intrinsic voids caused by processing and the intentional void, the hollow core of the sphere.***

introducing these voids is highly dependent on the type of material they are introduced into as well as the desired properties needed in the finished material. Details of these processes will be covered in Chapters 4–6.

When we discuss intentional voids in a material, it is important to remember that the intrinsic voids on the atomic and/or nanometer length scale may still be present. Figure 1.1 is an example of an intrinsic void in the wall of a hollow (intentional void) glass microspheres formed during the spray drying formation process. The hollow core of the sphere is in the micrometer range and the unintentional voids in the shell are in nanometers/ submicrometers. This intrinsic void weakens the shell of the sphere and can lead to a premature failure during service.

Independent of the material, voids can be categorized into *reinforced* or *unreinforced* and *open* or *closed cell*. We will discuss the concepts of open cell versus closed cell and reinforced versus unreinforced in Sections 1.2.2 and 1.2.3, respectively.

1.2.2 Closed and Open Cell

Whether discussing cells in foam or just general porosity, they are simply voids dispersed in a solid phase. Cells are made up of struts and faces, as shown schematically in Fig. 1.2, that surround the void space. In a closed cell, the face of the cell wall consists of a continuous solid phase. In an open cell material, a part of that wall is missing.

In an open cell foam, see Fig. 1.3(a) and (b), gas can freely flow in and out of the cells when the structure is compressed or extended. Because the cell faces are discontinuous, these materials typically have a lower modulus

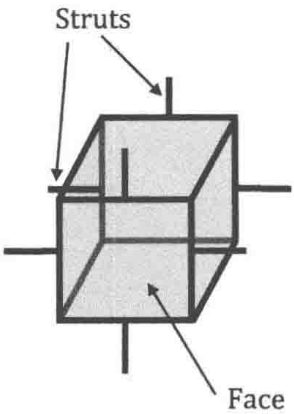

Figure 1.2 *An idealized structure of a cell consisting of struts and faces.*

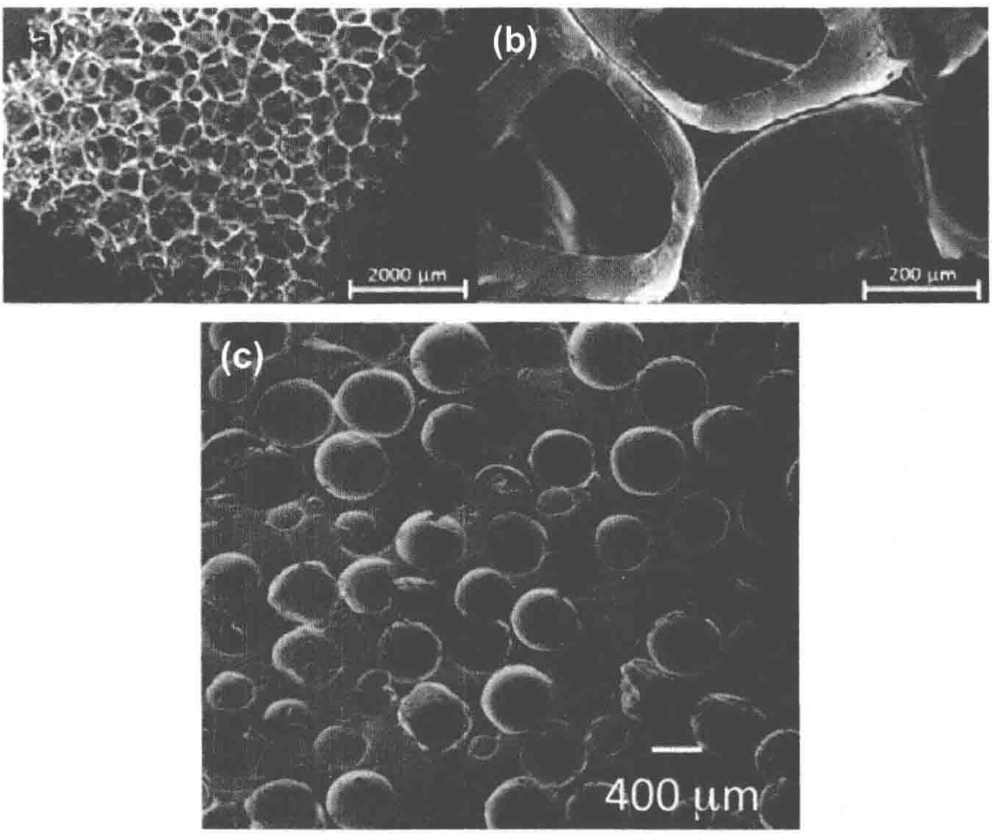

Figure 1.3 Examples of the structure (a) low magnification and (b) higher magnification of open cell reticulated foam (Lepage et al., 2012) (c) a closed cell silicone foam.

and strength than closed cell foams. The reticulated (meaning weblike) foam in Fig. 1.3 is an extreme example of an open cell foam as it is composed entirely of struts without faces. This material is a candidate for an electrode in microbial fuel cell (Lepage et al., 2012). There are some general conditions needed for a material to be open cell. According to Shutov (Shutov, 2004), the following two criteria must be met for a predominantly open cell structure:

1. Each polygonal cell must have at least two discontinuous or broken faces.
2. An overwhelming majority of the cell struts must be shared by at least three cells.

From the above criteria it is clear that the physical structure of open cell foams and resulting properties can vary widely. We discuss the structure–property relationships in more detail in Chapter 6. In general, open cell foams exhibit good absorption capacity for water and good acoustic damping properties (Zhang et al., 2012) compared to closed cell foams.

In closed cell foams (Fig. 1.3(c)) the faces are continuous, which leaves gases inside individual cells isolated from the surrounding cells. Because the faces are intact, closed cell foams typically have higher strength and modulus than open cell foams. In addition to superior mechanical properties, they are used extensively for their insulating properties (Jelle, 2011), because the air trapped in the cells is a good insulator.

1.2.3 Unreinforced and Reinforced Voids

Unreinforced voids are present in most materials that we deal with on a day-to-day basis. Conventional, single-phase, foams are the most recognizable materials that have unreinforced voids. An example of a single-phase foam containing an unreinforced void phase is the polyurethane foam used, for example, for cushioning in furniture and expanded polystyrene (PS) used for insulation. Examples of unreinforced voids are shown in Fig. 1.3(a), (b) and (c).

Foams containing unreinforced voids, as mentioned above, make a very large class of materials and find wide applications. There are many books and journals dedicated to the behavior of such foams so what we present in this book on this topic will be of a general nature and the reader will be directed to the suggested reading listed for more details.

Reinforced voids are mostly encountered in a class of materials called *syntactic foams* or *composite foams* (Gladysz and Chawla, 2002). They occur when one of the reinforcing phases is hollow or porous. Examples of hollow reinforcing phases are glass microballoons and hollow fibers such as carbon nanotubes.

The need to distinguish between reinforced and unreinforced voids became evident with the development of syntactic foams in the 1960 and 1970s. The first widespread use of syntactic foams was for use in deep-sea buoyancy and insulation applications. Voids are introduced in a syntactic foam by bonding together of a hollow material, typically in the form of microballoons, with a binder phase. The hollow particle or microballoon is the reinforced void phase; the shell is commonly made of glass, however the shell can be made of phenolic, carbon, ceramic, or metal also. The binder phase can be a polymer, metal, or ceramic.

Syntactic foams can be further categorized as two- or three-phase syntactic foams. A three-phase syntactic foam is made from microballoons, a binder phase, and interstitial voids. This interstitial void is an unreinforced void; it can be either an open or closed cell, and can be engineered into the syntactic material in order to minimize density. Although not referred to as such, hollow fibers, such as nanotubes when embedded in a matrix, can be viewed as reinforced void and a syntactic foam. Syntactic foams are used where high specific strength and modulus materials are needed.

Figure 1.4 compares two- and three-phase syntactic foams. Three-phase syntactic foams (Fig. 1.4(a)) are designed such that the microballoon and binder phase volume fraction is less than one; the remainder being the unreinforced, interstitial void. Two-phase syntactic foams (Fig. 1.4(b)) are designed so that the volume fractions of the binder phase and microballoons add up to unity; i.e., there is enough binder to fill the interstices between the microballoons. Typically the dimensions of the unreinforced voids in a syntactic foam are on a micrometer scale. Fig. 1.4(c) shows the microstructure of a three-phase syntactic foam, made of carbon microballoons and polymer binder.

There are several examples of hollow microspheres (micrometer scale in diameter) available commercially. Glass, phenolic, and ceramic particles are the most common ones. In large scale manufacturing, hollow particle formation processes rely on a *blowing agent*. The internal gas expands the skin of the hollow particle which then cools and hardens into a particle with a central void.

It is possible to make reinforced voids on nanometer, micrometer, and macrometer scales. On a nanometer scale hollow spherical shells have been made by templating nanoparticles on a sacrificial core material (Minami et al., 2005) or bubble (Hadiko et al., 2005). Another technique that can be used is plasma polymerization (Cao and Matsoukas, 2004). Figure 1.4(c) illustrates a three-phase syntactic foam; the binder phase having nanometer-scale unreinforced porosity, with a glass microballoon reinforced void. Figure 1.5 shows an example of hollow particle fabrication moving to the