Materials and the Development of Civilization and Science

Empiricism and esthetic selection led to discovery of many properties on which material science is based.

Cyril Stanley Smith

Materials—good hard solid stuff like wood, stone, metals, and clay—are generally dismissed as merely incidental to the things that are done with them. The archeologist recognizes successive material ages—Stone, Bronze, and Iron—but the analysis does not usually go much beyond this. Even art historians do not give much attention to the properties of matter through which an artist must realize his vision. To my mind, man's enjoyment, exploitation, and eventual explanation of the inner qualities of materials is one of the more fascinating aspects of human history (*1*).

Though man's imagination is not limited by materials (except those of which his brain is made), materials have fundamentally determined what man could do at every stage of history. There is a definite interplay between his knowledge of the properties of matter and the kinds of things he has thought worth doing. The Prometheus myth associates man's humanity with his ability to modify materials by fire. The earliest artists and the earliest philosophers were clearly sensitive to the range of qualities possessed by different substances. One may even claim that man's exploitation and enjoyment of the different qualities of material (explained today on the basis of composition, interatomic forces, and structure) had a great deal to do with man's finding himself. His discovery that he could play an almost God-like role in changing the very nature of matter may have played a considerable part in developing his intellectual awareness and giving him an aggressive confidence in his ability to control his environment—perhaps more than did his agricultural experiments, wherein his role was to aid and direct nature's normal biological processes, not to change its substance.

Man probably owes his very existence to a basic property of inorganic matter, the brittleness of certain ionic compounds. Some prehuman animal, bashing stones around, had discovered that the edge of a broken stone possessed useful properties, whereafter, as S. L. Washburn has so convincingly argued (*2*), any deviant who could crack and use stone a little more precisely gained great evolutionary advantage. The difference between the two types of tool shown in Fig. 1 lies in the fact that the maker of the fine axe had acquired a more complex brain and an opposable thumb. He was able not only to recognize and select materials that were brittle but strong (what an intricacy of atomic interactions these properties involve!) but to control the production and interaction of shock waves and tensile stresses in such a manner as to cause cracks to propagate in the directions necessary for producing useful shapes. Man appeared as the culmination of a series of mutations whose biological survival was favored by an increasing ability to select and manipulate materials.

Man's sensitivity to the esthetic qualities of matter is equally important, perhaps more so. After stone chipping, the next industry for handling inorganic materials was probably the selection and grinding of colored minerals for pigments (*3*). But paralleling color as a distinguishing characteristic of materials is texture, which is even more fundamentally related to their nature. Man has exploited the texture of different kinds of stone in toolmaking and in building, and has used various superficial and internal textures for his enjoyment, for identification, and as a guide during manipulation. Probably most early uses of complex substances involved esthetic pleasure based on their intriguing physical properties. For his delight man tries many things; for utility he employs only what he knows will work.

Esthetic Qualities of Ceramics

The cave paintings were an early exploitation of the properties of mineral substances, but real richness followed the discovery of the effects of fire in modifying the properties—even the very nature—of minerals. The plasticity of moist clay was widely exploited in Upper Paleolithic times in the modeling of figurines, and some of these may even have been fire-hardened. Figurines were certainly being fired by 9000 B.C. in the Middle East. Braidwood has suggested that the houses with sun-dried mud walls (*tauf*) that date from that time constitute a kind of shaped and hardened clay container as an antecedent to portable pottery, which, in turn, was perhaps an outgrowth of fire-hardened clay-lined pits for the storage of grain. Ceramics was well on its way to becoming the noblest of the pyrotechnical arts once the pot was seen to be not only useful but pleasing to the eye and potters found that both the beauty and the utility of their product could be increased by firing at higher temperatures and by admixing various minerals to give rich color and textural effects. By shortly after 7000 B.C. ceramics had come to include production of objects having strong esthetic appeal based on plasticity and on the modifications of viscosity, strength, surface tension, texture, and color which occur when certain natural materials are heated in association with each other. Even today we understand only "in principle" the whole range of physical and chemical properties and their interrelationships that were effectively used in making ceramics. Consider, for example, the pots shown in Figs. 2 and 3. Their esthetic appeal is based directly upon the potter's control of specific physical properties. The range of colors arises from the absorption of light of specific

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wavelengths by metal ions in the right state of oxidation. The wonderfully soft reflection of light from the glaze on the Korean pot is due to innumerable tiny internal bubbles skillfully nucleated by control of composition and temperature, and preserved by exploitation of the high viscosity of feldspathic glaze. The red glazes of Ming China required not only the addition of traces of gold or copper but also a particular sequence of kiln atmospheres and temperatures to give a precipitate of micron-sized particles of metal. The shaping of the pots involved familiarity with many subtle aspects of the behavior of colloids, with thixotropy, and with effects of interfacial energies, adsorption, and interatomic bonds of many types; their strength depends on a balanced array of amorphous and crystalline structures; their colors require atoms in excited states dispersed in unnatural environments (*4*).

These effects were discovered, reproduced, and enjoyed long before they were explained (in the main by solid-state physicists who are still living). As one looks at the past history of materials one must admit that the practical predecessors of Hamada, Cellini, and Masamuné, going right back to the legendary Hephaestos, were necessary forerunners of Aristotle, Lavoisier, Planck, Mott, Seitz, and other theorists. It was artistic empiricists who first showed with their fingers that there was something for man's mind to be concerned with. Cookery and tasteful selection disclosed most of the marvelous properties of matter; science has belatedly explained things previously known.

The Greek philosophers saw matter largely as the means toward the achievement of all-important form. Craftsmen saw matter as diverse materials which they themselves could select, transform, and shape. The alchemists marveled at the many changes of color and other qualities which resulted from mixing and heating different substances—the same phenomena that had given rise to metallurgy and ceramics at the beginnings of civilization. From studying these changes intensively they came to regard them as mystic symbols of the workings of the whole universe. Their aim was most noble, though their theories failed to bear fruit and their experiments added little to the repertoire of practical techniques. Only in the last few decades has science reached the position where it can lead practice in the development of new types of material. It has resolved the ancient dichotomy by relating qualities to forms: the properties are now seen to depend on the arrangement of atoms and on the distribution of electrons between geometrically based energy levels.

A material, to be useful, must have some specific shape, which is usually imposed on it by another material, in the form of a tool or mold, with which it is in competition. The material must be soft enough during manufacture to be given a shape, yet hard enough to retain this shape in use. These conflicting requirements can be satisfied by various means. Clay can be made plastic with water, molded intricately, and then dried to a fair rigidity because of the reestablishment of direct interatomic

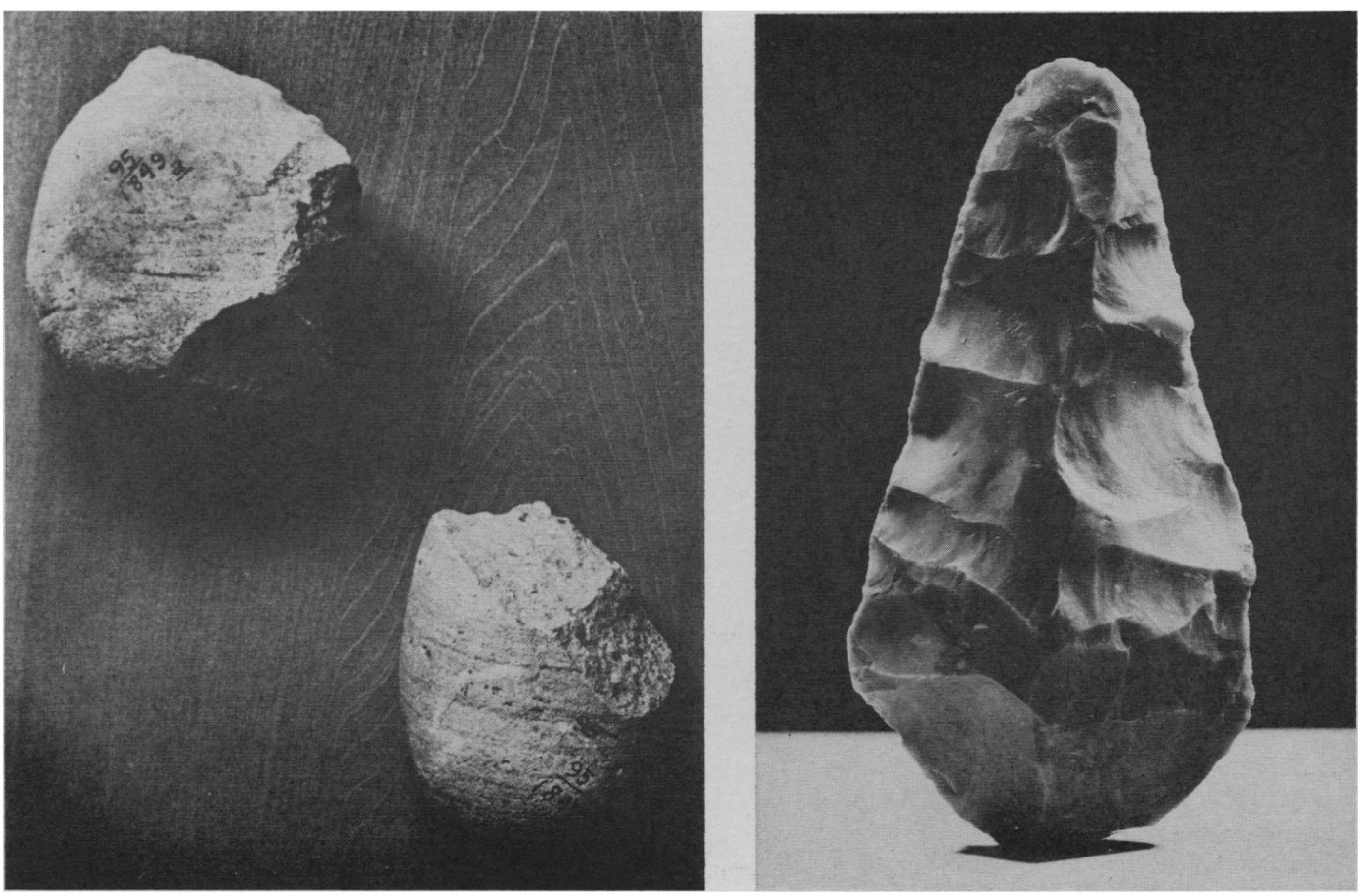


Fig. 1. Early stone tools. The pebble tools at left (similar to those found by S. B. Leakey in Olduvai gorge, dating from about 1,750,000 years ago) were made by a prehuman hominid. The Acheulian hand axe at right is much more recent, and required a hand capable of precision grip and a brain that could control it (slightly reduced). [Photograph at left, by Robert Saracco, reproduced courtesy of *Scientific American*; photograph at right, by the University Museum, Philadelphia]

forces between the clay particles. Still greater changes occur when molded clay is moderately heated; it is thereupon converted into a hard and strong body which will not revert to mud when wet because it has become partly crystalline—as indeed its components were in the granite from which it ultimately arose by weathering. It was truly one of man's greatest discoveries when he found that he himself could, by controlled heating, produce such profound irreversible changes in the structure and properties of common matter.

The Beginning of Metallurgy

At still higher temperatures clays melt, and they are useless thereafter. But melting is the basis of a primary means of shaping metals, for they solidify essentially unchanged. When solid, metals have the property of resisting stress only up to a certain point, beyond which they deform without breaking. Shaped by locally high stresses under the hammer, metals will resist the less severe stresses of use indefinitely. This property rests very intimately on the structure of the metal and on the state of its electrons, but the theory of deformation was not necessary for the discovery that metals are deformable, any more than the theory of alloys was needed for the discovery of bronze. The practical-cookbook method of handling materials revealed nearly all of the different types of behavior of metals and alloys long before man had any ideas concerning their atomic and electronic basis. It was enough to have found out that properties were reproducible. They were simply attributed to the different natures of materials which could be identified and put to use.

There are some metals (notably copper and gold) which occur in nature in conspicuous malleable lumps, and man could have found these in his early searches for toolmaking stones. The oldest known artificially shaped metal objects are some copper beads found in northern Iraq and dating from the beginning of the 9th millennium B.C. Two Anatolian finds date from the 8th millennium (*5*). (These have not yet been examined metallographically, but there is no reason to doubt that the objects are native copper that has been hammered, supposedly by means of a stone hammer and anvil, and perhaps abraded to shape.) The Indians of the Great Lakes region of America were using native cooper about 4000 years ago. Most metals, however, occur in nature in abundance only in the form of mineral compounds (oxides, carbonates, sulfides, or others), which, though they possess attention-catching color and density, have not the malleability of a metal. At some point in time—not well established but probably shortly after 5000 B.C., and in the mountains that form the northern boundary of the Fertile Crescent—it was found that heating certain greenish or bluish minerals in the proper kind of fire would produce metal—in other words, smelting had been discovered. This was a chemical event second in importance only to the initial discovery of the effectiveness of fire, and it vastly increased the amount of metal that could be made available (*6*). Separation of metal from ore requires a higher temperature than is commonly available in open fires, and many archeologists think it may have occurred first in a pottery, for clay pots were being fired in kilns at moderately high temperatures and oxide colors were probably being experimented with before copper was smelted. Or smelting may have been discovered by another route. Hammering of native copper may have been followed by the discovery that copper could be more extensively hammered if it were repeatedly heated (annealed) in a fire. Once the critical temperature had been reached, the melting and casting of native copper would have followed, making it possible to utilize previously useless scrap metal and small nuggets. A final step might have been the discovery that the green matter accompanying native copper could be transmuted to produce more metal when it was strongly heated with wood or charcoal. But this need not have been an entirely accidental discovery. Once the change-producing properties of a hot fire were known, the fundamental human instinct of curiosity could have led someone to experiment empirically, for no other reason than that he enjoyed the sight of unexpected things happening when colored and heavy stones were heated, alone and in mixture. A plot, against time, of the highest temperature regularly produced for any purpose by a given culture would serve as a good graph of the waxing and waning of technological skill in general.

Smelting, like most phase transformations or social innovations, had invisible beginnings and can only be recognized clearly after a certain stage of growth had occurred. However, regardless of

Fig. 2. An early ceramic pot, decorated with metallic oxides, from Susa (Iran), late 4th millennium B.C. [Photograph courtesy Musée du Louvre, Paris]

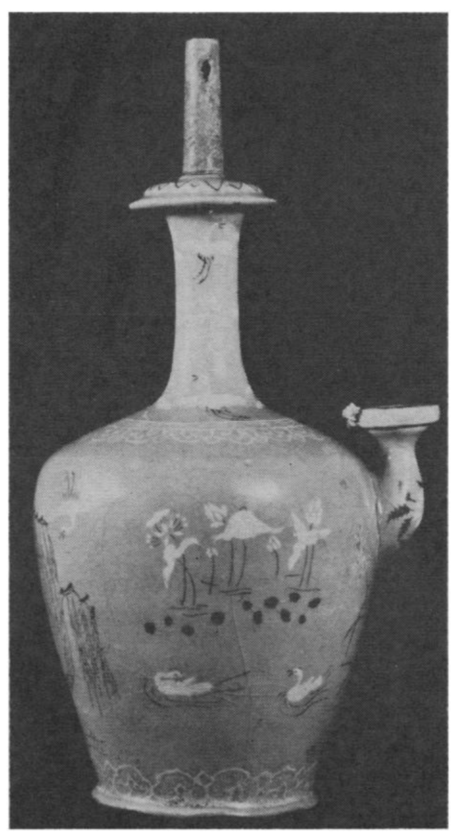


Fig. 3. Korean water jar of inlaid and glazed ceramic ware, Koryu dynasty, 11th century A.D. [Photograph courtesy Freer Gallery, Washington, D.C.]

the uncertain origin of smelting, it is well established that before the end of the 3rd millennium B.C. nearly all the metals that can be reduced by carbon from a common distinctive mineral had been discovered and put to some use; most of the useful alloys that can be made by mixing such metals had been discovered, and definite proportions had been selected; the effects of work-hardening and annealing (heat-softening) were known and used; and most of today's methods for shaping metal by casting, deformation, and joining were being used, except for those that require power or high-precision tools. Even iron was then known, though its wide utilization was delayed for a millennium. Steel was made with some degree of control by 1200 B.C.; cast iron was made by 500 B.C. (though only in China; it was not appreciated in Europe until 2000 years later). Zinc has an interesting history for it was used in an alloy (brass) long before it had been seen as a metal.

Aluminum cannot be reduced by carbon, and therefore, despite the vast abundance of its ores, the metal was not made until after electrolysis had revealed the electropositive alkali metals which were needed for its reduction (*7*). Many other metals, such as titanium and niobium, appeared on the scene relatively late, partly because they cannot be reduced with carbon except at very high temperatures, but principally because they are contaminated to the point of uselessness by carbon and the atmospheric gases, which the primitive metallurgist could not control (and which not even the advanced chemist could control until the present century).

Properties of Metals and Alloys

Figure 4 shows a comparison of the principal methods of hardening metals that were employed in antiquity. These are, (i) work hardening; (ii) hardening by the formation of solid solutions, as in the copper-tin alloys (bronzes); and (iii) hardening by partially restrained allotropic transformation, until recently known only in the case of the quenching of steel from a suitable high temperature, which produces the most spectacular change of properties. The three methods of hardening are now known to be simply three different ways of producing imperfections in the regularity of the stacking of atoms in the metal crystals. Work hardening breaks up the crystals mechanically and introduces "dislocations." Solid solution replaces some atoms of the main component in the crystal by others of a different size. The quench hardening of steel produces both of these effects and in addition produces extremely small crystals which oppose the deformation of each other. Tempered steel owes its hardness partly to a dispersion of tiny particles of iron carbide. (A somewhat similar dispersion, though produced without a major transformation in crystal form, is the basis of precipitation hardening, the only hardening technique not used by the ancients. It was discovered in an aluminum alloy in 1906, though hints of it could have been found previously in the behavior of sterling silver and certain dental alloys.) But theory was in no way necessary for discovery.

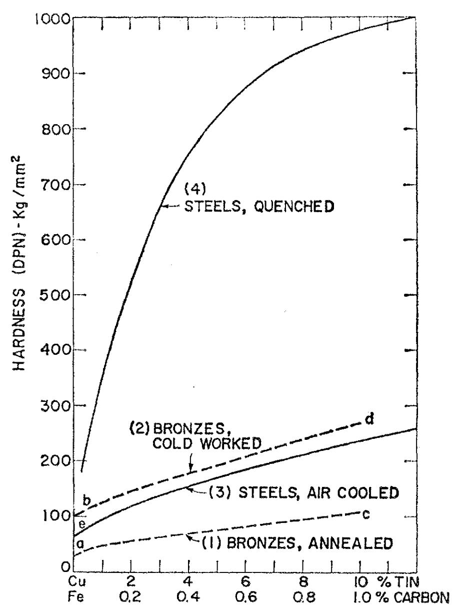


Fig. 4. Curves illustrating the principal ways of hardening metals. Pure copper when annealed has a hardness (DPH, measured with the Vickers diamond pyramid indenter) of about 40 kg/mm² (point *a*). Cold working hardens copper progressively to about 100 kg/mm² (point *b*) after 70-percent reduction in thickness, and to a maximum of about 120 kg/mm², which is reached after 95-percent reduction in thickness. Alloying copper with tin in amounts up to about 10 percent (curve 1) progressively raises its hardness to about 110 kg/mm² (point *c*) if the alloys are annealed, and the hardness can be further increased by cold work (curve 2) to about 270 kg/mm² (point *d*). Pure iron, which has DPH of about 60 (point *e*), is hardened by the addition of carbon, the essential element in steel. If steels are heated and allowed to cool naturally, the range of their hardness (curve 3) is slightly below that of the bronzes, but they become spectacularly superior if quenched (curve 4). The curves are approximate and the hardness varies considerably with impurity content, details of casting technique, prior annealing, and other factors. The brittleness of an alloy generally increases with its hardness.

Other critically useful modifications of metal properties that were used well before the origins of the classical civilizations were the changes of melting point produced by alloying, useful in soldering; diffusion in solids; and various chemical changes (particularly those involving oxides, sulfides, and silicates) which gave immiscible liquids useful in separating metals from earthy matter and from each other, as well as in refining.

A close relative of almost every one of the alloy compositions and methods of hardening that were employed for any purpose up to the very end of the 19th century had been found and put to use over 4000 years earlier! The engineering achievements of the Romans, the marvels of Byzantine architecture and ecclesiastical art, even the developments of the Industrial Revolution and 19th-century engineering were, with few exceptions, all based on materials of types, if not exact compositions, that had long been known (*8*). For most of this long period the history of metallurgy is mostly that of the geographic diffusion of techniques from the Middle East, where they originated, and that of an extending scale. Metallurgists were innovators only to the extent that they produced their materials in ever-increasing quantities at ever-decreasing cost. Craftsmen and engineers used their age-old materials with skill and with increasing reliability, but there was only trivial change in the range of characteristics available. For millennia, sophisticated alloys were associated with rather primitive mechanical technology. The empirical search and trials of the early metallurgists of the Middle East had indeed left little to be discovered. It seems that there was a personal immediacy in man's sensual contact with materials, in contrast to his more slowly developed, more intellectual, approach to mechanics. As R. J. Forbes has remarked, there is an important difference between the *discovery* of the properties of materials and the *invention* of things to do with them.

Figure 5 is a photograph of a silver vase now in the Louvre. It dates from about 2800 B.C. and, of course, comes from Mesopotamia. An ingot of metal had been hammered into a sheet, with frequent annealings, raised by local hammering on a stake into the present

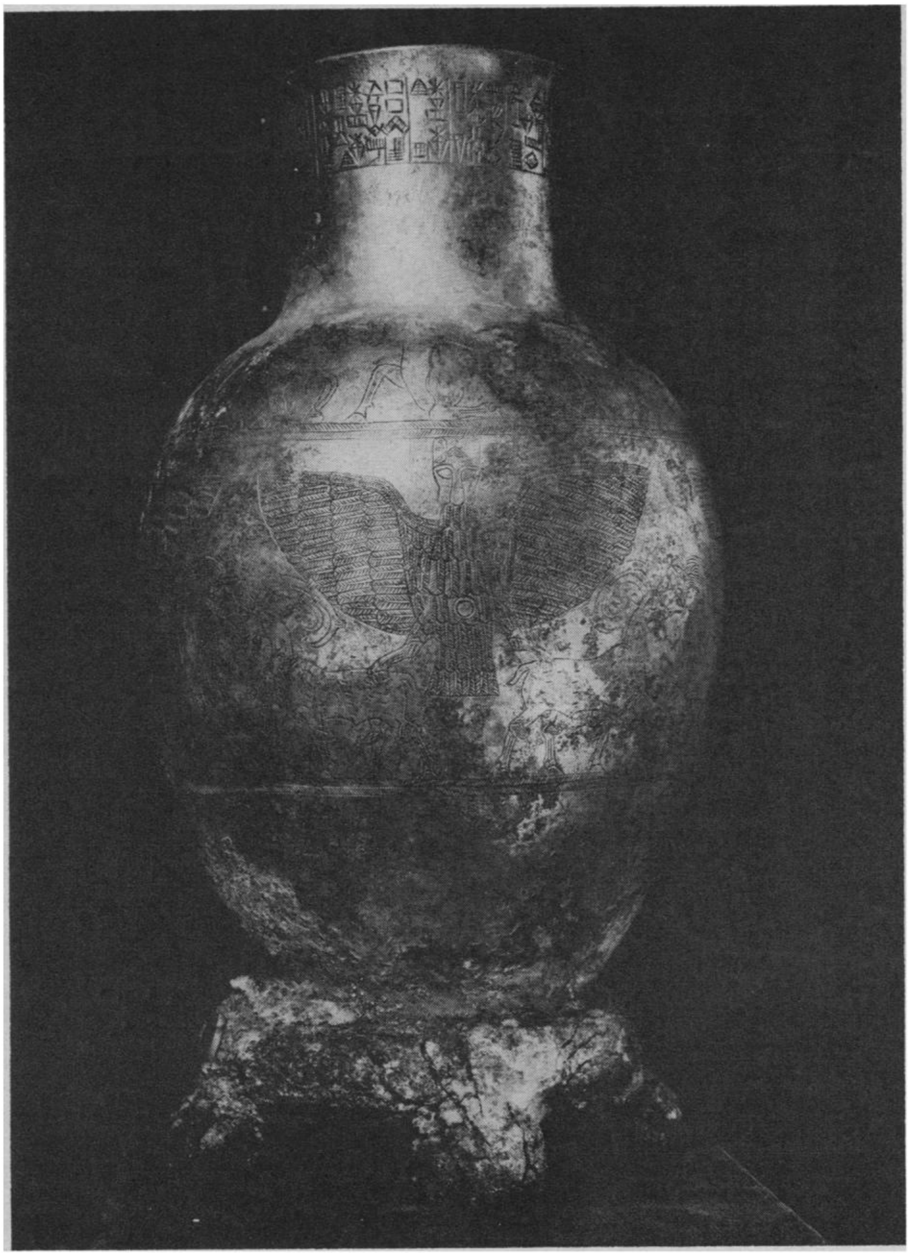


Fig. 5. The silver vase of Entemena, King of Lagash, Mesopotamia; about 2800 B.C. [Photograph courtesy Musée du Louvre, Paris]

magnificent form, and finally decorated and inscribed with lines impressed by a chasing tool. The gold jewelry from the royal graves at Ur (about 2600 B.C.) reveals a whole range of metallurgical techniques, including the use of wire (though not drawn wire). The use of alloy solder in this jewelry is particularly impressive; the solder has a lower melting point than the gold but retains most of the qualities of the pure metal (*9*). The designs are inseparable from the techniques, and the techniques, from the innermost properties of matter they exploit.

An even more ingenious soldering operation was the granulation technique. This technique was used in Crete and Mycenae about the middle of the 2nd millennium B.C. and beautifully employed by the Egyptians (as, for example, in the handle of the dagger found in Tutankhamen's tomb), but it reached a magnificent apex in the hands of Etruscan goldsmiths (Fig. 6). The invisible soldering into place of the spherical granules depended on coating the surface with an extremely thin surface of copper oxide (done by selective oxidation of the copper alloyed with the gold, or by application of a thin coating of paint containing finely ground copper oxide or carbonate). The copper oxide was then converted, by the reducing action of the furnace gases, into metallic copper, which formed a low-melting-point alloy with a little of the underlying gold. Capillarity caused the molten alloy to flow into the most minute crevices and the result was nearly invisible junctions. The technique required knowledge and control of the ductility of metals, of the effect of alloying on melting point, of differential oxidation and reduction, of diffusion, of surface tension and interfacial tensions, and of the optical properties of smooth and curved surfaces. Scientific understanding of these properties may have been lacking, but they were known and used effectively in the creation of pleasing designs based intimately upon the nature of the technique.

Technique versus Design

Chinese bronzes. The cover photograph shows a bronze vessel produced about 1200 B.C. in China. It is a magnificent exploitation of the casting process. The design is intimately related to the method of manufacture, which utilized the plasticity and refractoriness of sandy clay for the mold, and the fluidity of the metal in filling it (*10*). The most emphatic aspect of the design is the strong symmetry of the flanges, a characteristic of most Sung and Chou bronzes. These flanges did not originate in the artist's fancy but are a direct consequence of the fact that the molds had to be made in several pieces to allow removal of the pattern around which they were shaped and to give access to their inside surfaces for carving the fine details (*11*). Now, it is difficult to assemble such a mold without leaving some cracks into which the metal can run, forming fins on the resulting casting. The Chinese artisans or artists exploited this inevitable defect when they intentionally opened up the divisions of the mold, making them into a basic feature of the design.

The shapes of castings became freer, though on the whole less organically satisfying, when the foundrymen learned how to make almost any shape in wax, then bury this in clay, burn out the wax, and pour molten bronze into the cavity where the wax had been. (This technique had been devised very early in the Middle East but was slow to diffuse to China. It was used extensively in Peru and Ecuador in pre-Hispanic times.) Many beautiful things have been made in this way, but the technique is easily abused because it is so little subject to restraint imposed by the nature of the materials.

Early History of Iron

The history of iron is particularly interesting for it illustrates all the major themes of metallurgical development. Iron, like copper, was first used in the form of native metal (from meteorites), but the limited supply kept it a rare curiosity. Once appropriate methods of smelting and working had been discovered, the abundance of iron ores gave iron the ascendency over copper and bronze, despite the fact that its properties were, at first, inferior.

Throughout most of its history iron has been reduced from its ores at a temperature below its melting point, the resulting metallic sponge being hammered to remove slag and to weld the particles into a compact and ductile mass. Bits of man-made iron appeared in the first half of the 3rd millennium B.C., and iron was not uncommon in the Hittite empire around 1500 B.C., but it did not become important until about 1200 B.C. Though most of the product, then as later, was in the form of wrought iron, by that time man had learned how to make steel by prolonged heating of iron in a deep charcoal fire and he was hardening it, though ineffectively, by quenching it.

The early history of steel is murky, for objects made of it have not, like objects of bronze, been avidly sought by collectors and museums for their beauty. Moreover, the crucial distinction between iron and steel can only be determined on the basis of analysis or microscopic examination, and until very recently (*12*) this could be done only with metal, not with the rust or other corrosion product which is often all that remains. Good steel was certainly being made by the smiths of Luristan (in the mountains in western Iran) at a date within two centuries (plus or minus) of 1000 B.C. Luristan bronzes are to be found in every major museum, but the steel and iron found in the same graves, though magnificent metallurgical achievements, are hardly known. The handle of the short sword shown in Fig. 7 is composed of several pieces of intricately shaped iron, at least some of them forged in dies, as in 18th-century attempts at mass production, so that they will fit together (*13*). The blade is steel, *real* steel, and it had been hardened by heat treatment. One sample of Luristan steel which I have examined had a hardness (DPH) of over 400 kg/mm^2, and hardnesses of more then 250 are common, although not infrequently the structure of the blades shows that they had been annealed and very slowly cooled, supposedly in a funerary fire. After the Luristan period, knowledge of hardening techniques waxed and waned through the centuries. Superb steel swords were made in Japan even before the 12th century A.D. (*14*), but in other parts of the world the consistent production of high-quality steel is recent.

Cast iron (iron containing about 3

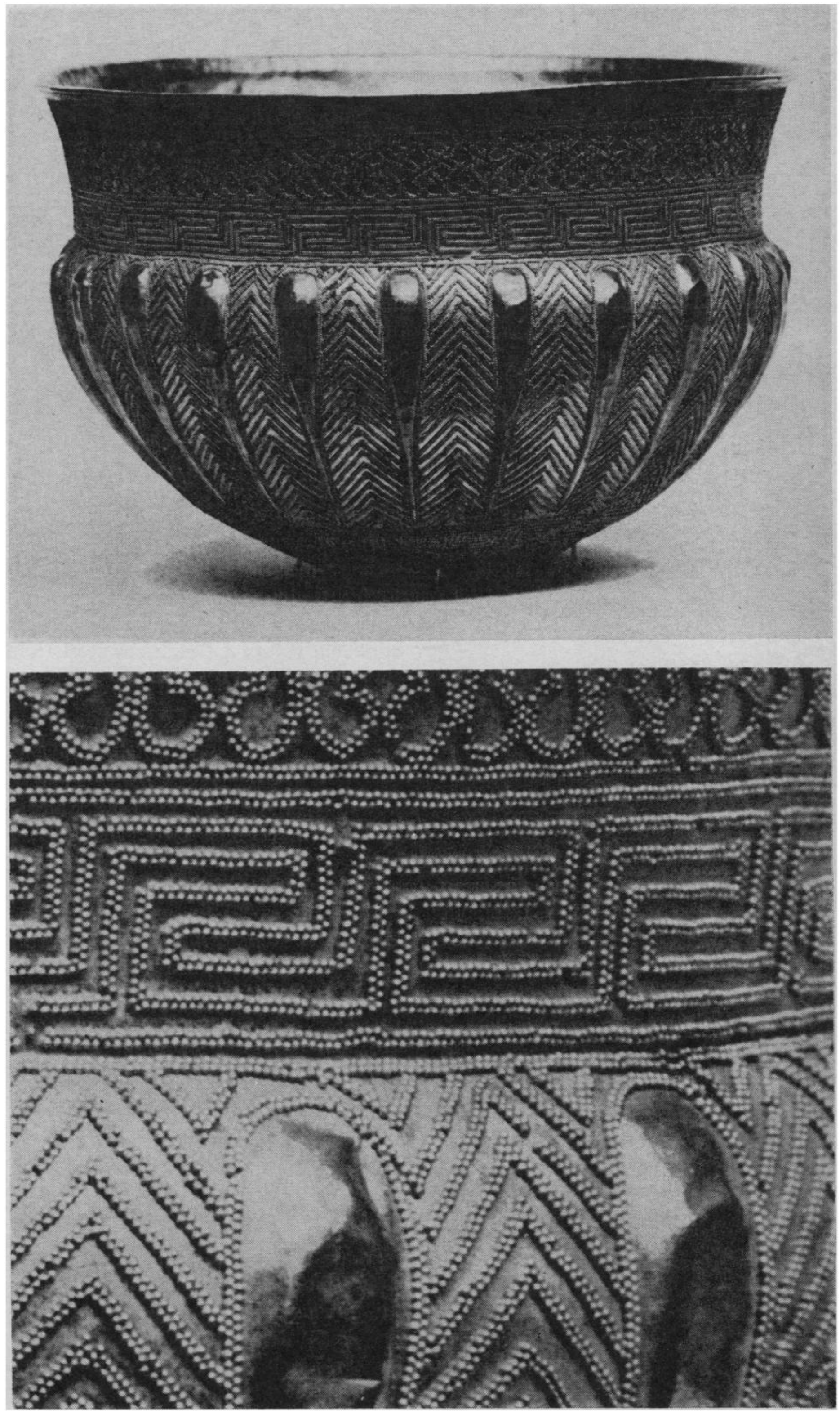
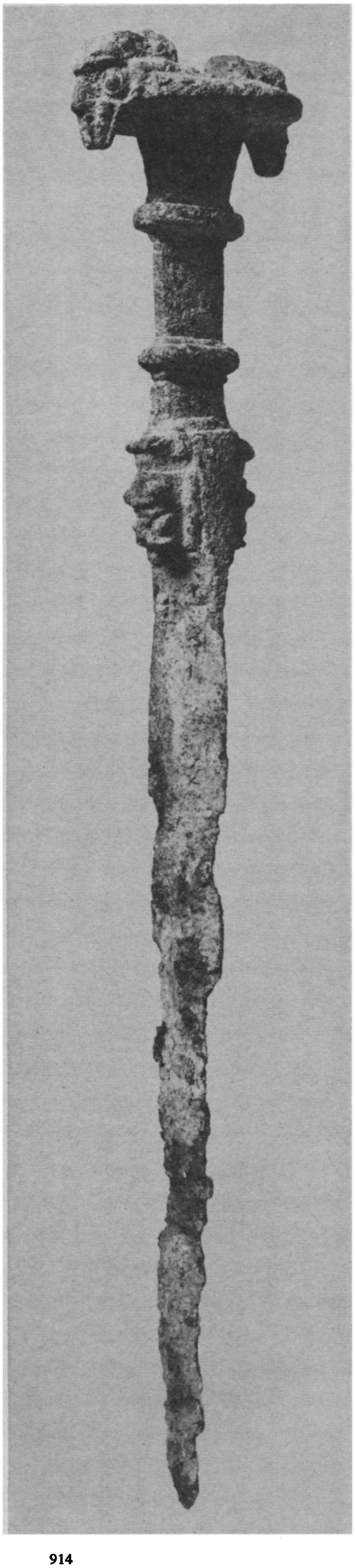


Fig. 6. Etruscan gold bowl with granular decoration, about 600 B.C. (actual size), and enlarged detail (about × 4.4). The bowl is about 11.1 centimeters in diameter, and the individual spherical granules are about 0.033 millimeter in diameter. [Photograph courtesy Victoria and Albert Museum, London]



percent of carbon, relatively easy to melt and cast to shape in molds, but brittle) was used from about the 5th century B.C. in China, where the casting process long took precedence over forging (*15*). It does not appear in Europe until the very end of the 14th century A.D., and then principally as an intermediate stage in the production of wrought iron from its ores (it is easier to separate the metal from earthy impurities when it is in the molten form) (*16*).

We know today, of course, that the difference between wrought iron, steel, and cast iron lies mainly in the increasing amount of carbon that its alloyed with the metal. This became part of scientific knowledge only at the end of the 18th century, at the time of the Chemical Revolution. Prior to that it had generally been thought that steel was a more pure form of iron (as Aristotle believed)—a reasonable enough assumption, for steel was made by prolonged heating in a fire, which common experience showed to be a powerful purifying agent. The fact that steel contained some real matter derived from the charcoal fuel was discovered only when Europeans attempted to duplicate textured Damascus steel from the Orient, for it was found that the visible texture of this steel resulted from a material residue that remained when steel, but not wrought iron, was dissolved in acid. This residue was tentatively identified in cast iron as plumbago (graphite) by the Swedish metallurgist Sven Rinman in 1774, and later fully analyzed by Swedish and French chemists (*17*).

It is significant that Damascus and Japanese swords, which are deservedly famed for their superiority to European weapons, both have surface patterns visible to the naked eye (Figs. 8 and 9). The textures are directly related to the way in which steel is made and provide a guarantee of proper composition and fabrication. They are, indeed, forerunners of modern metallographic control of the structure of metal. It is not an accident that such methods of handling metals were developed in the Orient, for Orientals (influenced by Buddhist and especially Taoist philosophy) have always been sensitive to texture. Subtle jade, not glittery diamond, is the preferred stone. The use in Western languages of the term *damask* or *Damascus* for several quite different kinds of material suggests how starved Europeans must have been for decorative textures when they first encountered them at this famous international market town.

Fig. 7 (left). Luristan short sword, 800 B.C. or earlier. The blade is of carbon steel; the handle, of forged iron, is assembled from several pieces. Total length, 42 centimeters. [Photograph courtesy University Museum, Philadelphia]

Beginnings of the Science of Metals

Though the compositions of useful alloys remained nearly constant during a long period, understanding of metals advanced in pace with the development of science as a whole. The mass of information on the reaction of substances which the practical smelter, assayer, and smith had gathered, by suggesting problems to the natural philosophers, was at least as important to the development of modern science as were the empirical data of the astrologer and astronomer. The color changes which alloying or surface reaction produces in metals led to the idea of transmutation, and to alchemy, which inspired interesting experiments, though few of them had any effect on practical metallurgical operations. However, the alchemists were right in seeking a theory, just as practical metallurgists were right in using empirical techniques. More than half of the reactions listed in the first tables of chemical affinity (1718) are from assaying practice, and it was the assayer who laid the basis for quantitative chemistry. Intensive chemical study of stones and of crystallization was sparked by attempts to make porcelain in Europe early in the 18th century, and many of the great arguments in chemical theory that culminated in Lavoisier's new chemistry arose from the metallurgists' studies of oxidation and reduction.

Studies of Damascus steel led not only to the discovery of carbon in steel but also to the discovery of the basic role of crystallinity, the fact upon which most of the modern science of materials is based (*18*). The concept has an interesting history, which has been largely ignored by historians of science in their concern with extremes of knowledge—of the atom and the universe. Many of the properties which the 17th-century corpuscular philosophers explained in terms of particles of various shapes and aggregations actually arise in microcrystals, not in atoms, and the first qualitative speculations were closer to the truth than the refinements that arose as science, after Newton, became more mathematical. Most of the properties of solids that were attributed to "molecular" behavior by 19th-century physicists and chemists are in fact crystalline or microcrystalline phenomena. The fact that the "molecule" concept had numerological support from both the kinetic theory of gases and the law of simple combining proportions in solids effectively discouraged further consideration of other forms of aggregation.

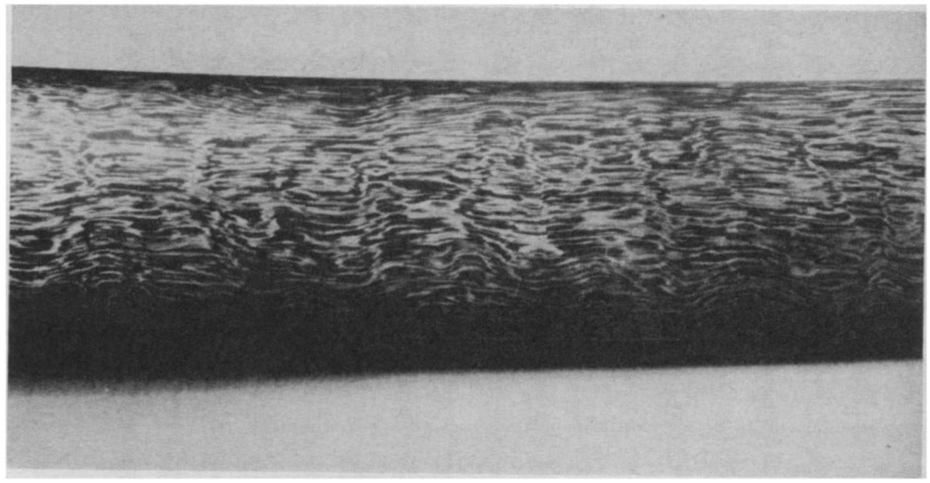


Fig. 8. Detail of Persian sword, late 17th century, showing the "Damascus" pattern in the steel, which reveals the distribution of areas of high and medium carbon content; the swordsmith developed the pattern by chemical etching after final polishing (actual size). [Photograph courtesy Wallace Collection, London]

Microcrystallinity

The slow discovery of the pervasive polycrystallinity of inorganic matter was, in the main, due to the metallurgist, whose work took on real physical meaning after pioneering studies on the microstructure of steel were made by Henry Clifton Sorby almost exactly a century ago. There is a long tradition of using the texture in metals, as revealed by the characteristics of their fracture, as an index of serviceability and as a basis of process control. Though the microscope was used to make important observations in the field of biology soon after its invention early in the 17th century, it showed nothing in metals, for significant surface detail was destroyed by burnishing or breaking.

Superficial attack with chemicals, which eventually was to reveal the structure, was used in Europe for purely decorative etching of armor. It was first applied to expose gross local differences in composition in the Damascus sword (Fig. 9), and it first revealed crystalline structure in 1804, when it was applied to meteorites, in which a composition variation is geometrically distributed as a result of a crystallographic precipitation process (Fig. 10). (It is amusing to note that space research had useful "spin-off" so long ago.) It was this observation in meteorites which eventually turned Sorby's interest to terrestrial steel, in 1864, after he had made pioneering studies of the microstructure of rocks, using thin sections and polarized light. His metallographic technique, which disclosed in detail the complex crystallinity of steel and its changes with changes in carbon content and with heat treatment, has not often been surpassed (*19*) (Fig. 11).

Sorby's work (published only as an abstract, in 1864) was noted favorably, but it was not emulated for 20 years, when research in Russia, Sweden, Germany, and particularly France began to explain the diverse properties of steel after different treatments in terms of its structure. From steel, the technique spread to show the behavior of microcrystals of the nonferrous metals during casting, working, and annealing. By 1900 it had been proved that most of the age-old known facts of metal behavior, (which had first been simply attributed to the nature of the metals and had later been partially explained in terms of composition) could best be related to the shape, size, relative distribution, and interrelationships of distinguishable microconstituents.

The early understanding of the structure of metals grew almost entirely out of work with steel, an extremely complex material which is far from ideal for scientific study. Could it be that scientific study of a phenomenon in controlled and comprehensible isolation marks the end rather than the beginning of an exciting period of research? The metallurgist has had to make, and the engineer has had to use, materials, whatever the state of their understand-

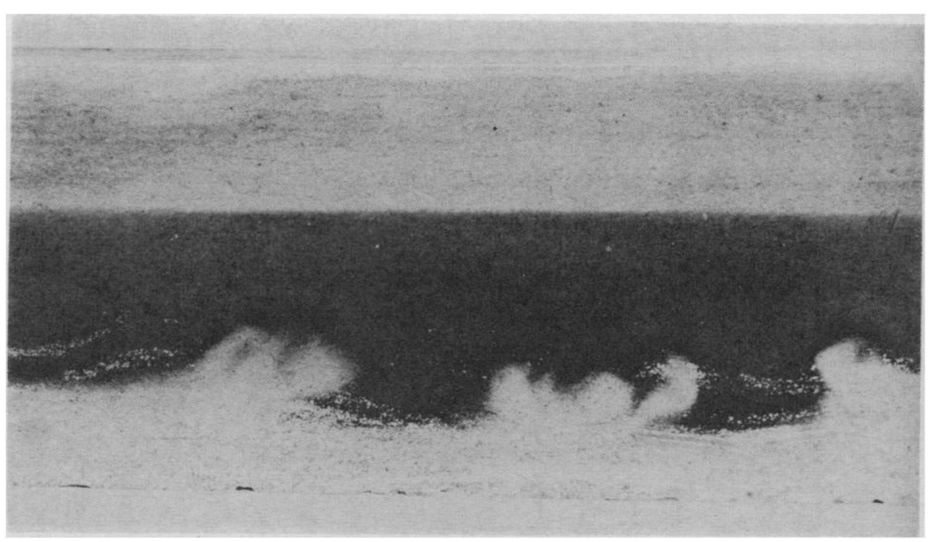


Fig. 9. Japanese sword blade, 16th century (detail). The cutting edge is at the bottom. The lighter parts are fully martensitic in structure, and glass-hard (hardness, typically 800 to 900 DPH), while the darker areas, which were locally masked by clay to cause slower cooling during quenching, are of a softer, pearlitic structure. This blade was lightly etched to emphasize the structure for photography, but the normal Japanese polishing process leaves a beautiful matte finish in which the pattern is subtly visible to a trained eye (about $\times$ 2.5).

ing of them. The metallurgist handled, not simple isolated crystals, but aggregates in which the useful properties depend less on perfect crystallinity than on the disordered material at the interfaces between the crystals, and on their internal imperfections.

While metallurgists slowly worried out their rather naive explanations, physicists and chemists remained relatively uninterested in real crystals, though there was magnificent mathematics dealing with crystal elasticity and space-groups and, after 1880, some good work in crystal chemistry. The molecule was king. In January 1912, a month before he made the famous suggestion that opened up the study of crystals by x-ray diffraction (*20*), the great physicist Von Laue did not know that crystals were believed to have a regular arrangement of atoms! The marvelous new diffraction techniques, developed particularly in England by W. L. (now Sir Lawrence) Bragg, led inevitably to models that were, for a time, too simple and rigid, for they overemphasized symmetry. There was even a belief that there could be no atom movements in a solid crystal, and experiments were made which seemed to prove it; but metallurgists had for millennia been making brass and steel by cementation, and measurements of diffusion soon became a prime index of the role of imperfections in crystals, the study of which is now an important branch of physics.

A particularly active phase in the development of solid-state physics occurred in the 1950's, due, I believe, quite largely to the circumstance that in World War II physicists of the first rank came intimately in contact with "materials" people and each came to appreciate the value of the other's viewpoint and knowledge. It may now be that some of the freshness of that discourse is being lost as the new and very effective discipline, materials science, begins to crystallize.

Conclusion

It will be apparent from this far-too-hasty view that, in the past, most knowledge of materials has been gained by the intelligent empiricist, and that the role of science has been to explain and to provide better control rather than to open up new areas. It may be that in complex fields this is inevitable, for science invokes subtle abstractions which are necessarily concerned sequentially with parts rather than simultaneously with a whole system. But how enormously better off we are now than we were in 1900, for we at least now understand the physical principles behind most of the properties of ceramics and metals, and more than one practical achievement stems directly from a scientist's suggestion. No practical man now understands metals better than the solid-state physicist; this was certainly not true even as little as 20 years ago. Yet the likelihood that pure science will lead directly to the discovery of really new materials will be only slightly greater in the future than it was in the past unless methods for handling wholes can be developed that are precise enough to be called scientific and communicable enough to be taught. This is a task that the scientist has in the past rightly and profitably refused to accept. We need a supergenius to develop some principles, not of simple particles and their interactions, but of extremely complex structures with parts interacting with other parts, on all levels, and with a hierarchy of interpenetrating substructures combining to form many levels of interpenetrating superstructure (*21*).

At present, I think, there is a regrettable tendency for people who have to deal with complex things to lose interest in their richness. While the old artisan—blacksmith, goldsmith, potter, bronze founder, painter, or sculptor—used to develop a feeling for the whole material, the modern worker is trained to look intellectually at the unitary parts of its behavior. The coordinated sensual reaction of the whole body to the material itself, yielding turmoil twixt hammer and anvil, has been replaced by the touch of a switch, the sight of a meter, and the intellectual solution of an equation.

Though it is undeniable that definite communicable knowledge can best be

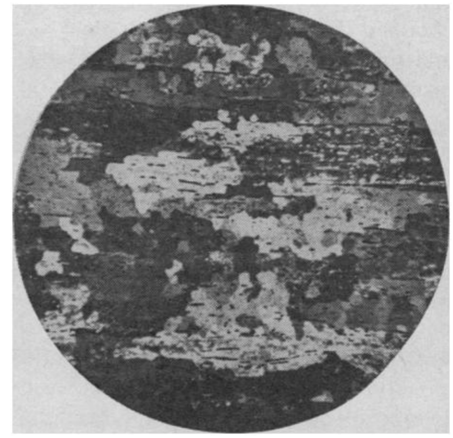


Fig. 11. Photomicrograph of wrought-iron armor plate (made in August 1864 by Henry Clifton Sorby in Sheffield) (about × 8).

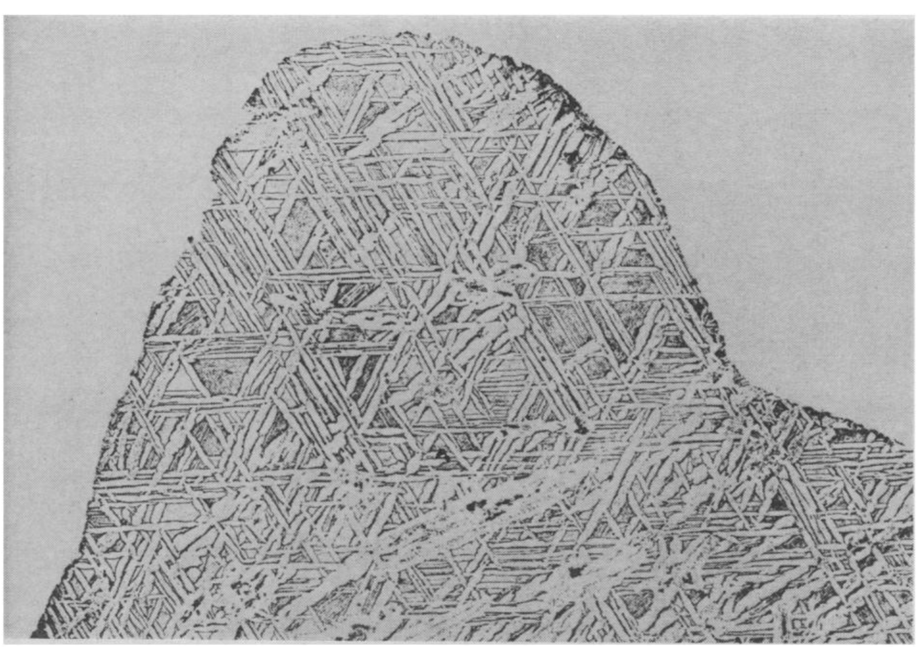


Fig. 10. Detail of typographic impression from a polished and etched section of the Elbogen meteorite (made by Widmanstätten and Schreibers in 1813). The structure was first described in 1804 by W. Thompson, an Englishman residing in Italy (detail about × 1.3).

obtained by the methods of science, and the artist and the mystic can never prove that they are right, science is now secure enough to admit some of its limitations and to reach toward those things which in the past it has rightly rejected. In the future the materials engineer may perhaps develop generalizing principles as he designs the structure of the material itself to fit the design and structure of the machine in which it is to be used, but he has not yet done so and it seems a shade more likely that a viewpoint which is at once scientific and capable of comprehending complex wholes may come out of biology. At present the biologist scorns the naturalist, and even cells are somewhat neglected in the excitement over studies at the molecular level, but sooner or later he, like the highbrow metallurgist with his crystal imperfections and electronic energies, must return to a concern with balanced whole organisms.

Now that the atomic and molecular bases of behavior are fairly well understood, we can hope to understand the larger aggregates with which we have to deal in engineering and in life—complicated systems which have frustrated scientists but have pleased artisans and naturalists. The powerful and essential tool of scientific abstraction must somehow be used at a higher level, perhaps by incorporating some of the methods by which the artist exploits complex interrelationships. It would be a marvelous thing if science could put things together, if it could understand more of the interactions and transactions between units, small groups, larger groups, and still larger aggregates. The innumerable combinations that *could* exist obviously cannot all be computed, and the analysis must, at least partly, be related to the particular structures that have come into existence as a result of the individual evolutionary history which is behind any complexity.

An intellectual approach tempered in this way would be good for human affairs in general, and those who used it would be less isolated than are today's scientists from the ordinary man who sees wholes and learns to enjoy and exploit sensed relationships which defy detailed analysis. Only thus can we avoid the ever-present and increasing danger of assuming that things or events that can be intellectually analyzed, and preferably computed, are the only ones of significance. One can even think of a distant future in which science (that is, analytical science as we now know it) is dead (or at least dull); but art, and materials, will live as long as man does, and they will be enriched to the extent that they, in turn, serve to enrich science.

References and Notes

1. A reader has objected to the obvious bias of this article. The bias, however, was intended to rectify an imbalance. Of course, materials per se were not responsible for anything. There was no simple cause and effect, but always a complicated multidirectional interaction of many factors, the interaction bringing out what was needed from each. The importance of environmental factors in later metallurgical history are emphasized in a paper [C. S. Smith, *Four Outstanding Researches in Metallurgical History* (American Society for Testing and Materials, Philadelphia, 1963)] which points out how "society," or rather the scientific and technological part of it, selected what was recognizably needed at a given time and ignored, for a time, other discoveries of comparable value. Natural and artificial organic polymers match in interest and importance the materials discussed here and merit specialized historical study.
2. S. L. Washburn and F. Clark Howell, in *Evolution after Darwin*, S. Tax, Ed. (Univ. of Chicago Press, Chicago, 1960), vol. 2, p. 33; S. L. Washburn, *Sci. Am.* **203**, pt. 3, 63 (1960); see also J. Napier, *ibid.* **207**, pt. 3, 56 (1962). For a discussion of the details of stone-working techniques see S. B. Leakey, in *A History of Technology* (Clarendon, Oxford, 1954), vol. 1, p. 128, and especially S. A. Semenov, *Prehistoric Technology* (London, 1964).
3. Minerals in later art are the subject of an interesting article by R. J. Gettens, *Smithsonian Inst. Ann. Rept. 1961* (1962), p. 551.
4. The principal studies of the physical and chemical basis of Chinese ceramic glazes are those of W. E. S. Turner, summarized by A. L. Hetherington, *Chinese Ceramic Glazes* (Cambridge Univ. Press, London, 1937).
5. H. M. Schmeck, Jr., New York *Times* (25 October 1964) (report on work of R. S. Solecki on copper from northern Iraq, which apparently dates from 8500 B.C., and on Anatolian copper of 7000 B.C. by R. J. Braidwood and H. Cambel).
6. On the origin of metallurgy and its relationship to the other pyrotechnic arts, see T. E. Wertime, *Science* **146**, 1257 (1964).
7. Once aluminum has been reduced it is an ideal material for primitive smithing. I was delighted last year to see a smith in Yazd (Iran) melting down scrap aluminum from the West, casting the metal into partly shaped ingots, and hammering it into soup ladles; one of these now hangs in my kitchen. Because it lends itself so well to simple operations, aluminum may perhaps be the metal of the future, being mined as already reduced metal from the radioactive ruins of our defense establishments.
8. A notable exception to this generalization (and one which suggests the modern approach of developing materials in specific relation to their application) is the case of printing. Though the Chinese were the first to use movable type (of ceramic, or of cast bronze made by conventional methods), once Europeans started to develop the idea in the 15th century they devised methods that far outstripped those of the Orient. The adjustable permanent rectangular mold with replaceable matrix gave different letter faces on type bodies that would fit exactly together and could be easily cast in quantity. Though the essence of the technique and the first alloy probably came from the pewterer, printers soon used bismuth- and antimony-hardened tin and eventually changed to cheaper, harder, alloys of lead and antimony. The development of type had to be accompanied by development of an ink quite different from writing ink and, of course, presses and new methods for the production of paper. Even the steam engine was not so dependent on new materials for its realization.
9. H. J. Plenderleith, in *Ur Excavations*, C. L. Wooley, Ed. (British Museum, London, 1934), vol. 2, p. 284.
10. Recent unpublished analyses by William Samolin of Columbia University have shown that many early Chinese bronzes are *phosphor* bronzes, although the effect of adding phosphorus (which, in amounts of the order of 0.1 percent, has a spectacular effect on fluidity) was supposedly a European discovery of about 1870 A.D! It is easy to reduce phosphorus from bone, provided the vapor is absorbed by copper. The process is analogous to the making of brass, which was also done many centuries before the discovery of the volatile element involved in the alloying.
11. Although some authorities continue to believe that the lost wax process was used by the Sung bronze founders, the evidence provided by the details of the vessels themselves overwhelmingly suggests the piece-mold process [see N. Barnard, *Bronze Casting and Bronze Alloys in Ancient China* (Australian University, Canberra, 1961; also published as *Monumenta Serica Monograph No. 14*, Nagoya, 1961)].
12. R. Knox, *Archaeometry* **6**, 44 (1963); O. Schaaber, *Carinthia* **153**, 129 (1963).

→ H. Maryon, *Am. J. Archaeol.* **65**, 173 (1961).

14. For a detailed study of the metallurgy of Japanese sword blades see C. S. Smith, *Documenti e Contributi per la Storia della Metallurgia*, No. 2, p. 42 (1957).
15. N. Barnard, *Bronze Casting and Bronze Alloys in Ancient China* (Australian National University, Canberra, 1961).
16. H. R. Schubert, *History of the British Iron and Steel Industry from c. 450 B. C. to A.D. 1775* (Routledge and Kegan Paul, London, 1957).

→ C. S. Smith, *Technol. and Culture* **5**, 149 (1964).

18. The true crystalline structure of high-carbon Damascus steel was first duplicated in Europe by Bréant in 1821 [see C. S. Smith *(17)*]. A general history of ideas on the structure of metals, with emphasis on their microcrystallinity, is given in C. S. Smith, *A History of Metallography* (Univ. of Chicago Press, Chicago, 1960).
19. Sorby's discovery of the microstructure of steel was commemorated by a centennial conference on the history of metallurgy, held in Cleveland, Ohio, in October 1963. The *Proceedings* [C. S. Smith, Ed., *Proceedings of the Sorby Centennial Symposium on the History of Metallurgy* (Gordon and Breach, New York, in press)] will contain critical studies of Sorby's life and work, and an analysis of many of the developments in metallurgical science in the last century.
20. P. P. Ewald, *Fifty Years of X-Ray Diffraction* (International Union of Crystallography, Utrecht, Netherlands, 1962).
21. C. S. Smith, *Rev. Mod. Phys.* **36**, 524 (1964).