New Materials and Composites

Recent major advances in new metals, organics, ceramics, and composite materials are surveyed.

William B. Hillig

The search for new, better, and more available materials probably dates back to the beginning of mankind. The selection by early man of the best natural materials from which to make his implements must have involved the elements of discovery, observation, comparison, need, and capability. With time, specialized needs emerged, made possible by and requiring a correspondingly wider range of materials. Synthetic materials such as glass, ceramics, and metal alloys were discovered. These materials offered advantages in terms of performance, fabricability, and appearance over natural materials. These same general forces have persisted to the present in a continuing quest for new, better materials and have led to today's materials-oriented sciences, technologies, and arts, in which vast numbers of people are employed. These workers were creating or identifying new substances (*1*) at the rate of 250,000 entries per year in 1967, and this rate is increasing by about 5 percent per year. Of necessity, this article will be highly selective and will focus on materials having actual or perceived potential or significant utility, and on which exceptional progress has been made.

First, let us consider briefly the nature of the activity leading to new materials, the associated "driving forces," and the environment in which these forces operate today. Substantial progress in materials generally originates with a provocative discovery or concept. This stage is followed by a period of expansive exploration, often with other workers rapidly joining in to define the scope and potential of the original discovery. Later, more detailed and complete information is gathered, and the often long, difficult process of practical demonstration, optimization, and conversion into a product commences. These stages can be termed (i) the original discovery, (ii) the exploration of bounds, and (iii) exploitation. The substance of this article is concerned primarily with the first two stages.

Significant discovery can come about through the scientific exploration of new classes of substances or through unsought chance observation. Examples of the latter are the discovery of polyamide polymers (for example, nylon) and crystallizable glasses; examples of the former are the high-strength crystal whiskers. In each case the original discovery was followed by the other two stages. The first two examples led to substantial industries, whereas the latter discovery has not yet been translated into a practical product.

Another path to substantial materials progress is the discovery of a phenomenon that is scientifically challenging or one that offers potential for new kinds of devices. Phenomena, such as superconductivity or laser action, are often intimately associated with particular kinds of materials. Thus, once the phenomenon has been discovered, an exploration often follows for materials which can enhance the observed effect or achieve it more conveniently. A particularly successful example of the essential interplay between materials and phenomena is the achievement in solid-state microelectronics of almost inconceivably fine-scale and complex material structures of highly specified compositions. These devices have had a pronounced qualitative effect on modern society.

An increasingly better traveled path in the search for new materials results from the pressures to satisfy extremely important functions for which existing materials are only marginally successful, if not totally inadequate. For example, the aerospace accomplishments of recent years depended on the development of new materials and structures with high strength and high stiffness-to-weight ratios. This effort has stimulated work on low-density, high-performance composites reinforced with B and graphite fibers. More recently, the changing fuel supply situation is placing new emphasis on metals and ceramics having higher temperature capabilities for use in heat engines. These materials are needed to achieve greater Carnot efficiency and to withstand the increasingly hostile chemical environments due to the expected deterioration in the quality of economically affordable fuels.

The above paths are not mutually exclusive but rather serve to define the approaches taken by particular individuals or organizations. With the passing of the recent "golden age" of scientific support for exploratory materials research in the period from 1950 through 1970, increasing emphasis has been placed on the search for materials that meet specific "hardware" requirements. Economics and good design dictate that materials be used as efficiently as possible. Thus, materials are being worked increasingly hard. This hard working of materials can be done when the use conditions for the materials are carefully defined and controlled. However, it can also lead to problems when the same apparatus is operated under a new set of conditions. We are becoming increasingly skilled in learning to use scarce and expensive materials locally only where needed. The substitution of one class of materials for another and the reexamination of designs in terms of their functional requirements place a continuing challenge on the materials and design communities to establish better mutual realistic awareness of their respective capabilities and limitations.

The drive toward working materials increasingly hard implies an increase of materials research and development activities on near-term materials improvement and problem-solving, relative to the more speculative, high-risk exploratory materials work. This trend also suggests that locally tailorable materials systems and hybrid materials will become increasingly important, as will composites which can result in new combinations of properties not available in single homogeneous materials. Examples are claddings for high-temperature turbine alloys and fiber-reinforced composites.

In identifying "new" materials or materials advances for citation, I was unable to arrive at a very precise definition of what constitutes newness, except perhaps a judgment that the impact on society or the technical community has not yet crested. Another concern was how to organize the selected new materials. One approach could be in terms of the paths by which they emerged, as just discussed. A second approach could be to group them according to their applications, such as structural, optical, electromagnetic device materials or the like. Another scheme might be to

---

The author is manager of the Composite Materials Program at the General Electric Research and Development Center, Schenectady, New York 12301.

classify them according to the nature of their newness, that is, new substances, new molecular or crystalline structures, or discontinuous advances in existing materials. However, materials can be grouped in a more natural way if they are classified as (i) polymers, (ii) metals, (iii) ceramics and inorganic materials, or (iv) composite materials. This is the plan I have followed below. New filamentary materials useful for composites are discussed under the composite materials heading.

New Polymeric and Organic Materials

Work in this important class of materials is presently concentrated in the exploitation and optimization stages. There has been major preoccupation with feedstock costs and availability as a result of the changing situation with respect to petroleum and natural gas supplies. Increasing emphasis on safety and consumer issues has resulted in increased industry efforts and predictable progress in reducing flame and smoke hazards, mainly through the use of additives. A relatively new emerging family (*2*) of polymers that may offer particular advantages in this regard are the polyorganophosphazenes. These polymers have a -(PN)- inorganic backbone; the specific characteristics are conferred by the organic side groups. By analogy with the silicones, this family of polymers can form rubbers that remain flexible to very low temperatures. These polymers have good hydrolytic stability and oxidation resistance but are somewhat difficult to synthesize. They have been described (*2*) as being at the state of development at which silicones were in the early 1950's.

A strong driving force for new polymer work is based on the fact that these materials can compete successfully against metals, especially in areas where low-temperature nonferrous die castings have been used. There is opportunity for widely expanded use in high-volume applications, such as appliances and automobiles. Their use in engine compartment components depends on solving the problems of creep (deformation with time under load), chemical stability at temperatures above 100°C, and resistance to petroleum solvents. In many such applications, the ability to fill space economically is an important consideration. Hence, structural foams (*3*) are a new, emerging material form in which voids are purposely introduced into the structural polymer at typical concentrations of 10 to 50 percent. Foams such as shown in Fig. 1 can also be introduced to achieve greater rigidity and creep resistance.

There are many other critical engineering applications, such as in aircraft, not ideally met by other materials, in which temperature capabilities of 300°C or more are desired. Hence, substantial efforts are being made to develop high-temperature thermoplastics (materials that soften upon heating), such as polysulfones and polyimides, as well as high-temperature thermosets (materials that remain rigid when heated), based on heterocyclic systems, such as the benzimidizoles and quinoxalines.

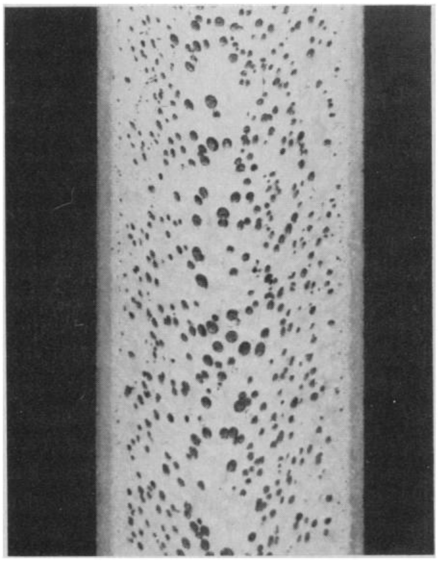

Fig. 1. Foamed polycarbonate resin. Introduction of about 20 percent voids increases the flexural stiffness on an equal weight basis by a factor of 2.

Other materials which may develop significant practical importance are certain electrically active compounds, which have been described (*4*) as having metal-like properties. The salts of tetracyanoquinodimethane (TCNQ) exhibit electronic conductivities equal to about 1 percent of that of graphite at room temperature. This conductivity is strongly anisotropic and increases with decreasing temperature until a metal-insulator transition occurs, below which the material no longer conducts. However, a TCNQ salt has recently been discovered that retains metal-like conductivity at near 0°K. A second material, $(SN)_x$, an inorganic polymer, has been found to exhibit superconductivity at temperatures below 0.3°K. This work has been confirmed by repeated measurements. This bronze, shiny material exhibits appreciable electronic conductivity above 0.3°K and becomes superconducting in spite of the fact that it possesses considerable disorder, and it offers the hope (*5*) that improvements are possible. Piezoelectric behavior has recently been reported (*6*) in polyvinylide fluoride, polyvinyl fluoride, and certain other polymers. These are highly orientable, readily crystallizable polymers containing dipolar chain elements, and they have sensitivities nearly equal to those of the semiconductor counterparts. The polymers can be made into piezoelectric films in which the dipoles are aligned by first a stretching of the films to produce a highly oriented structure and then a polarization through the application of large electric fields. These polymers can be used as strain sensors, acoustic transducers in microphones, and loudspeakers. Other advances in polymeric systems are discussed in the sections dealing with composites.

New Metallic Materials

Because metals are a mature class of materials, the opportunities for the discovery of new substances or structures might seem to be relatively remote. Nevertheless, there have been noteworthy discoveries in the categories of new substances, new structures, old materials in which quantum advances have been made, and known materials having newly discovered properties.

Since the discovery of superconductivity in 1911, a search has been under way (*7*) for practical materials that retain this behavior to as high a critical temperature T_c as possible, especially for materials that could operate at liquid hydrogen temperature, 20°K. Two alloys, V_3Si and Nb_3Sn, which have the A-15 (β-tungsten) structure, were discovered in 1953 and 1954 to have T_c values of 17.1° and 18°K, respectively. Interestingly, it took 13 years of further intensive search to reach the milestone goal of a T_c value of 20°K with $Nb_3Al_{0.8}Ge_{0.2}$, and this achievement was then surpassed in 1973 and 1974 by Nb_3Ga and Nb_3Ge, all A-15 materials. The latter alloy has a T_c of 23.2°K, the present record. This search is hampered by the lack of an adequate theory which connects composition to T_c. It remains to be seen whether these materials can now make practical the potential of superconductivity for such uses as electric power transmission lines, and new high-energy density motors, generators, and the like.

The so-called glassy or amorphous metals have been receiving accelerated attention since their discovery (*8*) in 1960. Since then, numerous noncrystalline alloys have been identified (*9*) and have been formed into continuous ribbon and wire. Cooling rates of about 10^5 degrees per second or more are required to produce amorphous metals. The most favorable compositions are those which correspond to eutectics with particularly low melting points and which contain transition elements, such as Ni, Pd, Zr, and La, as well as metalloids, such as B, C, P, and Si. Discernible ordering in the metal glasses extends only a few atom distances as is the case for conventional oxide glasses. These glasses have Young's moduli about 30 percent less than that of the crystalline state and high ultimate strengths that rival those of conventional glass fibers. In contrast to conventional glasses, they show marked ductility, as much as 50 percent strain under bending; consequently, they are much less notch-sensitive. Their densities are nearly equal to the crystalline state values. These behaviors imply that the binding forces remain essentially centrosymmetric. Toughness in the metal glasses, as measured by the crack extension force, is almost an order of magnitude greater than for their crystalline counterparts. These properties, along with interesting magnetic behavior and the good galvanic corrosion resistance (*10*) of some compositions, have generated considerable interest and speculation about the place of glassy metals in materials technology.

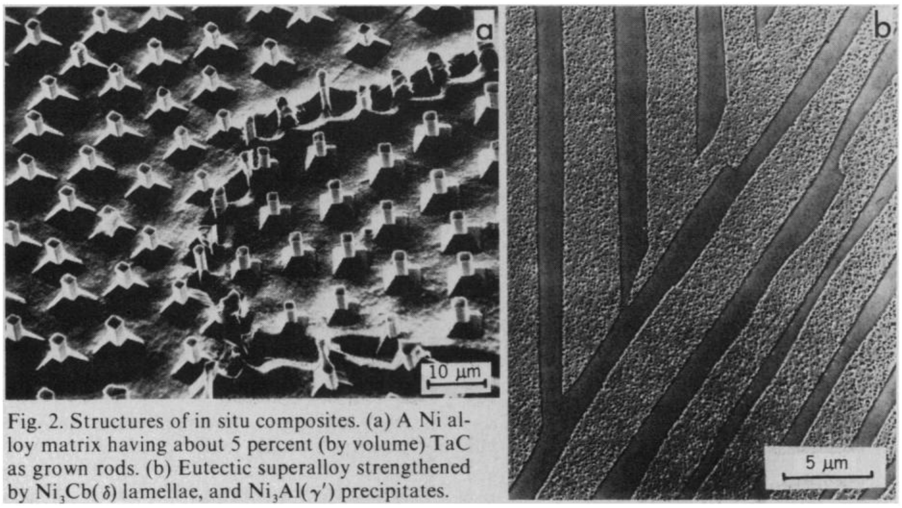

Fig. 2. Structures of in situ composites. (a) A Ni alloy matrix having about 5 percent (by volume) TaC as grown rods. (b) Eutectic superalloy strengthened by Ni$_3$Cb(δ) lamellae, and Ni$_3$Al(γ') precipitates.

The oriented eutectics (*11*), often called "in situ composites," are a relatively new class of metal structures that offer great potential for increasing the temperature capability of high-strength alloys. Such materials are needed to increase the efficiency performance of gas and aircraft turbines. Intermetallic compounds are known that have good high-temperature properties, but they tend to be brittle and difficult to fabricate. However, in favorable cases such intermetallics can be cast into useful shapes by the controlled solidification of eutectic alloy compositions. Plates or rods of strong intermetallic phases form as dispersions with a second continuous or lamellar phase. The compositions and proportions of the phases are fixed by phase equilibria constraints, and the fineness of the structure is adjustable by control of the growth conditions. The Ni$_3$Al and Ni$_3$Nb (*12*) and the TaC-containing (*13*) systems shown in Fig. 2 have shown particular promise for use as new turbine materials. The first material is a lamellar structure; in the second family of materials, the TaC is present as rods in a continuous matrix of Ni, Co, or other more complex compositions. Both systems have been produced in the form of turbine blades and appear to offer a quantum advance over the best earlier alloys. Oriented eutectic structures are not limited to all-metal systems.

An important discontinuous advance has occurred in a well-known commodity material, namely, silicon iron, used for transformer cores. Annual electric losses in the United States attributable to distribution transformer core loss are estimated to be about 3×10^{10} kilowatt-hours, that is, the electrical energy needed per year to supply about 3 million households. Silicon iron ideally requires a "cube-on-edge" texture for best properties. A good approximation to this texture is achieved by a complex process of rolling and annealing in which MnS is used as a grain growth inhibitor during certain critical steps. A breakthrough came about in Japan (*14*) where a new commercial process was developed in which two inhibitors, AlN plus MnS, were used to control grain growth. Not only was the texture improved, but a surface coating (*15*) was found to be effective with silicon iron for further reducing losses through an advantageous magnetostrictive mechanism.

An obstacle to the development of commercial fast breeder reactors was the unexpected swelling (*16*) of the stainless steels, considered as fuel-cladding materials, which occurred under irradiation with fast neutrons at reactor temperatures. As much as 7 percent swelling occurred when the neutron fluence had reached only 25 percent of the level needed for commercial operation. Some alloys swelled as much as 100 percent when subjected to a simulation of the full target fluence level. Internal voids cause the swelling. These voids result from the slight imbalance in favor of interstitial atom capture relative to vacant atom site capture at sinks such as dislocations. The excess vacancies then collect to form voids. The vacancies and interstitials are produced by the fast neutron collision processes. As shown (*17*) in Fig. 3, the propensity for such swelling varies by three orders of magnitude in the simple Fe-Ni-Cr alloy system. Certain trace alloying elements, such as Si, Ti, Zr, and Nb, also reduce swelling (*18*). The composition of the cladding steel initially selected was subsequently shown to lie in a high swelling region. If corrosion and other requirements can be satisfied, a satisfactory solution appears to be at hand for this particular problem of the fast breeder reactor.

Ceramic and Inorganic Materials

Advances in new ceramics have resulted, largely but not entirely, from the control of microstructure and purity. This accomplishment has required major advances in processing. For example, an old material for which an important new use has emerged is sodium β-alumina. This material has the nominal composition Na$_2$O · 11Al$_2$O$_3$, and consists of NaO$^-$ planes sandwiched between spinel blocks. It

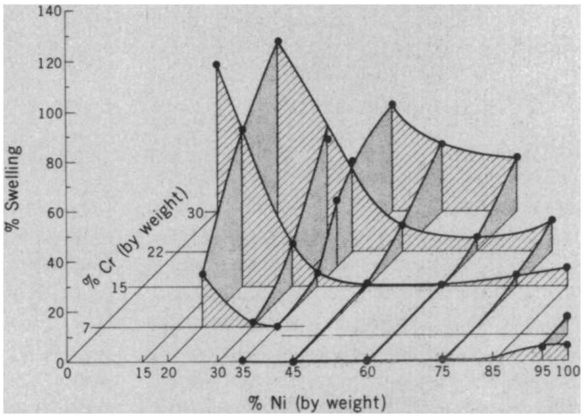

Fig. 3. Dependence of fast neutron-induced swelling in Fe-Ni-Cr alloy on the Cr and Ni contents.

Table 1. Physical properties of reinforcing fibers relative to stainless steel.

Material	Relative density	Equal volume basis		Equal weight basis	
		Tensile strength	Stiffness	Tensile strength	Stiffness
304 stainless steel	1	1	1	1	1
Glass metal, 34Ni/29Fe/15Cr/22(P+B)	0.9*	1.2	0.7	1.3	0.8
S-glass	0.31	1.7	0.45	5.5	1.45
Boron (W-core)	0.31	1.7	2	5.5	6.5
Graphite	0.22	1.1–1.4	1–2	5–6.4	4.5–9
Kevlar-49 Aramid	0.18	1.3	0.7	7.2	3.9

*Estimated value.

has long been used as a lining for the huge tanks used to hold molten glass for manufacturing. In 1966 it was noted (*19*) that this material has a remarkably high ionic conductivity, which at 350°C exceeds that of saturated brine (at room temperature). The compound β-alumina is the most useful of a class of materials (*20*) known as superionic conductors and has particular importance for high-energy battery systems, such as sodium-sulfur cells, or for fuel cell applications. It can be used not only as a nonaqueous electrolyte but also as a structural element. It has electrical properties that depend on the crystalline microstructure (*21*) as well as on the presence of dopants. However, it is difficult to sinter, especially to the desired microstructure. In most applications impermeable structures are required. Sound, good-performing material has been made. Because of the difficulty of satisfying all of the necessary conditions, work on β-alumina and its structural variant β''-alumina is the continuing subject of intensive work in many laboratories.

The achievement of higher-efficiency thermomechanical engines requires the availability of high-temperature, high-performance structural materials. The compounds SiC, Si_3N_4, and more recently Al_2O_3-Si_3N_4 alloys have received particular attention (*22*) for such applications because of their good strength and good corrosion and thermal shock resistance. Nonionic ceramics, such as SiC and Si_3N_4, have been difficult to fabricate by standard methods. In these materials, as in many other ceramics, the making of the material is inseparable from the making of the component.

The compound Si_3N_4 can be made directly from the elements with excellent shape fidelity. However, this lengthy process results in material that contains about 20 percent voids but, nevertheless, has strengths up to 50,000 pounds per square inch (14.7 pounds per square inch = 1 atmosphere). Dense Si_3N_4 can be made by hot-pressing the powder with small amounts of MgO used as a sintering aid. The hot-pressed material is about three times as strong as the reaction-sintered material and, for a ceramic, is relatively tough. However, only approximate shapes can be made, and this material exhibits creep at elevated temperatures. The replacement of MgO by Y_2O_3 appears to be beneficial (*23*) in ameliorating the creep problem.

The situation with SiC is somewhat analogous in that both reaction-bonded and hot-pressed grades are now commercially available. The former results from mixing SiC with graphite, shaping, and then reacting with molten Si, and produces a fully dense material with a strength of about 75,000 pounds per square inch. Hot-pressed SiC can also be made to approximate shapes with reported strengths somewhat less than for the corresponding Si_3N_4 material. The creep properties depend on aids used to promote consolidation during hot-pressing. The use of W and Al_2O_3 results in substantially higher creep rates than when B is used. A major recent scientific and technical advance (*24*) was the discovery that SiC can be conventionally sintered at 2100°C by standard ceramic techniques through the addition of small amounts of B and C. This procedure makes possible the production of complex shapes. The resulting properties are comparable to those of the hot-pressed material and, in addition, the SiC exhibits greater creep resistance.

SiAlON's, which are alloys of Al_2O_3 and Si_3N_4, are possible candidates as high-temperature structural materials. The phase equilibria relations in this quaternary system are complex and may account for various conflicting reports regarding the merits of SiAlON's. This system offers some promise of easier fabrication. However, much more work is needed to determine its ultimate importance.

The ability to form polycrystalline dense compacts (*25*) of diamonds and cubic BN is another notable achievement in the area of refractory nonionic solids. Even though these substances are the hardest known materials, single crystals exhibit marked anisotropy in their hardness and strength. As a result, cleavage fracture can occur. Hence, for cutting tools to be used in rock drilling, metal cutting, or wire dies, it is advantageous to have all crystal faces exposed to provide uniform wear and resistance to extended crack propagation. The synthesis of these compacts, therefore, has great significance for increasing productivity in areas of increasing economic importance.

Finally, among the inorganic glasses, the achievement of ultraclear glass fibers (*26*) in which the optical transmission loss is as little as 1 decibel per kilometer is a remarkable accomplishment. This achievement was made possible by an extremely careful synthesis process in which all traces of deleterious impurities are held to concentrations in the range of parts per billion. Such glass fibers are needed as optical wave guides if the promise of lasers in communications is to be realized. A second area of new materials advance in glasses results from the rapidly expanding interest in the so-called "chalcogenide" glasses (*27*).

This interest stems from such properties as bistable electrical switching behavior, light-induced nucleation, strain-induced nucleation, as well as other unusual structure- and transport-related characteristics. In a sense, these glasses are the complements of the metallic glasses. They consist mainly of combinations of the nonmetals and metalloids, such as As, Ge, S, Se, Si, and Te, but they may also contain appreciable concentrations of such metals as Ag, Cd, Cu, and Tl. These glasses continue to be a fruitful area of research for experimental and theoretical scientists and, in addition, offer many device possibilities as nonlinear elements and memories. However, it remains to be seen what their technological importance will be in the competition with other electrical and photoactive materials.

New Composite Materials

Composites are heterogeneous materials systems in which several substances are combined into a coherent structure. Many common materials, not usually classed as composites, are nevertheless heterogeneous structures, for example, carbon-filled rubber, ABS plastic, carbon steel, superalloys, porcelain, and ruby glass. However, in contrast to the case for composites, the proportions, size, and shape of the various phases in these heterogeneous structures are often determined indirectly through such factors as solubility, nucleation, and growth kinetics. The in situ composites cited above are examples of an intermediate class of composites for which great care is taken to produce a desired heterogeneous structure; however, in the case of fiber glass–epoxy composites, the fiber choice, arrangement, and proportions are independently controlled by the fabricator. Such control or tailorability contributes to the importance of composites. In the discussion that follows, I have found it useful to distinguish between structural and functional composites. The former are used mainly for their mechanical properties and the latter for their special electrical, chemical, or other characteristics.

Structural composites. The search for materials having exceptional strength and stiffness, and useful over a wide range of conditions, has stimulated wide activity in the search for new reinforcing fibers. For rotating components or for air- or spaceborne components, high mechanical performance at low density is important. The standard high-performance fiber of longest standing is E-glass. However, usage of the stronger and stiffer S-glass is increasing. Although these fibers are strong, they lack the stiffness needed for many applications. Another common filament is high-strength steel wire, which is strong and stiff but has a relatively high density. Steel and glass are the commodity filamentary materials against which the more advanced fibers can be compared.

Vapor-deposited B on a W- or C-core has been available for more than a decade. This fiber has the strength and density of glass but twice the stiffness of steel. However, its high cost of about $180 per pound ($0.40 per gram) limits the use of this reliable fiber material to special applications. This price is estimated to drop by about a third if sufficient volume develops. Carbon fiber is actually a family of fibers available over a range of strengths and stiffnesses. These properties plus density are functions of the starting material and processing conditions. Carbon fiber is produced by pyrolyzing and subsequently further heat-treating textile or pitch fibers. Carbon fiber has a typical diameter of 8 μm, whereas that of the B fibers ranges from 100 to 200 μm. Thus, the B fibers are usually handled as monofilaments, whereas the C fibers are gathered in bundles of 1000 or more individual fibers. The cost of continuous high-strength C fiber is currently about $60 per pound, and it is projected that the price will drop to about $10 per pound.

Recently a quantum advance was achieved in the mechanical properties of polymer fibers. Although it was recognized (*28*) that the C–C bond is intrinsically stiff in stretching, the tetrahedral –C–C–C– bonding in polymers results in a "coiled spring" structure. Hence, uncoiling and flexing rather than stretching account for the ordinarily observed low modulus of organic polymers. A high-modulus polymeric fiber (*29*) has been produced that is 50 percent stiffer than S-glass, comparable in strength, but less dense. The polymer is poly-aromatic-amide (aramide) in which geometric factors in the molecular structure prevent coiling. This fiber has the interesting, unusual characteristic of behaving like a chain; that is, it is strong in tension but weak in compression. This fiber is produced by spinning from a liquid crystal solution. Because of the close kinship between this process and the spinning of conventional textile fibers, lower cost can be anticipated for this material when it reaches high production volumes than would be expected for B or graphite. The current price is $3.50 to $8.50 per pound. Forms having Young's moduli of 19×10^6 and 9×10^6 pounds per square inch are available. The latter form is finding use as tire cord.

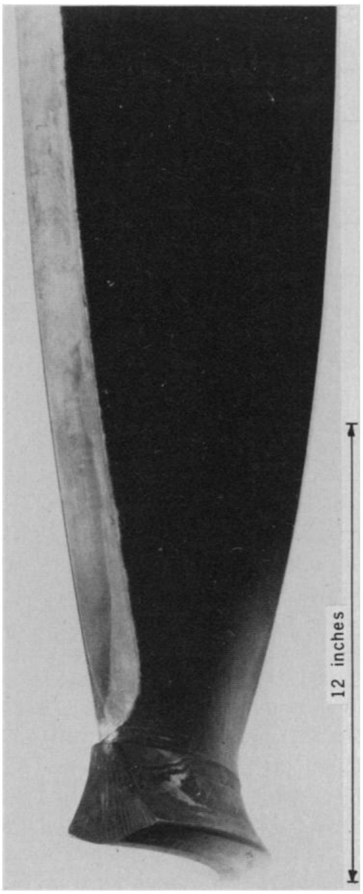

Fig. 4. Experimental aircraft engine fan blade made of graphite fiber-epoxy composite. The light-colored metal strip on the one edge protects the blade should birds accidentally enter the engine. The blade is about 60 centimeters long.

A recent laboratory achievement (*30*) has been the production of polyethylene with a strength and stiffness comparable to that of E-glass. Instead of the usual spherulitic crystallite structure, these fibers consist of parallel crystalline polymer fibrils which result from extrusion under very high pressure (2500 atmospheres) at 134°C. A one-component composite consisting of these fibers embedded in a matrix of normal polyethylene has been given preliminary study.

Table 1 shows a comparison of the properties of the various fibers relative to type 304 stainless steel wire, which has a characteristic strength of 300,000 pounds per square inch and a Young's modulus of 27×10^6 pounds per square inch. Because strengths can depend on the time at stress and on the number of loading and unloading cycles, the rankings can vary significantly depending on how the material will be used.

Advances in the making of oxide fibers have been substantial. There are several ingenious methods for producing continuous single crystals of oxides and other materials as well with a range of cross sections, shapes, and sizes. One method (*31*) is based on solidification from the melt with the use of a special shape-defining orifice. A second method is a controlled floating zone technique (*32*) in which laser heating is used. Very fine, continuous polycrystalline fibers (*33*) of Al_2O_3, ZrO_2, and mixed oxide compositions have also been achieved. Although their strengths are less than those of the other fibers cited, these fibers are relatively inexpensive and appear to offer the potential for high-temperature use. The polycrystalline materials are being used as catalyst supports and high-temperature insulation.

A wide variety of composites (*34*) have been made with the use of the above-mentioned fibers. Glass, B, graphite, and the aramide fibers have been used variously to reinforce epoxy, polyester, polyimide, and other resins. Materials with outstanding strength, toughness, and stiffness can be produced. Failure in these materials is often more benign than for the monolithic materials. Thus, composites find use in pressure vessels, aircraft, high-specific-energy flywheels, textile equipment, and sporting goods. An example is shown in Fig. 4. The weight savings and good mechanical properties suggest that these materials will find increasing use in automobiles as their costs for a given function become competitive with those of steel. The polymer matrix composites can be characterized as (i) being convenient to fabricate, (ii) having high strength parallel to the fibers, (iii) being weak transverse to the fibers, (iv) having low density, and (v) having a useful upper temperature of 100° to 300°C depending on the resin.

Certain of these limitations can be overcome by the use of metal matrices such as Al or Ti. Among the benefits that derive from the use of these matrices are better transverse properties and higher temperature capability. However, these materials are more dense and more difficult to fabricate. Boron and steel and, more recently, graphite, SiC, and Al_2O_3 filaments in combination with Al alloys are among the most successful metal matrix composites. These materials are being considered for such applications as turbine compressor blades and aircraft skins. However, degradation of properties due to reaction between the matrix and the fibers is a basic problem, especially in very-high-temperature systems.

This degradation has frustrated most attempts to produce very-high-temperature composites. The use of refractory metal filaments to reinforce superalloys and Si_3N_4 has had some success, the main disadvantages being high density and limited fabricability, respectively. However, an approach that results in a readily fabricable, temperature-stable, fully dense material, useful to 1370°C or perhaps more, is the Si-SiC composite (*35*). This material is somewhat analogous to the in situ composites in that the microstructure is the end product of a high-temperature reaction; the C fibers are converted to SiC upon infiltration with molten Si. This composite can be precision-formed into a wide range of complex shapes. Its mechanical properties are tailorable to a considerable degree. It can be produced so as to exhibit limited ductility at elevated temperatures. Its strength behavior is somewhat similar to that of reaction-bonded SiC. This composite material is expected to find use in high-temperature and corrosive environment applications, such as in gas turbines.

An important and rapidly growing class of composites is the reinforced thermoplastics (*36*). Typically these composites consist of a random mixture of oriented chopped glass fibers combined with an injection-moldable polymer, such as polypropylene, polycarbonate, or the like. The result is a material that has markedly improved dimensional stability, an extended temperature range, and improved strength by comparison with that of the base resin, while retaining ease of manufacture and low cost. One of the advantages over the corresponding reinforced thermosets is the shorter forming times needed to produce shapes, since only heatup and cooling are involved. Another advantage is that it is possible to rework material, thus cutting down on scrap. The use of reinforced thermoplastics is growing at the astonishing rate of 27 percent per year. These materials are used for a wide variety of general purpose applications, such as automotive and appliance components.

Functional composites. These composites exhibit special chemical, electrical, and optical characteristics resulting from special materials combinations and configurations. For example, high degrees of separation from a mixture of gases can be achieved by selective permeation (*37*) through immobilized liquid membranes. These membranes function via reversible chemical reactions that can occur in the solutions contained within them. The separation of CO_2 from air in the ratio of 1500 : 1 is made possible by the use of HCO_3^-/CO_3^{2-} buffer solution supported within porous polymeric films to produce the membrane structure. By comparison a film of silicone rubber, a highly permeable but chemically passive material, exhibits a CO_2/O_2 separation of 5. Other gases, such as H_2S, SO_2, and N_2, which when dissolved can ionize or complex, can also be selectively separated by appropriate choice of the active liquid material. Such membrane structures and the principles outlined offer promise for dealing with the increasing environmental problems of fuel and combustion gas cleanup.

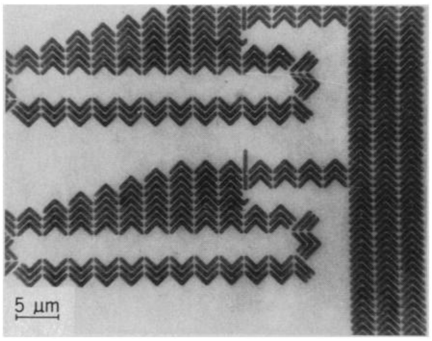

Fig. 5. Patterns formed in permalloy by the use of x-ray lithography. The spacing between chevrons is 0.2 µm.

Substantial advances (*38*) have also been achieved in passive functional composites. These materials consist of claddings and laminations, among other things. Such coatings applied to high-temperature metals by evaporation and plasma spraying have been very effective in further increasing the temperature capability and corrosion resistance of high-temperature alloys. Aluminides, chromides, and even precious metals are used to protect turbine blades and chemical process equipment.

Laminated metals (*39*) have been developed in which as many as five or six alloy materials can be placed in furrows in a base metal ribbon. Thus, thin strips of Au, Cu, and Sn alloys can be embedded in the surface of a steel strip to provide good electrical contacts, soldering capability, and good mechanical strength. Furthermore, such structures can greatly minimize the need for costly or scarce materials.

The extremely fine control and complex heterogeneous structure of advanced solid-state devices represents a state of the art of structural and compositional control of composite material systems on a scale incomprehensible less than a generation ago. Very uniform P-doping of Si base structures has been produced by neutron irradiation of the Si to produce the P by isotope transmutation (*40*). With the new techniques of ion implantation (*41*) and x-ray lithography (*42*), the latter shown in Fig. 5, it is possible to produce extremely sharply delineated junction regions and structure on a scale smaller than the wavelength of light. The result of such advances is an array of electronic multifunctional devices of greater complexity compressed into smaller structures and higher performance in terms of the switching times and frequency capabilities. For example, defect-free sensors (*43*) have been constructed, with the use of Si integrated circuit technology, which over an area of about 1 square centimeter have 244 lines of 248 elements—over 62,000 individual sites, each of which is interrogated as to the light level to which it is exposed. Such sensors closely approach the goal of a TV camera on a chip.

Conclusions

The numerous examples cited here offer ample evidence that great ingenuity is being used in providing new materials to meet current problems. There have been relatively few truly new materials, in the sense of materials that were not known before. However, substantial improvements in all classes of materials are readily identifiable. Although the details of such advances may not have been predictable, it is no surprise that substantial improvement could result from the application of talent to today's pressing problems. What is of more concern is the fact that there is not more advanced materials research and development being directed at major basic materials phenomena.

References and Notes

1. Based on an analysis of the formula index of Chemical Abstracts.
2. H. R. Allcock, *Chem. Technol.* **5**, 552 (1975).
3. A. M. Houston, *Mater. Eng.* **82**, 38 (1975).
4. W. D. Metz, *Science* **190**, 450 (1975).
5. G. B. Street, H. Arnal, W. D. Gill, P. M. Grant, R. L. Greene, *Mater. Res. Bull.* **10**, 877 (1975).
6. M. G. Broadhurst, Coordinator, "Proceedings of piezoelectric and pyroelectric symposium-workshop" (Interagency Report NBSIR 75-760, National Bureau of Standards, Washington, D.C., September 1975), p. 7.
7. V. Rivlin and D. Dew-Hughes, *New Sci.* **67**, 261 (1975); B. W. Roberts, *J. Phys. Chem. Ref. Data*, in press.
8. W. Klement, R. H. Willens, P. Duwez, *Nature (London)* **187**, 869 (1960).
9. J. J. Gilman, *Phys. Today* **28**, 46 (1975); T. Masumoto and R. Maddin, *Mater. Sci. Eng.* **19**, 1 (1975).
10. D. Lee and T. M. Devine, paper presented at the Second International Conference on Rapidly Quenched Metals, Boston, Mass., 17–19 November 1975.
11. L. M. Hogan, R. W. Kraft, F. D. Lemkey, *Adv.*

Mater. Res. **5**, 83 (1971); *Conference on in situ Composites* (Publication NMAB-308-1, National Academy of Sciences, Washington, D.C., 1973), vols. 1–3.
12. F. D. Lemkey and E. R. Thompson, in *Conference on in situ Composites* (Publication NMAB-308-1, National Academy of Sciences, Washington, D.C., 1973), vol. 2, p. 105.
13. J. L. Walter and H. E. Cline, *ibid.*, vol. 1, p. 61.
14. T. Yamamoto, S. Taguchi, A. Sakakura, T. Nozawa, *IEEE Trans. Magn.* **8**, 677 (1972); A. Sakakura, T. Wada, F. Matsumoto, K. Ueno, K. Takashima, K. Kawashima, *Magnetism and Magnetic Materials—1974*, C. D. Graham, Ed. (Conference Proceedings No. 24, American Institute of Physics, New York, 1975), p. 714.
15. T. Yamamoto and T. Nozawa, *J. Appl. Phys.* **41**, 2981 (1970).
16. C. Cawthorne and E. J. Fulton, *Nature (London)* **216**, 575 (1967).
17. W. G. Johnston, T. Lauritzen, J. H. Rosolowski, A. M. Turkalo, in *Radiation Damage in Metals* (American Society for Metals, Metals Park, Ohio, in press).
18. E. E. Bloom, J. D. Stiegler, A. F. Rowcliffe, J. M. Leitnaker, in preparation.
19. Y. Y. Yao and J. T. Kummer, *J. Inorg. Nucl. Chem.* **29**, 2453 (1967).
20. W. vanGool, Ed., *Fast Ion Transport in Solids* (North-Holland, Amsterdam, 1973).
21. R. W. Powers and S. P. Mitoff, *J. Electrochem. Soc.* **122**, 226 (1975).
22. J. J. Burke, A. E. Gorum, R. N. Katz, Eds., *Ceramics for High Performance Applications* (Proceedings of the 2nd Army Materials Technical Conference) (Brook Hill, Chestnut Hill, Mass., 1974). This volume contains numerous papers on SiC, Si_3N_4, and SiAlON.
23. G. E. Gazza, *J. Am. Ceram. Soc.* **56**, 662 (1973).
24. S. Prochazka, *Spec. Ceram.* **6**, 171 (1975).
25. L. E. Hibbs, Jr., and R. H. Wentorf, Jr., *High Temp.-High Pressures* **6**, 409 (1974); M. D. Horton, B. J. Pope, H. T. Hall, in *Diamond—Partner in Productivity* (Industrial Diamond Association of America, Moorestown, N.J., 1974), p. 19.
26. W. G. French, A. D. Pearson, J. B. MacChesney, *Annu. Rev. Mater. Sci.* **5**, 373 (1975).
27. For comprehensive sources, see: *J. Non-Cryst. Solids Spec. Vol.* **2** (1970); *ibid.*, **4** (1970); *ibid.*, **8–10** (1972). These volumes contain the collected papers on nonoxide glasses presented at three separate conferences.

→ P. I. Vincent, *Proc. R. Soc. London Ser. A* **282**, 113 (1964).
29. J. Preston, *Polym. Eng. Sci.* **15**, 3 (1975).
30. N. J. Capiati and R. S. Porter, *J. Polym. Sci. Polym. Phys. Ed.* **13**, 1177 (1975); *J. Mater. Sci.* **10**, 1671 (1975).
31. H. E. LaBelle, Jr., and A. I. Mlavsky, *Mater. Res. Bull.* **6**, 571 (1971).
32. J. Haggerty, in preparation.
33. A. M. Houston, *Mater. Eng.* **81**, 33 (1975).
34. Because the literature on structural composites is so extensive, no special references are cited. For further information, see L. J. Broutman and R. H. Krock, Eds., *Composite Materials* (Academic Press, New York, 1974), vols. 1–6.
35. W. B. Hillig, R. L. Mehan, C. R. Morelock, V. J. DeCarlo, W. Laskow, *Am. Ceram. Soc. Bull.* **12**, 1054 (1975).
36. A. Hall, *Plast. World* **1974**, 34 (1974).
37. W. J. Ward III, in *Recent Developments in Separation Science*, N. Li, Ed. (CRC Press, Cleveland, Ohio, 1972), pp. 153–161.
38. B. N. Chapman and J. C. Anderson, Eds., *Science and Technology of Surface Coating* (Academic Press, New York, 1974).
39. R. J. Russell, *Mater. Eng.* **81**, 48 (1975).
40. M. Schnoller, *IEEE Trans. Electron Devices* **21**, 313 (1974).
41. G. Dearnaley, *Nature (London)* **256**, 701 (1975).
42. D. Maydan *et al.*, in *Technical Digest, 1974 International Electron Devices Meeting* (Institute of Electrical and Electronics Engineers, New York, 1974).
43. G. J. Michon, H. K. Burke, D. M. Brown, M. Ghezzo, in *Proceedings of the 1975 International Conference on the Application of Charge Coupled Devices* (Naval Electronics Laboratory Center, San Diego, Calif., 1975).

Materials for Advanced Energy Technologies

Richard S. Claassen

Materials and energy are inextricably linked. Industrial materials cannot be produced without energy, nor can energy be produced without specialized materials. For example, the recovery and processing of industrial materials required about 16 percent of the total U.S. energy consumption in 1974. The interdependence of the two has been increasing and will continue to increase with time as the more easily won raw materials are exhausted and as the energy conversion and utilization schemes become more sophisticated. Although research and development on ways to recover and process materials with less energy is a challenging opportunity for the materials community (*1*), I will focus on the materials technology that will be required in major developing systems for extracting, converting, distributing, and using energy.

Figure 1 is a schematic representation of the energy sources; methods of processing, conversion, transmission, and storage; and forms of fuel energy that may exist in the near term (about 1990). The boxes with hatching indicate the elements which I believe require significantly improved materials technology if meaningful contributions are to be made to the national energy balance. At a later time breeder reactors may be added as converters of uranium, and eventually some form of pure fusion may provide an entirely new source of energy. The successful development of these new nuclear energy technologies will be heavily dependent on achieving substantial improvements in the performance of materials.

The fact that most fuel sources must be processed in some way or converted to another form before they are suitable for consumption is emphasized in Fig. 1. With the exception of solar heating, all systems being considered in this country for replacement of petroleum and natural gas depend on processing and conversion; that is why materials will dominate the resolution of our energy problem. Diminishing supply of low-cost and easily obtained fuels, increased environmental protection measures, and fuel conservation through increased efficiency are all factors which combine to place higher performance demands on every part of the energy supply system. Development of higher-temperature or longer-wearing materials, for example, can yield improvements for every step in Fig. 1. For some elements in the newly evolving program, indicated by hatching in Fig. 1, a significant materials development or improvement is essential to economic operation or even technical feasibility. I will emphasize those elements after some observations on availability of materials.

Supply of materials. Since the shortfall of domestic petroleum supplies was dramatized by the Arab boycott, it has been natural to ask whether there will also be shortages of the materials required to implement our new energy programs. I believe the answer is "No," but it is easy to point out a number of examples where careful attention and action are required (*2*).

1) High chrome alloys are needed for virtually every energy use—from oil refinery pipes to cryogenic structures in the magnets used in magnetic confinement fusion reactors. For chromium we are completely dependent on foreign sources of unknown future political stability.

2) Gallium arsenide cells are attractive for solar photovoltaic use, but a simple computation indicates that for even 8×10^9 watts, 10 percent of the estimated electric generation capacity in 1990, 10^5 tons (metric) of gallium would be required compared to an estimated world resource of 1.1×10^5 tons (*3*).

3) Through catalytic oxidation, fuel cells provide direct conversion of hydrogen-rich

---

The author is director of materials and processes at Sandia Laboratories, Albuquerque, New Mexico 87115. This article derives partly from deliberations of an ad hoc committee organized by the National Research Council's Commission on Sociotechnical Systems and chaired by the author, which held a workshop with invited consultants at Airlie House, Virginia, in July 1974 to discuss the impact of critical materials in the near-term energy program.