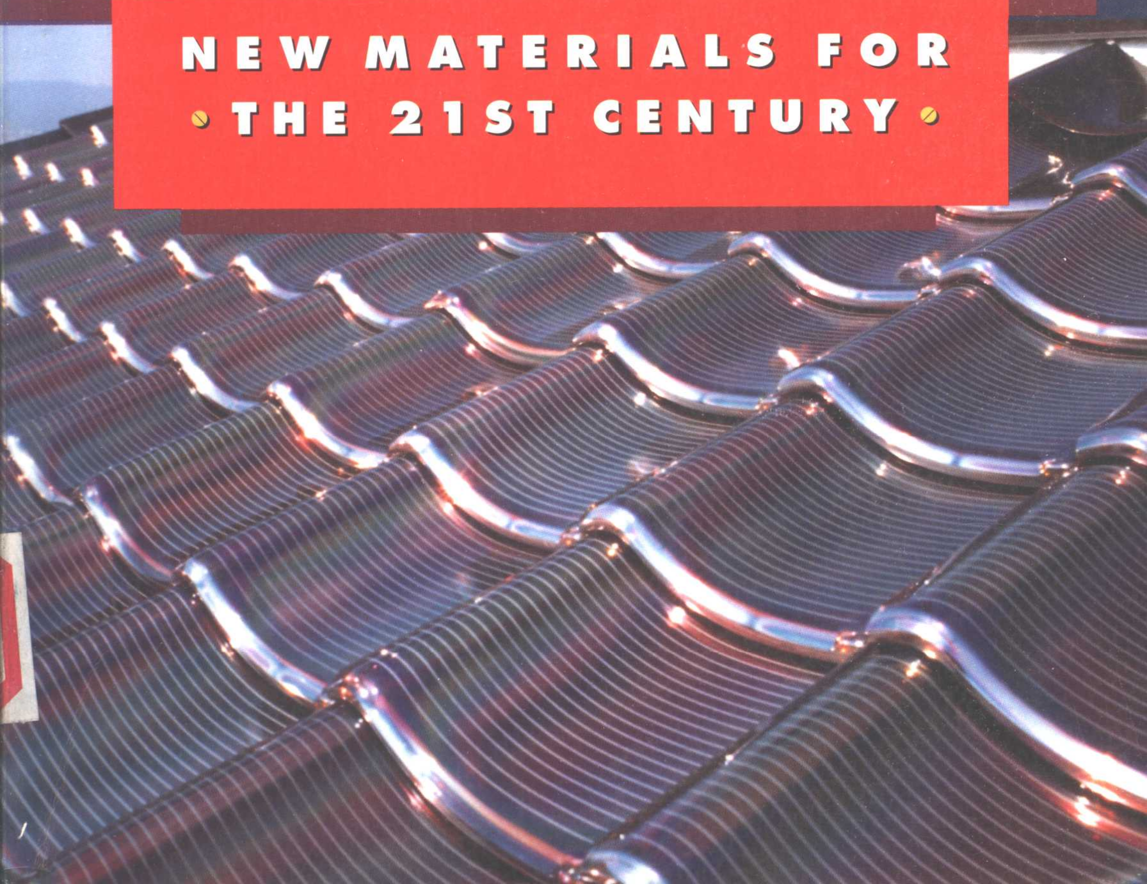
PHILIP BALL

MADE TO MEASURE

NEW MATERIALS FOR THE 21ST CENTURY



MADE TO MEASURE

NEW MATERIALS FOR THE 21ST CENTURY

Philip Ball

PRINCETON UNIVERSITY PRESS · PRINCETON, NEW JERSEY

Published by Princeton University Press, 41 William Street, Princeton, New Jersey 08540
In the United Kingdom: Princeton University Press, Chichester, West Sussex

Fourth printing, and first paperback printing, 1999
Paperback ISBN 0-691-00975-9

The Library of Congress has cataloged the cloth edition of this book as follows

Ball, Philip
Made to measure : new materials for the 21st century / Philip Ball
p. cm.
Includes bibliographical references and index.
ISBN 0-691-02733-1 (cloth : alk. paper)
1. Materials—Technological innovations. I. Title.
TA403.B2247 1997
620.1′1—dc21 97-4027

This book has been composed in Times Roman

The paper used in this publication meets the minimum requirements
of ANSI/NISO Z39.48-1992 (R1997) (*Permanence of Paper*)

http://pup.princeton.edu

Printed in the United States of America

4 5 6 7 8 9 10

ACKNOWLEDGMENTS

THAT THE writing of this book was a far less fraught experience than was my last is due to the generosity of my colleages at *Nature* to permit me to work a three-day week. I am deeply grateful for comments on the text from John Angus, Robert Birge, C. Jeffrey Brinker, Paul Calvert, Leigh Canham, Don Eigler, Jean Fréchet, Paul Gourley, Larry Hench, Allan Hoffman, Mark Kuzyk, Robert Langer, Stephen Mann, Jeffrey Moore, Stanford Ovshinsky, Geoffrey Ozin, Wim Sinke, and Kenji Uchino. I am also indebted to Frank Bates, R. Malcolm Brown, James Coleman, Norbert Hampp, Martin Pollack, Keith Prater, Deanna Richards, and David Tirrell for supplying useful reference material, and to the many others who have generously provided figures.

Emily Wilkinson, Kevin Downing, and their colleagues at Princeton University Press have been consistenly supportive and tolerant. For ensuring that my writing hours remain within sensible bounds I have again to thank Julia.

CONTENTS

MADE TO MEASURE

INTRODUCTION

The Art of Making

> As to the inventions of printing and of paper, we generally consider these in the wrong order, attributing too much importance to printing and too little to paper.
>
> —Norbert Wiener, *Invention*

THIS BOOK is made possible by the leaking of one of the best-kept industrial secrets of all time. It happened twelve hundred years ago in Samarkand, and it was not a pleasant affair. Chinese prisoners captured during an attack on the Arab city were coerced, by means that we can only guess at but which were clearly persuasive, into revealing how to make a coveted material. Using local flax and hemp, the prisoners showed their captors the art of papermaking—an art developed in China during the first two centuries of that millennium, and jealously guarded ever since. When the Moors invaded Spain in the eighth century, they brought with them a culture that had many things to teach the Europeans, and papermaking was not the least of them. Around 1150, the first paper mill in Europe was built in Valencia, and after that the word was out.

I can think of no better illustration of the power of materials technology as a force for social change. The invention of the printing press is widely and rightly held to have heralded the beginning of a revolution in information that today is accelerating as never before; but like all conceptual advances in technology, its realization required the right fabric. Paper was surely to medieval information technology what silicon is to today's, and what optical fibers and so-called photonic materials will be to tomorrow's.

But we have been taught to revere ideas more than fabrics. That's a habit acquired from ancient Greece, where the artisans and craftsmen were at best humble members of society, and at worst slaves. Because the Chinese were not infected by this attitude, their materials technology was far richer than that of the West for centuries, so that we would go begging, or more often battling, for silks, for ceramics, for explosives. Today, I suspect that as a result we take materials for granted—we appreciate their benefits, perhaps, but how often do we wonder where they come from? Sold on the idea of science as discovery and revelation, we have relegated mere invention—mere creation—to the realm of engineering, a grubby business for sure. "Invention," says Norbert Wiener, the founder of cybernetics theory and a mathematician of a rare practical persuasion, "as contrasted with the more general process of discovery, is not complete until it reaches the craftsman." By that stage, it no longer seems heroic, and the rest of the world has generally lost interest.

This is a book about invention, and I think also about a craft: the craft of making new materials, of designing new fabrics for our world. I find these fabrics astonishing. We can make synthetic skin, blood, and bone. We can make an information superhighway from glass. We can make materials that repair themselves, that swell and flex like muscles, that repel any ink or paint, that capture the energy of the Sun. I'd like to tell you how.

Advanced Materials

It has been said that, while historical periods may define their own, unique style, a living culture never reflects just the most contemporary of these. Life in the 1990s differs from that in previous decades largely by the addition of a few new artifacts and ideas to the vast collection of cultural baggage that has been accumulated over centuries. Visitors to Britain can fly supersonically to see a twelfth-century church, yet the church is still here—it has not (one hopes) been replaced by a hypermarket. Since materials are as much a part of this cultural baggage as are music, architecture, and philosophies, they too reveal a mix of the old and the new. The houses that have appeared across the road as this book has been written have wooden timbers, cement foundations, steel joists. There are no fancy new materials that threaten to replace these trusty items. And yet I suspect that the floors are carpeted with synthetic textiles, the bathrooms contain a rich selection of plastics and plastic coatings, and the central heating system may house a silicon microchip or two.

The encroachment of new materials into the marketplace is generally slow and subtle, and never complete. I don't think that we shall ever see wood replaced as a building material, nor stone blocks, bricks, and mortar. They are simply too cheap to be threatened—the supply is abundant, the processing is minimal. For a while in the 1950s and 1960s it might have seemed as though plastics would one day replace everything, but that is clearly not going to happen. On the other hand, I think it is safe to say that this century has seen a shift in the use of materials that is like nothing that has gone before. Not only do we have a far, far greater range of materials from which to choose in fabricating any artifact, but the whole decision-making process is radically different. For the first time in history, materials are *designed* for particular applications. Often the application, the requirements, come first—"I want a material that does this and that"—and the material will then be concocted, invented if you will, to meet those demands.

This is true even for materials that we might imagine are off-the-shelf items. You want to make steel suspension springs? It is no good telling your production manager to go out and order a hundred tons of steel—that is like an interior decorator requesting a dozen cans of paint. Will that be mild steel, stainless steel, medium- or high-carbon steel, nitrided steel, steel with nickel, chromium, manganese, titanium . . .? Steels today are designed materials, a delicate blend of elements whose strengths span a factor-of-ten range—and whose cost varies likewise. While in one sense we might imagine that making steel boats is a traditional use of an old material, you can bet that the stuff of today's metal vessels is a far more carefully selected and more skillfully engineered material than that which Isambard Kingdom Brunel, the first iron-boat builder, had at his disposal.

But the development of new steels is nothing compared with the way that some of today's new materials are put together. They are literally designed on the drawing board in the same way that a house or an electronic circuit is designed. The difference is that the designers are working not with skylights and alcoves, not with transistors and capacitors, but with atoms. The properties of some new materials are planned from and built into their atomic structure. This means, of course, that we have to be able to understand how the characteristics of a particular molecular constitution translate into the bulk properties that we wish to obtain. In practice, it means that materials scientists must enlist the help of physicists, chemists, and, ever increasingly, biologists to be able to plan successfully. Frequently the strategy is a modular one—in this regard it is not really so different to the circuit designer who knows what combinations of components will give her an oscillator or a memory unit. You want a flexible molecule? Then let's insert some flexible molecular units here. You want it to absorb green light? Then we'll graft on these light-absorbing units here, equipped with atomic constituents that tune the absorption properties to the green part of the spectrum. Alternatively, the design process might involve a careful adjustment of a material's crystal structure—for example, to place the atoms in a crystal a certain distance apart, or to ensure that the crystal contains gaps or channels of specified dimensions.

In this book I will talk largely about materials whose properties are designed in this way—whose composition and structure are specified at the smallest scales, right down to the atomic, so as to convey properties that are useful. On the whole, this control requires clever chemistry (to arrange the molecular components how we want them), physics (to understand which arrangements will lead to which properties), and fabrication methods (for example, to pattern materials at microscopic scales). What all of this means is that such materials are generally expensive to make. Most are not materials for building bridges with—their applications will be highly specialized, and will require only small amounts of the material. The high cost, it is usually hoped, will be bearable because the materials will do things that no others can. In other words, they will find new niches on the market, rather than replacing older, cheaper materials. These new materials will augment our technological palette, not replace the old primary colors with new, subtler shades. Many will scarcely be noticed by the user, at least in a tangible sense. While you will appreciate it when your bicycle frame is made of a lightweight fiber composite rather than steel, you will be less likely to recognize that your desktop computer contains photonic semiconductors, which process light signals, rather than silicon chips. But you *will* notice the change in speed and data-handling capacity that this will bring.

These new, sophisticated, designed materials are often called *advanced materials*. That is an ambiguous term, and I don't suppose that it tells one anything much more than does the label "modern art." Will today's art still be "modern," and our latest materials still be "advanced," in a hundred years' time? But it might help to draw the distinction that advanced materials are generally costly, created by rather complex processing methods (at least in comparison to cutting down trees) and aimed at highly specialized applications. They are, in the parlance of economics, "high-value-added"—their uniqueness and the consequent high commercial cost of the products that use them offset the high cost of their production. In contrast, older materials like brick, wood, and cast iron are "low-value-added," available in large quantities at a low cost for a broad range of applications in which there is usually a considerable tolerance to variability of properties and performance.

A word of caution is needed. I have attempted here to skim across the top of the breaking wave of the new materials science, and to pick off some morsels that I hope will be appealing. But inevitably, when the current wave breaks, not all of these will surface. At the forefront of any science are ideas and enthusiasms that have not yet been exposed to the exacting test of time. A road that looks exciting today may turn out to end in a cul-de-sac next week, or next year. In short, I can be certain that not all (perhaps not even many) of the new materials that I discuss will ever find their way into the commercial world (although some have already). But that is not the point. What I hope to show is the way that materials science works at the frontier: how a problem, a need, is identified, and how researchers might then go about developing a material that will solve that problem, meet that need. I hope to capture emerging strategies and trends rather than to alight on specific materials that will become marketable items in the next few years. It might be as well, then, to say something very briefly about that long and rocky road from the laboratory to the corner store.

Making It Work

All Part of the Process

Materials scientists are pretty good at figuring out how to make things, and that is a skill worth having. But most are not industrialists, and this can be something of a hindrance. Let us say that a materials scientist has just figured out how to make a plastic that will turn blue when warmed past water's freezing point, and realizes that this is just what the Plaxpax company wants for packaging its frozen foods; you can see at a glance when it has become too warm, he tells them. So the Plaxpax chemists come to see how the stuff is made, and the scientist explains that you dissolve this organic material in that solvent, heat it to 500 degrees Celsius under pressure, and an amorphous sticky substance will separate out on cooling—at least it will usually, but sometimes not (on those occasions the whole mixture just turns to a black goo).

The Plaxpax people love the product, but the synthetic method is useless. The solvent is toxic, the high pressures are hazardous, and success is variable. So the Plaxpax industrial chemists face a challenge every bit as daunting as the original synthesis: to turn it into a process that can be conducted safely and economically on an industrial scale.

The processing route used to turn a material into a commercial product is generally as important for its success in the marketplace as the properties of the material itself. Scientists can conduct syntheses in the lab that no one would dream of doing in an industrial plant, because they are too costly, too dangerous, or simply impossible to scale up. A material can switch from being a lab curiosity to a crucial company asset merely through the identification of a processing method that is industrially viable. The choice of material for a particular application can depend as much on the availability of a suitable processing technique for forging that material into the required form as on the properties of the candidate materials. Alternatively, even when a given material has been selected for an application, the engineer may be faced with a further choice of processing method best suited to that situation.

Nowhere is the importance of processing more clear than in metallurgy. In recent years, new methods of processing metals have substantially improved the performance that can be extracted from metal parts, and this in turn has presented subtle economic questions in metals manufacturing. To the old-style fabrication methods of casting and forging have been added new methods whose application requires a balancing of cost against performance of the products. A technique called powder-metallurgy forging (also known as hot isostatic pressing) makes components from a metal powder (usually an alloy), which is loaded into a mold and subjected to high temperatures and pressures. Because the shape of the cast product can be made very close to that of the final metal part, less subsequent machining of the cast object is needed, reducing both labor and materials wastage. Moreover, by using different powders to fill different parts of the mold, a single component can be fabricated from two different metal alloys. But a disadvantage that must be weighed into the balance is the high cost of the molds.

If cost is less critical than performance (durability and strength, say), a new processing method called directional solidification is often used. Here the metal part is formed by pouring the molten metal into a mold that is subjected to a highly controlled heating and cooling regime to influence the way that the metal crystallizes, so as to remove the microscopic flaws that limit the strength of conventional cast components. This process is expensive but is used to make turbine blades for jet engines, where long life and strength at high temperatures are critically important.

The importance of manufacturing methods extends not only to a material's consumer (insofar as the processing method plays a part in determining the material's cost and properties) but to everyone affected by an industrialized society—and today no one is any longer excluded from that category. For manufacturing has an environmental cost as well as a financial one. There can be no denying that in the past these two costs were frequently traded against one another to the detriment of the former. Making materials can be a messy business, and manufacturing companies have often been none too careful with their wastes. Toxic organic solvents have made their way into water supplies. Thousands of tons of toxic heavy metals, including lead, cadmium, thallium, and mercury, are emitted every year into the atmosphere from smelting, refining, and manufacturing processes. The CFCs used as refrigerants, foam-blowing agents, and solvents have proved to be far from the inert, harmless compounds originally envisioned: when they reach the stratosphere, they fall apart into ozone-destroying chemicals.

So materials manufacturing has a bad name, and not without cause. In the United States alone, something like eleven billion tons of nonhazardous waste and three quarters of a billion tons of hazardous (inflammable, corrosive, reactive, or toxic) waste are generated each year. Around 70 percent of the hazardous waste is produced by the chemical industry, and most of it is dealt with by physical, chemical, or biological treatment of the water streams that contain it. But there are signs that these dirty habits are changing. Some engineers are beginning to talk about "industrial ecology," which is concerned with developing industrial systems that make optimal use of energy, minimize or ideally eliminate (or make beneficial use of) their wastes, and are ultimately sustainable rather than simply consuming available resources. Industrial ecologists recognize the futility (indeed, the danger) of looking at a manufacturing plant in isolation, in terms of bare economic indices such as productivity and overheads—just as it makes no sense to look at one niche of a natural ecosystem, or one trophic level of a food web, as if it were independent of the rest of the system. They recognize that there are human and social facets to manufacturing systems, and that here, as in the economic sphere, there are costs, benefits, and risks to be evaluated.

This is not an exercise in altruistic idealism. It is becoming increasingly apparent that an industrial ecosystem view makes commercial sense too. By reducing their waste emissions by nearly 500,000 tons in 1988, the 3M company actually saved $420 million.

Increasingly, legislation punishes polluters with taxes, levies, and fines. (And as demonstrated by the recent boycotting of Shell gasoline stations in Europe over the threatened dumping of the Brent Spar oil rig in the North Sea, the public is prepared to punish them too—regardless, perhaps, of the scientific pros and cons.) But in addition, profligate use of raw materials and energy, and disregard for products labeled as waste, can be economically foolish. Many so-called waste products contain potentially valuable materials. Depending on the value of the material, its concentration in the waste, and its ease of extraction, there will be some threshold at which waste becomes a viable materials resource. Thousands of tons of heavy metals such as mercury, copper, cadmium, and silver are discharged as hazardous industrial waste each year when analyses suggest that they could be *profitably* recovered and recycled.

Within the paradigm of industrial ecology, the ideal is to move beyond waste reduction and recycling to its eventual elimination. This implies a shift in the whole concept of manufacturing. At present, most attempts to deal with manufacturing pollution are "end-of-pipe" methods, which look at the noxious substance dribbling from the waste pipe and worry over what to do about it. But we would like to have no need for that pipe at all. Commonly this requires the development of entirely new processing methods. A major source of hazardous waste is organic solvents such as hexane, benzene, and toluene, which are used in all manner of processes ranging from the manufacture of electronic printed circuit boards to paints. There is now much interest in developing "dry" processes for circuit-board manufacture, which involve no solvents at all. One of the most striking advances in this arena in recent years is the appearance of nontoxic solvents called supercritical fluids: these are commonly benign fluids such as water or carbon dioxide which, when heated and pressurized to a "supercritical" state (described on page 308), are able to reproduce many of the characteristics of the toxic organic solvents. Union Carbide has introduced a paint-making process that reduces the use of volatile organic solvents by 70 percent by thinning the paint with supercritical carbon dioxide.

But the environmental cost of materials in fact extends far beyond the effects of their manufacture. The raw materials have to be mined, refined and transported, and the final products might ultimately have to be disposed of. All of this has an environmental price, and it is frequently met not by the supplier, manufacturer, or consumer, but by the world—all too often by disadvantaged parts of it. Within the viewpoint of industrial ecology, these "hidden costs" are no longer ignored but are weighed into the balance in the choices that are made.

Spoiled for Choice

You want to make an engine part? A vacuum cleaner? A coat hanger? Then take your pick—at a very rough count, you have between 40,000 and 80,000 materials to chose from. How do you cope with that?

Well, I don't propose to answer this question. It's simply too big. Primarily I want to demonstrate only that it is into a crowded marketplace that the new materials described in this book are entering. That is why it pays to specialize, to be able to do something that no other material can, or at least to find one of the less-congested corners of the market square. It is seldom a good idea, however, to focus single-mindedly on refining just one aspect of a material's behavior until it outperforms all others in that respect. The chances are that you'd find you have done so only at the expense of sacrificing some other aspect (commonly cost) that will prevent the wonderful material from becoming commercially viable. For while in the laboratory there may be a certain amount of academic pride and kudos to be gained by creating, say, the material with the highest ever refractive index, in practice the engineer will be making all manner of compromises in selecting a material for a particular application. He might want a strong material, say—but the strongest (diamond) is clearly going to be too expensive for the large components he wants to make. And he doesn't want a material that will be too heavy, for it is to be used in a vehicle and so he wants to keep the weight down. And the material has to be reasonably stiff too—strength against fracture will be no asset if the material deforms too easily. Then he has to think about whether corrosion will be a problem . . . and how about ease of finding a reliable supplier? Will the cost stay stable in years to come? How easy is the material to shape on a lathe?

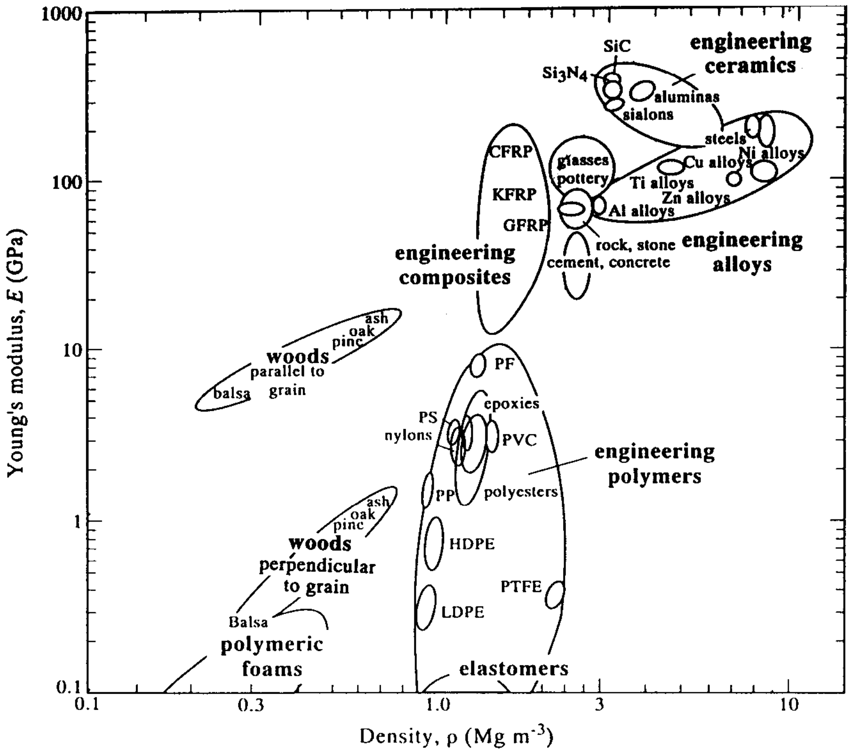


FIGURE I.1 Materials selection charts help a designer to make the right choice from the bewildering array of engineering materials now on offer. The best choice generally represents a compromise between different factors, such as weight (density), strength, stiffness, or cost. A single chart displays the ranges of two such factors spanned by different materials, and so allows the designer to determine the permissible options. Here I show a chart depicting the relationships between density and stiffness, as quantified by a parameter called the Young's modulus. You can see that stiffer materials (toward the top) are generally also denser (toward the right). (CFRP, KFRP, and GFRP are carbon-, Kevlar-, and glass-fiber-reinforced plastics.) (Figure courtesy of Michael Ashby, University of Cambridge.)

To guide the engineer through this jungle of choices, Michael Ashby at Cambridge University in England has championed the use of materials selection charts, which attempt to render on a single graph those properties, for a range of materials, that are most salient to a particular application. The engineer can then circumscribe his design parameters on the chart and see which choices that leaves him. The selection charts plot two relevant materials properties—say, density and strength—along the two axes, and the ranges of these two properties for all manner of materials are depicted by closed curves (fig. I.1). Assume, for example, that we are seeking to choose a material for making table legs. The prime considerations, at least initially, may be stiffness (which is quantified by a parameter called the Young's modulus) and density (the legs should be lightweight). So we would take a look at the chart shown in figure I.1. The stiffer the material, the thinner we can afford to make the legs, and so the more we can sacrifice in terms of density. So we can draw a diagonal line across the plot, above which the materials are stiff enough, for their respective density, to do the job. This shows us which materials to focus on; typically, we can then do a similar exercise for other design constraints (such as cost) until we have narrowed the choice down to a small short list.

Promises, Promises

It is a common complaint that, of the scientific "breakthroughs" proclaimed in tomorrow's headline news, most will have vanished from sight a year hence. This is true, and largely inevitable. "Breakthrough" is not a very helpful word for scientists, although it has an unfortunate tenacity for science journalists. While it conveys the impression of revolutionary new technologies just around the corner, the reality is that almost all scientific "breakthroughs" are beginnings. They are seldom the final, critical step that will allow some fantastic new product to impinge on our lives, but more often the first firm step in a new direction. Breakthroughs usually come suddenly, from some unexpected direction; the hard work comes after, not before. It can take years, decades, for an exciting new discovery to lead to a useful application—if it ever gets there at all. For a breakthrough is usually a result pregnant with possibilities, but there is never any telling whether some very mundane hitch will subsequently make itself manifest and spoil the fun.

It is in this spirit that I suggest you read this book. For I will often be talking about research that is at the so-called breakthrough stage, at the breaking edge where scientists are still excited and have not yet gotten down to the graft of figuring out how to convert the possibilities of their findings into reality.

I'd like to illustrate this with an example. One of the most prominent advanced materials that I have not discussed elsewhere in the book is the class of solids called high-temperature superconductors. This omission is partly because they are one of the very few new materials to have received wide attention elsewhere, but also partly because they have reached the "graft" stage; after intense excitement in the mid-1980s, researchers are now laboring at the difficult business of turning them into useful materials. This example is instructive because, to have heard the story at the peak of the excitement, one would have thought that this was a new material that just couldn't fail.

Superconductors carry electrical currents without resistance. As a consequence, they do not dissipate electrical energy as heat—a superconducting power line would not lose power over large distances, as conventional power lines do. It is a dramatic property: a current circulating around a superconducting ring will, in theory, circulate forever without dissipating its energy. Surely there must be valuable uses for a material that conducts without resistance? And what is more, a superconductor expels a magnetic field and so repels magnets: a magnet will hover above a superconductor, levitated by this repulsive force. This effect has conjured up visions of magnetically levitated trains, running almost friction-free on superconducting rails.

Superconductivity is not a new discovery; it was first seen by the Dutch physicist Heike Kamerlingh Onnes in 1911. But the excitement of the 1980s came from the discovery of a class of materials that become superconductors at much higher temperatures than those known previously. Kamerlingh Onnes had to cool mercury to just 4 degrees Celsius above absolute zero before it became superconducting, and until the 1980s no material was known that would superconduct at a temperature greater than about 23 degrees above absolute zero. The need for expensive cooling systems restricted superconductors to rather specialized applications, for example in the coils of electromagnets that produce very strong magnetic fields, or in devices called superconducting quantum interference devices (SQUIDs) that detect very small magnetic-field fluctuations such as those that occur in the brain.

In 1986 Georg Bednorz and Alex Müller of IBM's research laboratories in Zurich, Switzerland, found a ceramic oxide material that became superconducting at 35 degrees Celsius above absolute zero. So dramatic was this jump above the previous record that laboratories all around the world immediately began experimenting with other, related oxide ceramics. By 1987 the record had shot up to 93 degrees above zero, and a year later it rose a further 32 degrees. These latter temperatures were well above the boiling point of liquid nitrogen (77 degrees above absolute zero), which meant that this could be used as a coolant rather than the liquid helium necessary for the old superconductors, making the refrigeration technology cheaper.

The field looked set to produce levitating trains, ultrafast superconducting circuits, loss-free power lines, and who knew what else. A decade later, none of these things have materialized; so far, the only significant application of the high-temperature superconductors is in a new generations of SQUIDs, used for geological prospecting and for magnetic scanning of brain activity.

What happened? It turns out that the "hotness" of the superconducting transition is not the only, or even the most crucial, factor that determines the materials' usefulness. In most prospective applications, including transmission lines and levitation devices, superconducting wires are needed that carry large current densities. But as the current through the high-temperature ceramic superconductors is increased, there comes a threshold (a critical current) above which the superconductivity breaks down. For most applications, the critical current of available superconducting wires is too low.

It appears that this problem is mainly one of materials processing. Being ceramics rather than (like the older superconductors) metals, the new materials are brittle and not easily formed into wires. They are usually fashioned instead into tapes, made from powders pressed into hollow tubes of silver, and pressed and rolled flat. These tapes have some flexibility, but their superconducting core is a composite of tiny crystalline grains. Measurements on individual single crystals suggest that the high-temperature superconductors can in principle carry appreciably higher critical currents than the tapes, and it seems that the boundaries