1 Introduction

1.1 WHY HARDNESS MATTERS (A SHORT HISTORY)

A most characteristic property of a solid is its hardness. This ranges from very soft (talc) to very hard (diamond). Although hardness is an important general characteristic of materials, it also has great utility. It determines the resistances of surfaces to wear. It determines the effectiveness of all sorts of tools used for cutting everything from textiles to hard rocks. A closely related function is the polishing of gems, mirrors, lenses, and the like. It is an index of the strengths of materials; particularly metals. Geologists find it useful for identifying minerals; and it plays a key role in geophysical phenomena such as meteor impacts. Unfortunately it can also be very destructive in military ordnance. A property of more ubiquitous importance is hard to find.

The range of hardness numbers, measured in kilograms per square millimeter, is large. It runs from one for a soft material like KI to about ten thousand for the hardest material—diamond. In other words, it has a range of about four orders of magnitude.

As a result of its utility, mechanical hardness has been highly prized for millennia. It has often played a key role in the progression of civilization because it has enabled progressively more sophisticated devices and machines to be constructed. Initially the hardest available materials were rock, bone, and wood. Bone tools from 19,000 BCE have been found. The search for improved hardness extends back to char hardened wooden-spears as old as 120,000 BCE (Bunch and Hellemans, 2004). The first advanced material was probably flint which fractures conchoidally, so controlled fracture can give it atomically sharp edges (Wikipedia, 2006). Flint was a considerable improvement on obsidian (volcanic glass), starting in the Middle Paleolithic Age (≈300,000 to 30,000 years ago). Imagine the improvement that flint arrowheads made, compared with hard wood. Hardness was not the only factor that determined technological progress, but was a key factor. Technology often waited for improved hardness to become available before new technology could be introduced.

For example, consider copper. Native copper could be worked into various shapes, but was too soft for making tools and swords. Copper smelted from

ore was also relatively soft. This changed when it was discovered that calamine ore (mixed carbonates and silicates of zinc), when smelted together with copper ore makes brass (a Cu-Zn alloy much harder than copper alone). Further improvement came when tin became available, and could be mixed with copper to make bronze. Syrians did this in about 3000 BCE, thereby ending the Stone Age and beginning the Bronze Age.

One of the most important inventions of the late Stone Age was the wheel. It reduced the force needed to move objects by a factor of at least 100. But the first wheels were made of wood. An enormous advance came when wheels could be rimmed with bronze.

Since tin is much less volatile than zinc, bronzes are more versatile than brasses. The low volatility of tin allowed bronze alloys to be cast and forged into various shapes, including large bells. These formed the basis of the first large scale communication systems. Every settlement had its own bell tower for communicating with its residents, and with other settlements.

Bronzes with a variety of hardnesses and other properties can be made depending on the tin content, and by adding other elements as well as tin. These have included arsenic, magnesium, calcium, phosphorous, and antimony. The resulting bronzes had (have) a large variety of applications. Because it forms a protective oxide, bronze is excellent for fittings on boats where it resists seawater corrosion. Its friction coefficient is small so it makes excellent bearings and gears. Alloyed with phosphous, it is useful for springs. Since it fills casting molds precisely, it is used extensively for statues and other art objects.

In parallel with the development of the art of smelting metallic ores, the art of heating various oxides and silicates to make artificial rocks (ceramics) was being slowly developed. The first evidence of this development has been found in Moravia, dating from 28,000 BCE. Clay pottery was being manufactured in Egypt by about 5000 BCE, and glass glazes were applied to their surfaces from about 12,000 BCE. Glass shapes date from 7,000 BCE in Egypt. The availability of clay pottery revolutionized the transport of water, wine, and other liquids.

Special glass compositions have been invented, using a variety of oxides together with silica to obtain special characteristics. An early one was lead glass in England in 1624. For improving glass lenses, Zeiss, Inc. invented high boron glass in 1884, and Abbe-Schott developed high barium glass in 1888. A special boron glass (Pyrex) was developed at the Corning Glass Works in 1915. Precipitation-hardened glasses were developed at the same place during the mid-twentieth century. High purity, high strength glass fibers for optical communication systems began to be made in the 1970–80 period.

A dramatic change in the hardnesses of metallic materials occurred when the smelting of iron was invented in Egypt (4000 BCE). By 1550 BCE, it could be forged into wrought iron which considerably improved its properties.

By adding relatively large amounts of carbon (several weight per cent) to iron, it was found in China (500 BCE) that large and complex cast-iron shapes could be made readily. Through chill-casting, cast-iron becomes very hard (albeit brittle); this gives it considerable wear resistance.

Although pure iron is less hard than some bronzes, it was considerably hardened by converting it to pearlitic steel (iron + a small amount of carbon) (India, 500BCE). By adding more carbon (up to 1 wt.%), and other selected metals, plus heating, quenching, and tempering (reheating), iron alloys yielded very hard, tough martensitic steels.

Without these advances in hard, strong materials; based on abundant, and therefore low-cost iron ore, there could have been no industrial revolution in the nineteenth century. Long bridges, sky-scraper buildings, steamships, railways, and more, needed pearlitic steel (low carbon) for their construction. Efficient steam engines, internal combustion engines, turbines, locomotives, various kinds of machine tools, and the like, became effective only when key components of them could be constructed of martensitic steels (medium carbon).

The civilian advances were accompanied, and often led, by advances in military ordnance. Iron and steel became the basis of swords, spears, arrows, guns, cannon, armor, tanks, warships, and more. In fact, the motivation for inventing and developing new hard materials was often the desire for improved military ordnance. This continues with searches for better body armor, and the inverse searches for more penetrating projectiles.

An important sub-division of the industrial revolution was the discovery by Moissan in 1906 that carbon forms exceedingly hard tungsten carbide (WC) crystals. In 1928, workers at Krupp, Germany found that WC crystals can be cemented with cobalt metal to make aggregates that were unparalleled tools for cutting steel (Riedel, 2000, p. 481). Other hard compounds, such as silicon carbide (SiC) and aluminum oxide (Al_2O_3) are also used for cutting other materials. The hardest crystals of all, diamond and cubic boron nitride (BN), are very useful for cutting rock as well as steel, in the case of BN. Diamond is not useful for cutting steel because, being carbon, it reacts with iron. It began being used as a tool as early as 300 BEC (Riedel, 2000).

With the advent of aeronautics, aluminum alloys allowed major advances such as the monocoupe design. The first all metal airplane was the Junkers J-1 (1917). Pure aluminum is light in weight, but too soft for constructing aircraft, so it is hardened by adding to it copper, magnesium, and other metals. During heat treatments, these form precipitate particles that harden the alloy (e.g., particles of the compound, $CuAl_2$). This process is called age-hardening. It is the approach used for the alloy known as Duralumin which was invented by Alfred Wilm in Germany in about 1909, and has been a standard construction alloy for many years.

Aeronautics also stimulated the development of superalloys, largely based on nickel. They hold their strength (hardness) at very high

temperatures. Efficient aircraft-turbine engines could not be constructed without them. These engines have allowed mass commercial air transportation to develop.

The weakest parts of superalloys are the grain boundaries between the crystals. A desire to eliminate these boundaries led F. VerSnyder to fabricate turbine blades from very large individual crystals of nickel–aluminum alloys. This material consists mostly of the compound, Ni_3Al, and because of its lack of grain boundaries, the monocrystalline form has remarkable creep resistance and high temperature fracture resistance. The durability of these monocrystalline turbine blades has substantially reduced the costs of operating large jet airplanes by extending the time between repair operations. They have also reduced fuel consumption by increasing the maximum allowable operating temperatures.

In addition to mechanical devices, optical devices have benefited from improvements in the hardnesses of materials. A familiar example is scratch-proof lenses for eye glasses. Scratch-resistant aircraft windscreens are also important. Less familiar, but more impressive, is the importance of hardness in solid-state lasers. Early in the history of solid-state lasers, it was discovered that the best host material for the active fluorescent atoms is a very hard garnet (yttrium aluminum garnet—YAG). The standard fluorescent centers are neodynium atoms added to the garnet. YAG garnet is exceptionally rugged and hard at very high temperatures. Because of the intensity (energy/sec.cm^2) of the light beam in the lasing material, large electric fields tend to decompose it. Therefore, both its optical and mechanical properties contribute to desirable performance.

High pressure scientific research is an area of science that has benefited from high hardness. Here, individual diamonds are used as pressure vessels to contain specimens at ultra-high pressures (millions of times atmospheric pressure).

Because of the simplicity of doing scratch tests, hardness has been an important diagnostic tool for mineralogists and prospectors by helping them to identify various rocks and minerals.

Since it measures the susceptibility of materials to plastic deformation (as contrasted with elastic deformation), hardness is very important for diagnosing the mechanical state of a material, in particular toughness. Purely elastic materials are brittle. Plasticity, by blunting cracks and other defects, allows metals and, to some extent ceramics, to tolerate small flaws and thereby become malleable and tough.

An illustration of the impact that improved hardness has had on technology is presented in Figure 1.1. This shows the dramatic increase in performance of machine cutting tools (lathes, milling machines, saws, drills, and the like) as the tools became harder. It also shows how very fast cutting speeds have become. The top cutting speed ($\approx 5000\,m/sec$) is about 16% of the speed of sound in air!
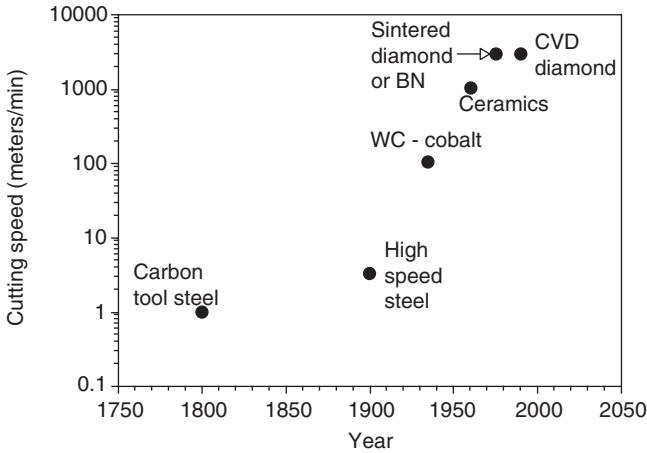
Figure 1.1   Improvement in cutting speeds with tool hardness. During two centuries of development machine tool performance increased by a factor of about 5000. Adapted from Riedel, 2000, p. 550.

1.2   PURPOSE OF THIS BOOK

Crystals of high purity metals are very soft, while high purity diamond crystals are very hard. Why are they different? What features of the atomic (molecular) structures of materials determine how hard any particular crystal, or aggregate of crystals, is? Not only are crystals of the chemical elements to be considered, but also compounds and alloys. Glasses can also be quite hard. Is it for similar reasons? What about polymeric materials?

Many decades ago, with the advent of convincing atomic theory, it was thought that a universal model for hardness could be found. This is not the case given the present state of solid-state physics. Much of physics, and therefore chemistry, is based on interactions between pairs of particles. This is adequate for understanding changes of sizes of objects, but hardness involves changes of shape, and this requires more complex interactions.

However, It has been found that in many cases, simple models of the properties of atomic aggregates (monocrystals, polycrystals, and glasses) can account quantitatively for hardnesses. These models need not contain disposable parameters, but they must be tailored to take into account particular types of chemical bonding. That is, metals differ from covalent crystals which differ from ionic crystals which differ from molecular crystals, including polymers. Elaborate numerical computations are not necessary.

The presentation here attempts to provide—for materials scientists, metallurgists, ceramists, chemists, and physicists—knowledge of how hardness

is related to other properties, and to the building blocks of everyday matter—atoms and electrons; that is, what information is contained in hardness measurements. The emphasis is on physical concepts so the general picture may be grasped and appreciated by most readers. Various materials types are discussed in individual chapters. Some chapters on general principles integrate the whole.

This is, by no means, the first attempt to relate hardness to other more precisely defined properties. As mentioned in the Preface, Plendl and Gielisse (1962) studied correlations between hardness and cohesive energies per atomic volume. Both quantities have the same units (energy/volume). These correlations are successful, but not completely. The shortcoming is that cohesive energy is a measure of the energy needed to *separate* atoms, but hardness is not a measure of this. Hardness is a measure of the energy needed to *shear* pairs of atoms; that is, to break chemical bonds by shearing them.

Other authors have studied other correlations. Two are Povarennykh (1964), and Goble and Scott (1985). The latter emphasized compressibility (inverse bulk modulus) as did Beckmann (1971). The bulk modulus is not a reliable measure for the same reason as the cohesive energy. It is volume dependent rather than shear dependent. Still another attempt to correlate hardness and compressibility was that of Yang et al. (1987). This was followed by a proposal by Liu and Cohen (1990) that hardness and bulk moduli are related. This proposal was refuted by Teter (1998) who showed that hardness values correlate better with shear moduli than with bulk moduli.

A measure of shear strength is the shear modulus. For covalent crystals this correlates quite well with hardness (Gilman, 1973). It also correlates with the hardnesses of metals (Pugh, 1954), as well as with ionic crystals (Chin, 1975). Chin has pointed out that the proportionality number (VHN/C_{44}) depends on the bonding type. This parameter has become known as the Chin-Gilman parameter.

The variation of the Chin-Gilman parameter with bonding type means that the mechanism underlying hardness numbers varies. As a result, this author has found that it is necessary to consider the work done by an applied shear stress during the shearing of a bond. This depends on the crystal structure, the direction of shear, and the chemical bond type. At constant crystal structure, it depends on the atomic (molecular volume). In the case of glasses, it depends on the average size of the disorder mesh.

There are at least four types of chemical bonding. Some crystals have open atomic structures, while others are close-packed. Also, many crystals are anisotropic. Therefore, although making hardness measurements is relatively simple, understanding the measured values is not simple at all.

Attempts to understand hardness from first principles have resulted in empirical equations that represent good curve fitting, but yield relatively little understanding (Gao, 2006).

1.3 THE NATURE OF HARDNESS

Hardness is a measure of the ease with which solids can be plastically deformed. This depends on the mobilities of dislocations, their multiplication, and their interactions. Dislocation speeds vary from Angstroms per second to 10^{13} Å/sec. Their concentrations vary from zero to about 10^{12} lines/cm^2 and the interaction possibilities number at least the squares of their concentrations. Fortunately, there are some limiting cases in which a few factors dominate the behavior.

The mobilities of dislocations are determined by interactions between the atoms (molecules) within the cores of the dislocations. In pure simple metals, the interactions between groups of adjacent atoms depend very weakly on the configuration of the group, since the cohesive forces depend almost entirely on the local electron density, and are of long range.

In covalently bonded crystals, the forces needed to shear atoms are localized and are large compared with metals. Therefore, dislocation motion is intrinsically constrained in them.

Ionically bonded crystals contain both long-range and short-range bonding forces because like ions repel each other, while unlike ones attract.
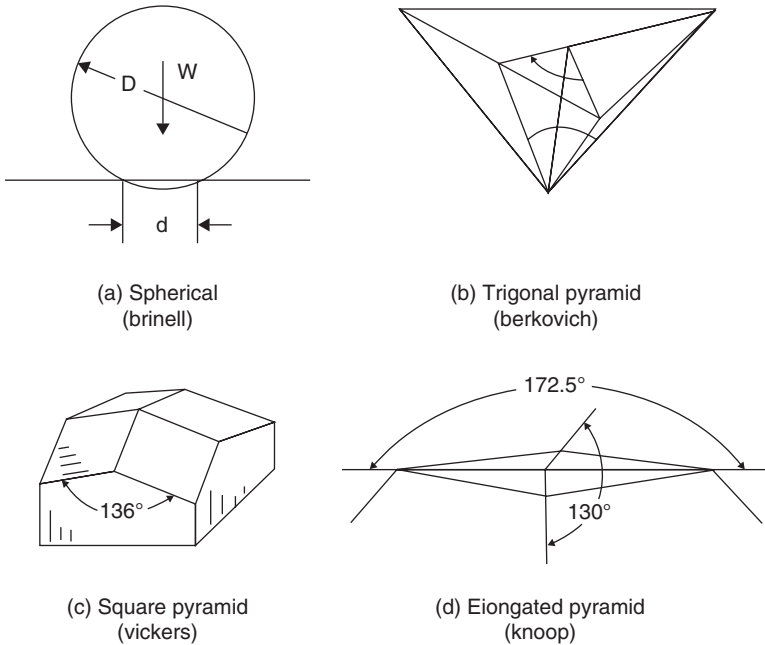
Thus, in simple metals, interactions between dislocations rather than interactions between atoms, are most important. The hardnesses of metals depend on deformation hardening (dislocation interactions) rather than individual mobilities. The elastic resistance to shear plays a dominant role because it is directly involved with dislocation mobility.

Since hardness and the shear modulus are usually proportional, the factors that determine the shear moduli need to be understood. The shear moduli are functions of the local polarizability and this depends on the valence electron density, as well as the energy needed to promote a valence electron to its first excited state. The latter depends on the strength of the chemical bond between two atoms. This will be discussed in more detail in Chapter 3.

Hardness is a somewhat ambiguous property. A dictionary definition is that it is: "a property of something that is not easily penetrated, spread, or scratched." These behaviors involve very different physical mechanisms. The first relates to elastic stiffness, the second to plastic deformation, and the third to fracturing. But, for many substances, the mechanisms of these are closely related because they all involve the strength of chemical bonding (cohesion). Thus discussion of the mechanism for one case may provide some understanding of all three.

The four rather distinct forms of chemical bonding between atoms are: metallic, ionic, covalent, and dispersive (Van der Waals). All of them are subtopics of quantum electrodynamics. That is, they are all mediated by electronic and electromagnetic forces. There are also mixed cases, as in carbides and other compounds, where both metallic and covalent bonding occur.

The principal type of hardness to be discussed here is indentation hardness in which a diamond of a standard shape is impressed into a specimen surface.

(a) Spherical
(brinell)

(b) Trigonal pyramid
(berkovich)

(c) Square pyramid
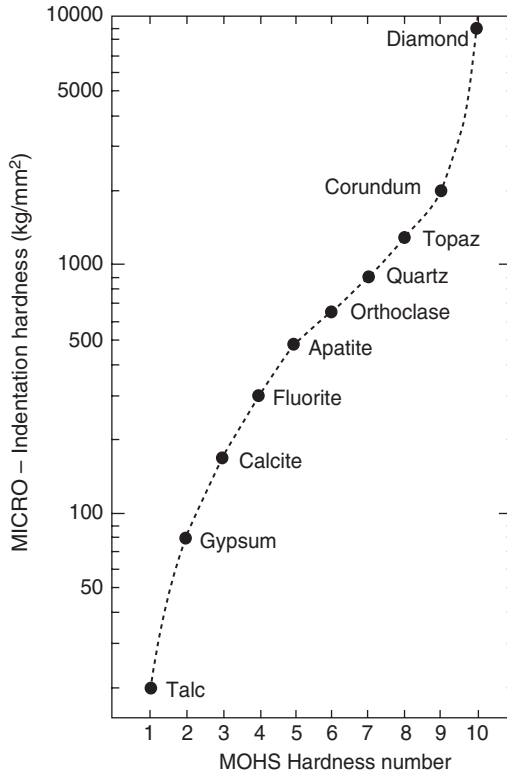(vickers)

(d) Eiongated pyramid
(knoop)

Figure 1.2 Shapes of various hardness indenters (adapted from Shaw, 1973).

The shape is usually either: a sphere (Brinell, and Rockwell B or C); a square pyramid with apex angle = 135° (Vickers); a trigonal pyramid (Berkovich); or an elongated four-sided pyramid (Knoop). (See Figure 1.2). For quality control in manufacturing operations, semi-automatic Rockwell machines, and their various indenters, are also useful.

A fixed force is applied to the axis of the indenter which makes an irreversible indentation into the specimen's surface. The projected length, or area, of this indentation is measured, and the ratio of the applied load to this projection is formed to obtain the hardness number which has the dimensions of stress (also expressable as energy/volume). The sizes of the indentations vary, depending on the indenter's shape and the amount of load applied to it. The size range is from macro- (millimeters), through micro- (microns), to nano- (nanometers).

There are other, less commonly used, methods for measuring hardness. One is an impact method in which an indenter is dropped from a known height onto a specimen, and either the size of the indentation, or the coefficient of restitution, is measured. Another is the pendulum method in which a rocking pendulum is applied to a specimen surface. The damping of the pendulum's oscillations is a measure of the hardness. Still another is Moh's scratch method in which the ability of one specimen to scratch another is observed. These methods are described in various books (McColm, 1990), but only the

Figure 1.3 Correlation between the Moh scratch hardness and Vickers indentation hardness scales.

Vickers indentation method will be pursued here (in both its micro- and nano-manifestations).

However, to develop some intuitive sense of hardness it is useful to consider the Moh scratch hardness scale. This is a rank-file scale consisting of ten levels. Each level has been assigned to a particular mineral such that the mineral at level n is capable of scratching the one at level $(n - 1)$. The mineral at the lowest level (designated 1) is talc, and the highest (designated 10) is diamond.

Figure 1.3 compares the Moh scratch scale with the more quantitative Vickers scale (Gilman, 1973). Clearly the two scales are not linearly related. Each has its own realm of application. For brittle minerals, and similar materials, the Moh scale is most useful. For ductile materials like metals the Vickers indentation scale can detect small differences more readily. Note that the range on the Vickers scale is large; about 1000, while range of the Mohs scale is about 10.

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