Making the Right Stuff

Scientists turn the materials of their dreams into custom-made realities

By IVAN AMATO

When engineers set out to design the B-2 "Stealth" bomber more than 10 years ago, they knew they wanted a versatile warplane that could evade radar detection. But at that time, materials with the detection-thwarting property and other unique attributes needed for the futuristic aircraft existed only in their minds. Undeterred, they turned the stuff of their imaginations into reality by inventing some 900 new manufacturing processes and materials.

Last month – more than $22 billion later – a prototype B-2 made its first test flight.

Throughout most of history, people have relied on things like stones, plants, metals and clay from their surroundings to survive and sometimes thrive. Only in the last few decades has a staggering variety of synthetic materials emerged, by-products of our increasingly sophisticated picture of how atoms build into molecules and how these assemble into different materials, each with its own personality of combined properties.

"Materials science and engineering over the millennia have gone from 'What do you find outside the cave?' to the beginnings of materials-by-design," says Stephen H. Carr of Northwestern University in Evanston, Ill., who envisions an explosion of new materials in the decade ahead.

The buzz phrase "materials-by-design," heard increasingly among chemists, materials researchers, physicists and engineers, denotes not just the materials themselves but also the bold new attitude spurring their development. Instead of relying primarily on the old tactics of serendipity, trial and error, craft knowledge and rules of thumb to modify existing materials, scientists now are learning to systematically assemble atoms and molecules into new materials with precisely the properties they need for designs too demanding for off-the-shelf resources. And in working with existing materials, they no longer view the traditional limitations of each type of material as a permanent state of affairs. At one company, for instance, researchers have made experimental springs out of high-strength cement (SN: 7/9/88, p.24).

B-2 "Stealth" bomber during first flight.

Northrop Corp.

Without this emerging attitude, the romantic feat of flying nonstop around the globe would have remained but another entry on a flier's wish list. Before pilots Dick Rutan and Jeana Yeager could achieve this goal three Decembers ago in their graceful flying ship Voyager, materials researchers had to develop a reinforced polymer/paper composite fuselage and wing material that combined high strength with the extremely low weight needed to save fuel during a nine-day, nonstop aerial circumnavigation.

Today, many materials researchers see themselves as creators of things not yet on Earth. As they gain insight into how molecular microstructures relate to a material's hardness, electrical and thermal conductivity, magnetic behavior, transparency and other properties, they are forging a brand new relationship to "stuff."

Many of the novel high-tech materials fall into the category of advanced composites, tailor-made from combinations of metals, ceramics and polymers. One type of material serves as a matrix, while fibers, whiskers or flakes of another (or the same) type reinforce the matrix or bestow other properties the matrix material lacks. The results include advanced composites that remain strong at high temperatures or withstand more stress than can steel and yet are lighter than the metal.

"The development of advanced materials has opened a whole new approach to engineering design," noted a 1988 report by Congress' Office of Technology Assessment. "In the past, the designer has started with a material and has selected discrete manufacturing processes to transform it into the finished structure. With the new tailored materials, the designer starts with the final performance requirements and literally creates the necessary materials and the structure in an integrated manufacturing process."

Adds Robert C. Dynes, head of chemical physics research at AT&T Bell Laboratories in Murray Hill, N.J., "It used to be the job of the physicist to understand the materials already in the world. Over the past 20 years, we've kind of turned the table on that situation to the point where we are synthesizing materials that do not occur in nature."

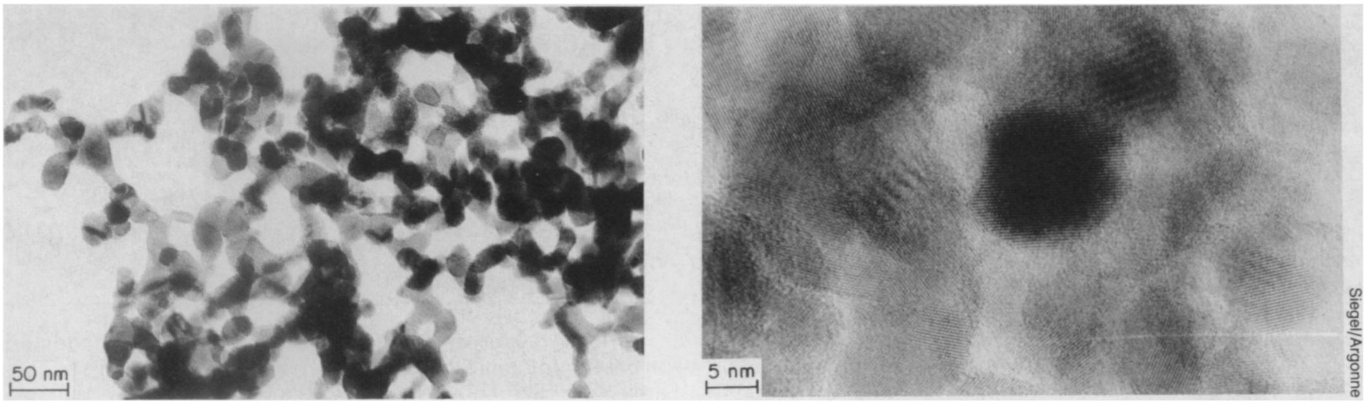
Optical communication using lasers and optical fibers provides an example. Making this technology work depends in part on the distance light signals can travel down an optical fiber before they need a boost to go farther. Scientists know enough about lasers made of thin films based on the synthetic material gallium arsenide, Dynes says, that they can calculate the optimal wavelengths of light for a particular optical fiber, then tailor-make a thin-film laser to emit them. Engineers have honed the skills and developed the tools to build such lasers atomic layer by atomic layer (SN: 2/4/89, p.69).

"Since the beginning of time," Dynes says, "people have been designing materials around applications," such as sharpening stone for axes. "But now people are designing materials on the atomic scale. We have sufficient understanding that we can relate the atomic configuration to macroscopic properties of materials."

Carr concurs. "Materials science by the late 1980s has evolved into an elegant exercise involving many levels of effort," he says. The materials-by-design movement is driven, he says, by the goal of making new materials that either improve on available materials for existing technologies or are so novel that they usher in new technologies.

For example, new lightweight superalloys containing aluminum and lithium make planes lighter and more energy efficient than aircraft fashioned of conventional, heavier metal skins and skeletons. For an unconventional aircraft like the planned National Aerospace Plane, which would fly at more than 20 times the speed of sound and generate huge amounts of heat at its shell, materials researchers are designing carbon-based and carbon-fiber-reinforced structural composites that are strong and heat resistant yet light in weight and low in density.

For materials such as electrically conductive polymers and the so-called optically nonlinear crystals crucial to the next wave of optical communications and computing technologies, Carr says the



Siegel/Argonne

Two views of nanometer-scale clusters of titanium dioxide molecules. Clusters start out loosely arranged (left) before being mechanically packed into a denser form for sintering. Some show visible molecular rows.

design cycle begins with researchers using theoretical rules linking the features of the bulk material to underlying electronic arrangements. In the case of a nonlinear optical material, the bulk property might double or triple the frequency of incoming light. At the second stage of the design cycle, scientists define the molecular or crystal architecture that will yield this electronic structure.

With the theoretical version of their new conductive polymer or optically nonlinear material in hand, chemists then can synthesize the appropriate ingredients. Processing experts can assemble these into the necessary architecture, and they and other materials researchers can test the products to see if they behave as intended. In the case of the nonlinear optical material, they might measure how the frequency of emitted light compares with the frequency of input light. "If you don't get the property, you travel the cycle again with the benefit of what you just learned," Carr says. "At each station of the cycle you learn something even if you don't succeed."

MIT materials historian Cyril Stanley Smith offers another perspective on the changing field of materials research. In the past, he notes, artisans such as metallurgists or potters knew the properties of the materials they worked with but not the chemical and physical theories underlying them. Though physicists have been developing a theoretical picture of matter for more than 150 years, Smith says they have focused more on understanding ideal forms of matter, such as perfectly symmetric crystal lattices, than on materials of the real world, which are always pocked with imperfections and asymmetries.

Magnified cross sections of metals and ceramics, for example, look like slices through soap froths (SN: 7/29/89, p.72). These grainy materials are made up of many crystal domains of different orientations packed together but with boundaries that play important roles in setting the materials' bulk properties, such as strength and electrical conductivity. Material properties stem from "a hierarchy of structural imperfections down to the atom," notes Smith. A material displays certain magnetic behavior, for example, when its molecular or atomic constituents have unpaired electrons.

Smith argues that materials scientists need to zoom in on how properties of materials emerge from what he calls an "aggregation of imperfections," instead of focusing on the symmetries in nature. Only recently, he says, have the seemingly opposed perspectives of symmetry and imperfections in matter begun merging into the multidisciplinary field of materials science.

A small community of researchers known as cluster scientists seems to have taken Smith's focus on asymmetry to heart. Cluster scientists concentrate on an intriguing level of material structure above the single molecule but below the larger assemblages that clearly behave like bulk metals or ceramics.

Richard W. Siegel of Argonne (Ill.) National Laboratory says a goal of cluster scientists is "to decide what materials properties one would like to have, and then actually construct the material from the building blocks of clusters." Unlike bulk materials – typically made of micron- or larger-scale grains, each comprising a million or more atomic or molecular units – cluster-assembled materials consist of nanometer-scale minigrains or clusters, each comprising tens to thousands of such units (SN: 5/6/89, p.284).

These quantitative variations emerge as qualitative differences in materials, Siegel says, largely because of the dramatically increased number of units involved in grain boundaries in the cluster-assembled materials. Compared with larger clusters, smaller clusters have proportionally more atoms or molecules sitting at surfaces than buried in their interiors. In a 100-nanometer cluster of atoms, for instance, 3 percent of the atoms sit at cluster surface boundaries. Shrink the cluster by a factor of 10 and the proportion of boundary atoms grows to 30 percent. Thus, compared with the boundary atoms in conventional materials made of micron-scale grains 100 or more times larger, the surface atoms or molecules of cluster-made materials play a more dominant role in determining bulk properties such as ductility and fracture susceptibility, Siegel says.

In his own work, Siegel explores differences between ceramics made from titanium dioxide (rutile) clusters 12 nm in diameter and conventional rutile ceramics made from commercially available titanium dioxide powders with particle diameters of 1.3 microns, or more than 100 times larger. The cluster-made ceramics sinter – a heat-intensive process that coagulates ceramic or metal grains into a stronger bulk structure without melting the grains – up to 1,000°C lower than do the larger-grained ceramics. The mechanical properties of the finely grained ceramics compare favorably to conventional materials sintered at higher temperatures, Siegel says. Yet the cluster-made material is more ductile – a property he says could enable researchers to make strong ceramic parts in net-like shapes and other configurations impossible to achieve today.

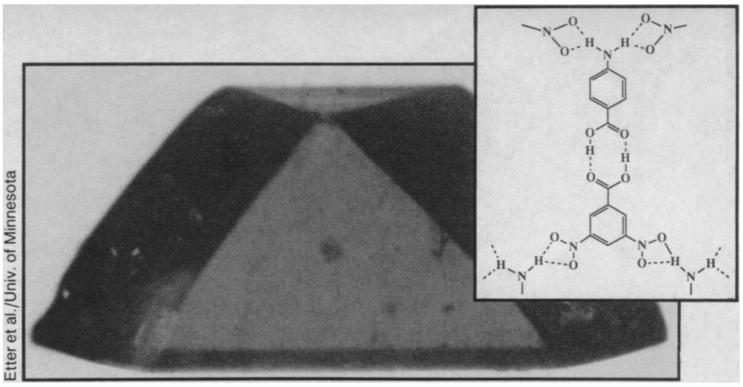
One potential payoff, researchers say, is better engines for running cars, planes and other machines. Ceramics withstand much higher temperatures than metal, and internal combustion engines run more efficiently at higher temperatures. Ceramic-based automobile engines, therefore, could yield cars that consume less fuel and pollute less than those with metal-based engines under their hoods.

Extending the horizon of materials-by-design is a new way of looking at organic chemistry – the carbon-based chemistry at the heart of most synthetic chemicals. In the conventional approach, scientists create these compounds by controlling how carbon atoms bond to each other and to a small cast of other atoms such as hydrogen, oxygen and nitrogen.

Chemist Margaret C. Etter of the University of Minnesota at Minneapolis describes traditional organic chemistry as the science of *intra*molecular bonds. "What we're doing is trying to unravel how to do synthetic chemistry of *inter*molecular bonds," she says. "If you could learn to put [collections of] molecules together in a preferred way, the potential is equally broad and promising as has been conventional synthetic chemistry," which has produced Saran Wrap, nylon and numerous pharmaceuticals, among other innovations.

"We're looking at how hydrogen bonds can be used to hold molecules together," Etter says. Chemists have not traditionally viewed hydrogen bonds – which are weaker than the covalent bonds linking atoms in typical molecules such as ethanol – as a chemical glue for assembling molecules into materials. "Here's where organic chemists' minds have been poisoned," Etter says. "In fact hydrogen bonds are weaker, but that doesn't mean they aren't good for doing syntheses."

"We now have a new synthetic method for designing materials" such as nonlinear optical crystals, she says. Normally, crystals are made up of identical atomic or molecular units. "But if I can take a single organic molecule and learn how it hydrogen-bonds to different kinds of molecules, I then can put it into a solid and surround it with molecules different from itself." In one example, Etter and her co-workers start with the molecule para-nitroaniline – used for making dyes – and assemble it with other molecules into 25 different crystals, or solid states, each with unique optical and electronic properties.



A 1:1 ratio of p-aminobenzoic acid and 3,5 dinitrobenzoic acid yields the designed co-crystal shown at right. Inset shows how the constituents assemble via hydrogen bonds, depicted here as series of dashes.

Etter et al./Univ. of Minnesota

"Until now, we have had to simply take Mother Nature's products – whatever grew out of solution, whatever crystallizes," Etter notes. And these natural crystals have unvarying microstructural features such as the interatomic or intermolecular distances. But by using hydrogen bonds to construct new crystal structures, she says she can gain control over these "invariables," thus loosening the strictures of nature. Scientists at the Du Pont Co. in Wilmington, Del., are learning to harness other intermolecular forces, such as electrostatic interactions, to control how different molecular building blocks assemble. Like Etter, they seek to develop new materials for optical communications technologies. They are also aiming to make molecule-scale versions of electronic components like transistors and wires (SN: 3/18/89, p.166).

"On a millennium time scale, we have had an explosion of activity in what materials are available and what we know we can do with them," says Carr. As scientists get a better feel for how a material's bulk properties stem from its microstructure at atomic, molecular, cluster and higher levels, they will improve their ability to custom-design materials for specific applications. "In the 1990s," Carr predicts, "we're going to be deft enough with our understanding to really chain it all together." ☐

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form a temperature inversion at its base. Both effects hasten cloud breakup.

Flight results show that changes in the cloud-condensation nuclei can influence climate in several ways, Radke says. An increase in the number of particles makes stratocumulus clouds brighter, and it also makes them last longer – two forces that cool the Earth's surface.

Climatologists need to understand how global warming might affect the number of condensation nuclei in these clouds, Radke says. Some scientists have suggested tiny ocean organisms called plankton may provide an important climatic feedback loop because they produce sulfur compounds that become cloud-condensation nuclei. Theoretically, if these plankton fared poorly in a future climate warming, the number of cloud particles would drop, intensifying the warming (SN: 12/5/87, p.362).

An individual water droplet in a cloud can measure as little as 10 microns across. At the opposite end of the size scale, a cloud system can span 1,000 kilometers.

"That's 100 billion orders of magnitude. It's no wonder we have problems," says atmospheric modeler Slingo.

The most advanced climate models – the general circulation models – break the atmosphere and oceans into thousands of boxes, their sides typically measuring a few hundred kilometers each. Within such a large grid, individual clouds fall through the cracks. Modelers therefore account for clouds through a process called parameterization.

"When I first came into large-scale modeling," says Slingo, "I thought [parameterization] was one of the most evil words I had ever come across. It's a little like an admission of failure."

To parameterize, modelers draw up equations that represent a general "cloudiness" factor based on physical principles and empirical observations. The equations might, for example, indicate that when relative humidity reaches a certain level in a box, the box begins to reflect sunlight and to rain.

As one of FIRE's main goals, researchers hope to develop better parameterizations by gathering detailed data on real clouds and testing the basic assumptions within their models.

In the future, as computing power grows and box size shrinks, computer experts will steadily improve the way they handle clouds, Slingo says. But the results of FIRE's cirrus and stratocumulus experiments may be opening a whole new dimension of problems for programmers. Those who work with general circulation models say they had hoped to avoid specifically including the complexities of microphysics. Yet the properties of minute drops strongly influence the entire cloud, and modelers can no longer overlook microphysics in an effort to keep things simple.

At present, clouds represent the weakest atmospheric link in climate models – a point illustrated by a study of 14 atmospheric general circulation models reported in the Aug. 4 SCIENCE. When researchers compared climate forecasts for a world with double its present amount of carbon dioxide, they found the 14 models agreed quite well if clouds were not included. But when the investigators incorporated clouds, the models failed to agree and produced forecasts ranging over a wide spectrum.

With such discrepancies plaguing the current generation of models, scientists find it difficult to predict how quickly the world's climate will change; nor can they tell which regions will face dustier droughts or deadlier monsoons.

Says Randall, a computer modeler himself, "If we can better include cloud effects in the climate models, those forecasts will become more reliable. The more reliable they are, the better we'll be able to plan for the future." ☐