Part one

Thinking About the Material World

ONE

Idealizing Material Response

1.1 A Material World

Steel glows while being processed, aluminum does not. Red lasers are commonplace, while at the time of this writing, the drive to attain bright blue light is being hotly contested with the advent of a new generation of nitride materials. Whether we consider the metal and concrete structures that fill our cities or the optical fibers that link them, materials form the very backdrop against which our technological world unfolds. What is more, ingenious materials have been a central part of our increasing technological and scientific sophistication from the moment man took up tools in hand, playing a role in historic periods spanning from the Bronze Age to the Information Age.

From the heterostructures that make possible the use of exotic electronic states in optoelectronic devices to the application of shape memory alloys as filters for blood clots, the inception of novel materials is a central part of modern invention. While in the nineteenth century, invention was acknowledged through the celebrity of inventors like Nikola Tesla, it has become such a constant part of everyday life that inventors have been thrust into anonymity and we are faced daily with the temptation to forget to what incredible levels of advancement man's use of materials has been taken. Part of the challenge that attends these novel and sophisticated uses of materials is that of constructing reliable insights into the origins of the properties that make them attractive. The aim of the present chapter is to examine the intellectual constructs that have been put forth to characterize material response, and to take a first look at the types of models that have been advanced to explain this response.

1.1.1 Materials: A Databook Perspective

What is a material? The answer to this seemingly nonsensical question strikes right to the heart of some of the key issues it is the aim of this book to examine.

From the most naive of perspectives, questions surrounding the defining qualities of a particular material are easily answered in terms of our everyday perceptions: weight, luster, color, hardness, susceptibility to heating. However, these simple notions are a reflection of a deeper underlying identity, an identity that is revealed quantitatively the moment one poses the question of precisely how a given material replies when affected by some external probe. If we subject a material to a force, it changes shape. If we apply a potential difference, electrical current might flow. And if the temperatures of the two ends of a sample are different, a flow of heat results. In each of these cases, these experiments reveal something further about the identity of the material in question.

One of the overarching conceptual themes that has emerged from such simple experiments and that rests behind the quantitative description of materials is the idea of a material parameter. For example, Hooke's original efforts, which were aimed at uncovering the relation between a body's extension and the applied force that engendered it, led to the recognition that there exist a series of numbers, namely the elastic moduli, that characterize the elastic response of that material under different loading conditions. Similarly, there is a well established tradition of subjecting materials to applied fields which result in the emergence of various fluxes such as the electrical and thermal currents mentioned above. Allied with these fluxes are material parameters that link the response (i.e. the flux) to the applied field. In these cases and many more, the central idea is that a particular material can be identified in terms of the specific values adopted by its material parameters. In fact, for some purposes, a particular material may be idealized completely in terms of a set of such parameters. For the elastician, single crystal Al is characterized by a density and three elastic constants, namely, $C_{11} = 106.78$ GPa, $C_{12} = 60.74$ GPa and $C_{44} = 28.21$ GPa (data for Al at 300 K taken from Simmons and Wang (1971)). By way of contrast, to the engineer concerned with the application of Al in thermal environments, Al is specified in terms of a density and a thermal conductivity $\kappa = 2.37$ W/(cm K) (data for Al at 300 K taken from Shackelford *et al.* (1995)). This type of idealization of a material in which its entire identity is represented by but a few numbers is one of far-reaching subtlety. In the context of the elastic constants, all of the relevant atomic bond stretching and bending has been subsumed into the three material parameters introduced above. Similarly, the full complexity of the scattering of phonons giving rise to the thermal properties of a material has also been subsumed into just one or a few numbers. One of our primary missions in the coming chapters will be to explore how such effective theories of material behavior may be built strictly on the basis of such material parameters and to examine what gives rise to the difference in these parameters from one material to the next.

From the standpoint of the idea given above, a particular material is characterized by a set of numbers that can be unearthed in a databook. For example, important parameters include the density ρ, the yield stress σ_y, the fracture toughness K_{IC} and the diffusion constant D. We note that in each case there is a number that can be looked up that characterizes the weight of a material in some normalized terms (i.e. the density), the resistance of the material to permanent deformation and fracture (yield strength and toughness), the ease with which mass can be transported within the material at elevated temperatures (diffusion constant) and any of a number of other possibilities. Our main point is to illustrate the way in which a given number (or set of numbers) can be used to introduce material specificity into continuum treatments of material response. For example, in considering the continuum treatment of mass transport, it is held that the flux of mass is proportional to the gradient in concentration, with the constant of proportionality being the diffusion constant. This same basic strategy is exploited repeatedly and always hinges on the fact that the complexity of the atomic-level processes characterizing a given phenomenon can be replaced with a surrogate in the form of material parameters.

The significance of the notion of a material parameter is further clarified by putting the properties of different materials into juxtaposition with one another. In figs. 1.1 and 1.2, we follow Ashby (1989) with some representative examples of the range of values taken on by a few prominent material properties, namely the Young's modulus, the yield strength, the fracture toughness and the thermal conductivity. The basic idea adopted in Ashby's approach is to allow the contrasts between the properties of different materials to speak for themselves. One of our aims in the chapters that follow will be to develop plausible explanations for the range of data indicated schematically in fig. 1.1, with special attention reserved for thermomechanical properties.

Despite the power of the idea of a material parameter, it must be greeted with caution. For many features of materials, certain 'properties' are not *intrinsic*. For example, both the yield strength and fracture toughness of a material depend upon its internal constitution. That is, the measured material response can depend upon microstructural features such as the grain size, the porosity, etc. Depending upon the extent to which the material has been subjected to prior working and annealing, these properties can vary considerably. Even a seemingly elementary property such as the density can depend significantly upon that material's life history. For a material such as tungsten which is often processed using the techniques of powder metallurgy, the density depends strongly upon the processing history. The significance of the types of observations given above is the realization that many material properties depend upon more than just the identity of the particular atomic constituents that make up that material. Indeed, one of our central themes will

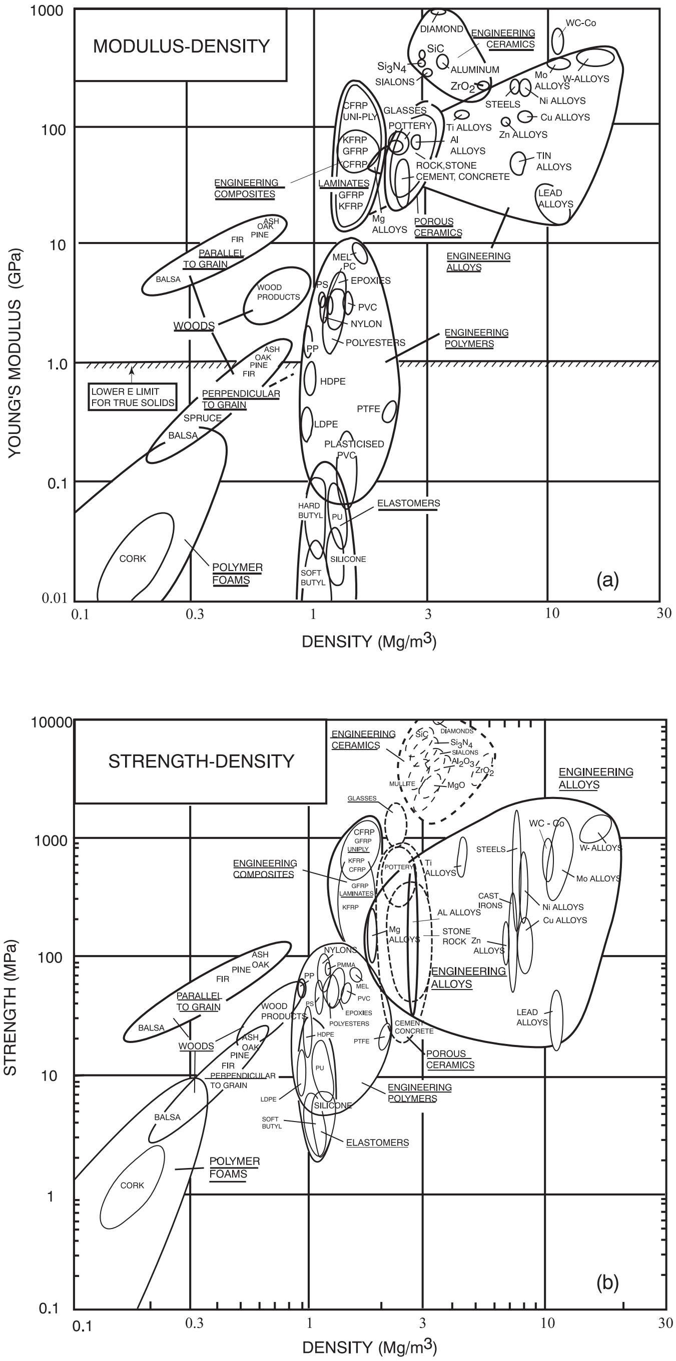

Fig. 1.1. Elastic and plastic properties of a wide class of materials (adapted from Ashby (1989)).

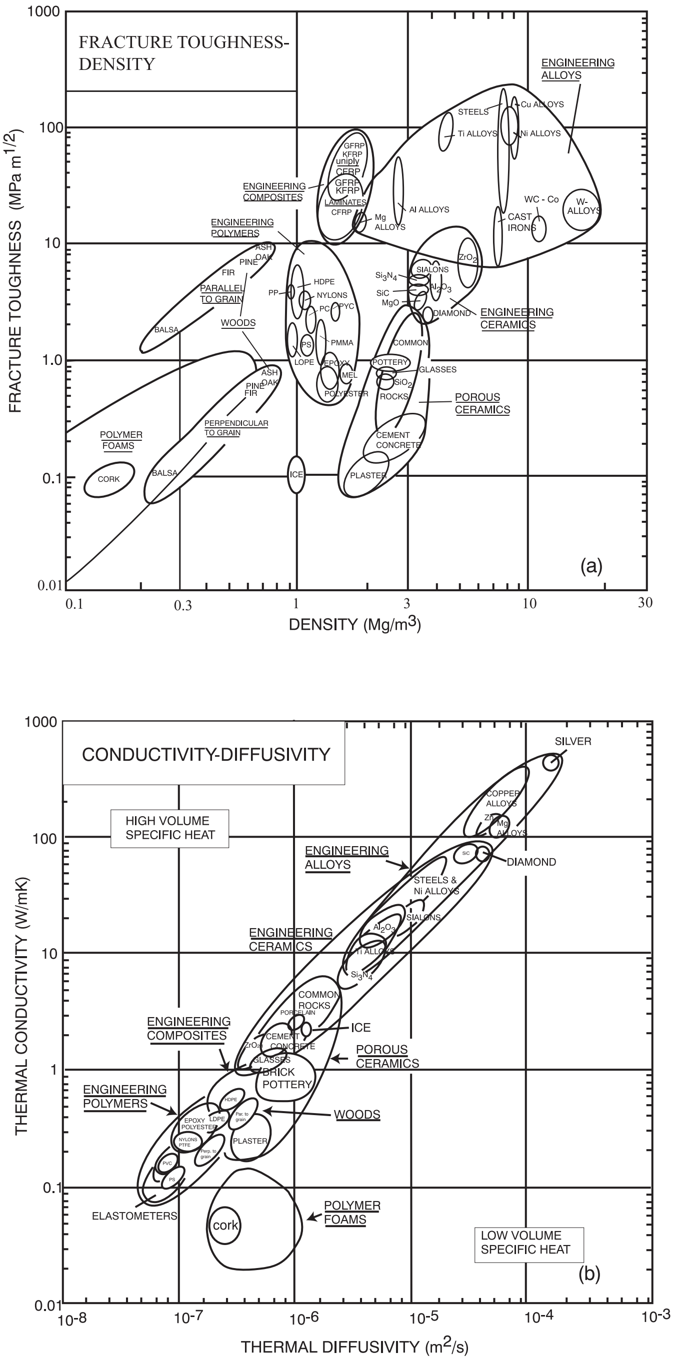

Fig. 1.2. Fracture and thermal properties of a wide class of materials (adapted from Ashby (1989)).

be the argument that microstructural features such as point defects, dislocations and grain boundaries can each alter the measured macroscopic ‘properties’ of a material.

One of our primary concerns in the pages that follow is to understand the emergence of material properties on the basis of the geometric structures that populate materials. This critical link between structure and properties has been canonized through the structure–properties paradigm which elevates the analysis of structure as a prerequisite to understanding properties. We have tried, in this section, to present something of the backdrop against which we will develop models of material behavior, especially with reference to thermomechanical properties. As an introduction to such models we first examine the role played by geometric structure in dictating material properties, followed by an overview of the ways in which materials may be tailored to yield particular values of these material parameters.

1.1.2 The Structure–Properties Paradigm

In the previous section we noted that, in the abstract, Al (or any other material) may be characterized by a series of numbers, its material parameters, to be found in a databook. However, as we already hinted at, because of the history dependence of material properties, the description of such properties is entirely more subtle. There is no one aluminum, nor one steel, nor one zirconia. Depending upon the thermomechanical history of a material, properties ranging from the yield strength to the thermal and electrical conductivity can be completely altered. The simplest explanation for this variability is the fact that different thermomechanical histories result in different internal structures.

A fundamental tenet of materials science hinted at in the discussion above is the structure–properties paradigm. The claim is that by virtue of a material’s structure many of its associated properties are determined. Structure is an intrinsically geometric notion and one of the abiding themes in this book will be the constant reminder that it is structure on a variety of different length scales that gives rise to many of the well-known properties of materials. From the atomic-scale perspective we will constantly return to the implications of the fact that a material has a given crystal structure, whether it be for its role in dictating the properties of interfacial defects such as antiphase boundaries or the elastic anisotropy that must enter elasticity theory if the crystal symmetries are to be properly accounted for. Next, we will devote repeated attention to the lattice defects that disturb the uninterrupted monotony of the perfect crystal. Vacancies, interstitials, dislocations, stacking faults, grain boundaries and cracks will each claim centerstage in turn. At yet lower resolution, it is geometry at the microstructural scale that comes into relief and will occupy much of our attention. At each of these scales we will return to

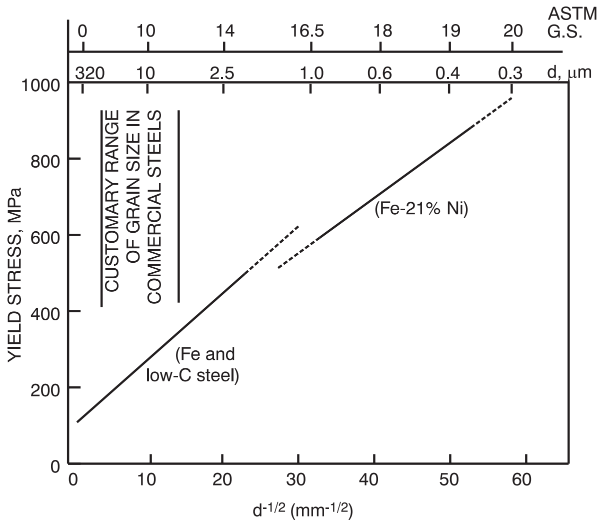

Fig. 1.3. Yield strength data for steel as a function of grain size *d* (adapted from Leslie (1981)). Plot shows dependence of yield stress on inverse power of grain size. The legends at the top of the figure show the actual grain size as measured in both µm and using the ASTM units for grain size.

the question of the structure–properties paradigm, always with a critical eye, to see just how far it may take us in our desire to unearth the behavior of real materials.

A celebrated example of the coupling of structure and properties is exhibited in fig. 1.3 in which the relation between the yield strength and the grain size is depicted. In particular, the Hall–Petch relation posits a relation between the yield stress and the grain size of the form $\sigma_y \propto 1/\sqrt{d}$, where d is the grain size of the material. The Hall–Petch relation leads us to two of the most important notions to be found in contemplating materials: the existence of microstructure and its implications for material properties, and the development of scaling laws for characterizing material response. An immediate consequence of the results depicted here is the insight that not only are structures at the atomic scale important, but so too are the geometric structures found at the microstructural scale.

We have noted that the attempt to understand materials demands that we confront a hierarchy of geometric structures, starting with the atomic-level geometries presented by the crystal lattice and increasing in scale to the level of the isolated defects that exist within materials to their assembly into the material's microstructure itself. The quest to understand the structure of a given material inevitably commences with the phase diagram. Phase diagrams are one of the primary road maps of the materials scientist. Such diagrams represent a summary of a series of tedious analyses aimed at determining the *equilibrium* atomic-scale structure of a given element or mixture of elements for a series of temperatures (and possibly

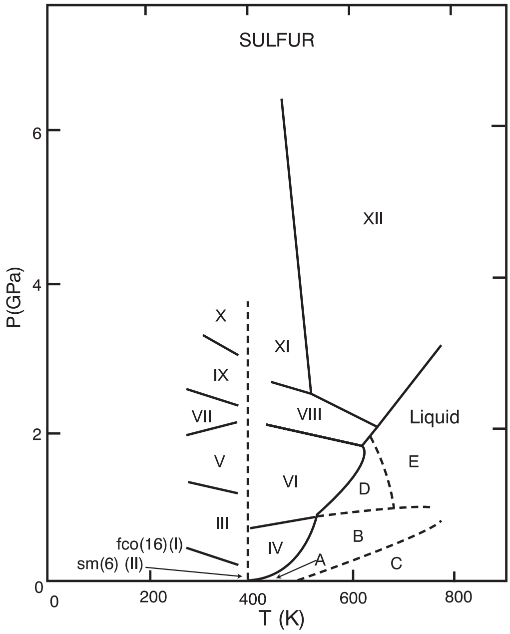

Fig. 1.4. Phase diagram of elemental sulfur (adapted from Young (1991)).

pressures). In figs. 1.4 and 1.5, we show the equilibrium phase diagrams of elemental sulfur and the iron–carbon system. The particular choices of materials shown here are meant to give a feel for the existence of the rich atomic-level complexity that is found in both elemental systems and their alloy counterparts. Note that in the case of elemental sulfur, there are not less than ten different equilibrium structures corresponding to different values of the temperature and pressure. These structures are built around molecular S_8 and range from orthorhombic to monoclinic lattices. The iron–carbon phase diagram illustrates a similar structural diversity, with each phase boundary separating distinct structural outcomes.

Phase diagrams like those discussed above have as their primary mission a succinct description of the *atomic-level* geometries that are adopted by a given system. However, as we have already mentioned, there is structure to be found on many different length scales, and one of the surprises of deeper reflection is the realization that despite the fact that phase diagrams reflect the equilibrium state of a given material, they can even instruct us concerning the *metastable* microstructures that occur at larger scales. The simplest example of such thinking is that associated with precipitation reactions in which an overabundance of substitutional impurities is frozen into a system by quenching from high temperatures. If the material is subsequently annealed, the phase diagram leads us to expect a two-phase

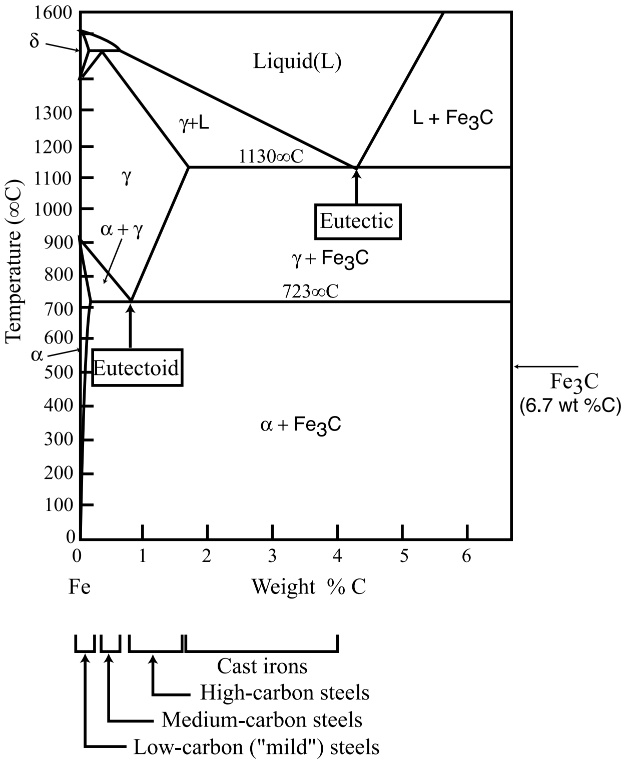

Fig. 1.5. Phase diagram for the iron–carbon system (adapted from Ashby and Jones (1986)).

microstructure in which the overabundance of substitutional impurities is now taken up in the relevant equilibrium phase. What this suggests is that strategies can be concocted for preparing particular metastable states with desirable properties. It is this insight that has led to many of the heat and beat strategies that have attracted pejorative attention to the materials engineer. A broad description of the significance of phase diagrams to materials science may be found in Massalski (1989).

As noted above, the phase diagram instructs our intuitions concerning the atomic-level geometries of materials. At the next level of geometric complexity in the hierarchy of structures that exist within a material, we must confront the defects that populate materials. Indeed, one of the key realizations that we will revisit from a number of different perspectives is that of the role of defects in the determination of material response. What this means is that the structure–properties paradigm makes an ambiguous use of the word ‘structure’ since in different situations, the structures being referenced can range all the way from atomic-scale structure to that of the nature of the grains making up a polycrystal. At the level of the defect