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Materials with Complex Electronic/Atomic Structures

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Abstract

We explored both experimentally and theoretically the behavior of
materials at stresses close to their theoretical strength. This involves the
preparation of ultra fine scale structures by a variety of fabrication
methods. In the past year work has concentrated on wire drawing of in situ
composites such as Cu-Ag and Cu-Nb. Materials were also fabricated by
melting alloys in glass and drawing them into filaments at high
temperatures by a method known as Taylor wire technique. Cu-Ag
microwires have been drawn by this technique to produce wires 10 μm in
diameter that consist of nanoscale grains of supersatuated solid solution.

Organogels formed from novel organic gelators containing cholesterol
tethered to squaraine dyes or trans-stilbene derivatives have been studied
from several different perspectives. The two types of molecules are active
toward several organic liquids, gelling in some cases at w/w percentages
as low as 0.1. While relatively robust, acroscopically "dry" gels are
formed in several cases, studies with a variety of probes indicate that
much of the solvent may exist in domains that are essentially liquid-like in
terms of their microenvironment. The gels have been imaged by atomic
force microscopy and conventional and fluorescence microscopy,
monitoring both the gelator fluorescence in the case of the stilbene-
cholesterol gels and, the fluorescence of solutes dissolved in the solvent.
Remarkably, our findings show that several of the gels are composed of
similarly appearing fibrous structures visible at the nano-, micro-, and
macroscale.

Background and Research Objectives

The theoretical strength of solids can be described by reference to the bonding forces and
estimated to be of the order of the elastic modulus divided by thirty. Many areas of
engineering would benefit immensely by the development of materials with strength
levels which approach this theoretical limit. This can be achieved either by refining the
scale of the microstructure to the order of a few manometers, or by devising methods to
store large densities of dislocations in materials. The objective of the study is two-fold.

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The basic science aspect deals with the study of the mechanisms of attaining ultra materials both by thermal mechanical sequences and by novel phase transitions. In addition, attention will be given to developing methodologies for the production of ultra high strength materials and rationalizing of these materials in engineering design.

The design and synthesis of new molecules with novel self-assembling properties (based on amphiphilicity or noncovalent aromatic-aromatic interactions or a combination thereof) and reactivity as supramolecular assemblies and the development of novel and efficient photoredox reactions of organic and inorganic molecules based on single electron transfer processes is also pursued. This project element builds on a novel scheme for amplifying reactions initiated by light, ionizing radiation or redox active reagents (free radicals, etc.) by coupling tandem chain fragmentation of donor and acceptor substrates. The key feature of the reaction is that the donor substrate, D, fragments upon one-electron oxidation to yield a stable product and a radical, DR, which is a better reducing agent than the starting material. In a counterpart reductive process, the acceptor substrate, A, fragments following one-electron reduction to yield a stable product and a radical or ion-radical, AR, which is a stronger oxidant than A. The consequence of the two fragmentations is that each of the radical products can initiate further reaction by attacking additional substrate molecules, DR reduces A, and AR oxidizes D. This can result in large amplification factors that can provide highly reactive materials for application as sensors, nonlinear optical materials, holographic substrates and photolithography. We plan to synthesize substrates which can self-assemble or are incorporated into polymers such that the reaction can be carried out in solids, films or other assemblies.

Importance to LANL's Science and Technology Base and National R&D Needs

The theoretical strength of solids can be described by reference to the bonding forces and estimated to be of the order of the elastic modulus divided by thirty. Many DOE and Laboratory programs and missions would benefit immensely by the development of materials with strength levels which approach this theoretical limit.

This can be achieved either by refining the scale of the microstructure to the order of a few manometers, or by devising methods to store large densities of dislocations in materials. The basic science conducted in this project deals with the study of the mechanisms of attaining ultra materials both by thermal mechanical sequences and by novel phase transitions. In addition, attention is given to developing methodologies for the production of ultra high strength materials and rationalizing of these materials in engineering design.

The design and synthesis of new molecules with novel self-assembling properties (based on amphiphilicity or noncovalent aromatic-aromatic interactions or a combination thereof) and reactivity as supramolecular assemblies and the development of novel and efficient photoredox reactions of organic and inorganic molecules based on single electron transfer processes is important to DOE and Laboratory programs in developing new sensors for biological detection and photoconversionof light into energy.

Scientific Approach and Accomplishments

<u>Dislocation Accumulation at Large Plastic Strains-an Approach to the Theoretical Strength of Materials</u>

The usual method of introducing engineers to the concept of dislocations and their role in plastic flow is to compare an estimate of the theoretical strength of solid (of order $\mu/30$ where μ is the shear modulus) and the observed strength of either single crystals ($\mu/10^4$) or practical engineering material such as structural steels where the yield stress in shear is of order $\mu/10^3$. However, if we consider the problem in reverse, we can consider the accumulation of dislocations as one important mechanism by which we can produce engineering materials in which the strength level approaches the theoretical strength. If we assume that the flow stress can be expressed in terms of the mean free path between stored dislocations or as the square root of the global dislocation density, then we can see the influence of dislocation density in a diagrammatic form.

If we are interested both in the understanding of the physics of deformation in materials with a high density of dislocations and in the development of ultra high strength materials with useful combinations of properties such as strength and ductility, strength and toughness, strength and electrical conductivity, etc. The salient factors to be considered in this regard are that in a number of systems with increasing imposed strain both the tensile strength and the ductility (measured by the reduction in area) increase as exemplified in Table I.

Table I Tensile Strength (TS) and Reduction in Area at Fracture (RA) of 0.2wt%Cr0.96wt%C hypereutectoid Steels

Isothermal Transformation Temperature (^{o}C)	TS before Drawn (Mpa)	TS after Drawn (Mpa)	RA (%) before Drawn (Mpa)	RA (%) after Drawn (Mpa)
575	1500	3910	31.6	38.6

It is clear that the strengthening by dislocation accumulation due to large imposed plastic strains represents an important approach both to the development of new, potentially valuable, engineering materials and an important area of basic understanding in terms of the mechanical response of materials close to their theoretical strength.

From the results outlined for a variety of materials, it is clear that large strain deformation provides a mechanism for the attainment of strengths close to the theoretical strength. The detailed mechanisms by which these strength levels are attained are not completely clear and careful microstructural studies are needed in many cases. However, a general frame work for the understanding of ultra high strength material can be constructed based on the basic concepts of dislocation accumulation and annihilation outlined by Kocks and Mecking plus the process of stage IV hardening at large plastic strains discussed by a number of authors. In pure materials, the hardening rate in stage IV, θ_{IV} is of order of $5 \times 10^{-4} \mu$, which is much less than θ_0 so we can express the hardening rate over a wide range of strain in equation.

We can now examine the various mechanisms by which strength of order E/100 to E/50 can be attained; a) By cryogenic deformation at 4.2K dynamic recovery is reduced to that dislocation can be stored up to a density of order 10^{12}-10^{13} cm^{-2} as shown in Figure 15(a), (b) We can add an additional hardening term by the creation of twins or martensite plate which adds to the hardening rage at large strain such that:

$$\theta = \theta_0 ((1 - \sigma / \sigma_s) + \theta_{IV})(1 - f) + (\sigma_m - \sigma)df(\varepsilon)/d\varepsilon,$$

(c) In dynamic precipitation, we can again have a situation where a new set of obstacles can be created as a function of plastic deformation. If we approximate these as a separate set of point obstacles which require bending the dislocation to angle ϕ to break them, the extra strength $\Delta\sigma$ is of order:

$$\sigma = (\mu b/L)(\cos(\phi/2))^{3/2}(0.8+\phi/5\pi)$$

where L can be approximately related to the number of obstacles per unit area by

$$L \approx n^{-1/2}$$

Thus, $\Delta\sigma = A\mu b \, n^{-1/2}$

And if we assume that n is proportional to the imposed stain. This gives an additional rate of hardening which is very significant at low strains and decreased with strain.

In the case of two phase materials we can consider that as the scale of the structure decreases, we create additional interface energy so that we consider not only simply the hardening rate but the rate of dislocation storage $\sigma d\sigma/d\varepsilon$. We have two stored energy terms as a function of strain one due to dislocations in which the rate of energy storage decreases with strain and one due to interfaces which increases with strain. This concept is outlined in Figure 15(c) and compared with data for Cu-Nb.

Taylor Wire Synthesis

An elegantly simple process technique which combines both rapid solidification and deformation is the Taylor microwire technique of melting materials in glass tubes and drawing the composite to very small diameter wires. The technique was originally developed by Taylor 1924 and has been reviewed recently in terms of both the resultant properties of the microwires and their potential applications.

The application of the Taylor wire technique to the Cu-Ag system is very interesting not only because the structures of the Cu-Ag Taylor wires can be compared with those produced by cold drawing, but also because non-equilibrium phases can be obtained in this system by rapid cooling, mechanical alloying and other techniques. To date there exists very little microstructural evidence to relate the properties of the Taylor wires to their detailed structure. Thus the investigation of Cu-Ag microwires produced by the Taylor wire method presents not only a rich area for detailed correlation of properties and structure in ultra-fine-scale materials but also the opportunities to produce new non-equilibrium structures.

Cold drawn rods of Cu-l6at% Ag were encapsulated in 7740 borosillicate glass tubes which had a softening temperature of 821°C and working temperature of 1252°C. The assembly was heated to a temperature between the softening and working temperatures of the glass and drawn vertically as shown schematically in Fig. 1. The glass coated wires cooled in air at rates estimated to be in the range of 10^2 °C /s to 10^5 °C/s depending on the diameter of the drawn wire.

Scanning electron microscopy (SEM) examination was performed using a Philips Microscope operated at 20kV. A back-scattered detector was employed in this work in order to detect atomic number contrast in the samples. An Energy-Dispersive Spectrometer (EDS) Link X-Ray system was used with the SEM to perform compositional analysis.

The preparation of thin samples of the Taylor wires for transmission electron microscopy (TEM) examination was conducted by first gluing the wires on a 3mm-diameter grid. The samples were then ion-milled using a Gatan 600 dual ion mill apparatus operated at 4kV. During the ion milling, the samples were cooled by liquid nitrogen and milled at an angle of 10° in order to minimize the ion beam damage. The specimens were examined in a Philips CM30 TEM operating at 300kV, and Jeol 3010F TEM (Cs=0.6mm) operating at 300kV.

A Cu-24wt%Ag alloy can be fabricated using the Taylor wire method to yield a series of various diameters. The wire diameter determines the cooling rate of the liquid and therefore the scale and nature of the microstructure obtained. Nano grains were obtained when the wire diameter was about 10 μm with a cooling rate of order of 10^5 C/sec. When the diameter of the wire was larger than 20 μm pro-eutectic Cu and eutectic CuAg were found. As the diameters of the wire increases, the microstructure becomes coarser. In the lamellar structure region (1 1 1) twins were observed in the 30, μm Taylor wire with the cooling rate of 10^4 C/sec. Both the Cu and Ag phases exist in two variants (T1 and T2). Cu_{T1} and Cu_{T2} have a (1 1 1) type twin relationship. Cu_{T1} and Ag_{T2} are also twin related across a (1 1 1) twin plane. However, Cu_{T1} and Ag_{T1} have an orientation relationship of (100)$_{Cu\,T1}$ /(100)$_{Ag\,T1}$ and [010]$_{Cu\,T1}$ /[010]$_{AgT1}$ The twinning boundaries are generally coherent, lying on (1 1 1) planes.

Organogels

An area of increasing recent interest is the formation of semistable gels by the addition of small amounts of low-molecular-weight organic molecules ("gelators") to relatively low-molecular-weight, nonviscous, organic liquids. While several different categories of gelators have been identified in recent studies, 2-15 gel formation can usually be best understood as resulting from competition between tendencies for the gelator to dissolve in the solvent and tendencies for it to self-assemble and crystallize.

Among the types of gelators found in different investigations thus far are single molecules or pairs which interact through hydrogen bonding, amphiphiles, substituted cholesterol derivatives, and various alkyl-aromatic compounds. Particularly interesting among the different classes of gelators studied thus far are a group of tethered "dyads" which contain two different groups, each having a strong tendency to self-assemble. Examples of these include several cholesterol-linked anthracene derivatives studied by Weiss and co-workers and by Weiss and Terech and cholesterol-linked azobenzenes studied by Shinkai and co-workers. Several of these compounds exhibit the ability to gel a diverse array of solvents at levels of 1% (weight/weight) or below; under these conditions one molecule of the gelator may (on the macroscopic scale) immobilize several thousand solvent molecules.

The structures of organogels have been studied by a variety of different techniques including neutron scattering and X-ray scattering techniques, various forms of imaging, and spectroscopic and calorimetric investigations. Although much has been learned in a number of recent studies regarding the structure and properties of these organogels, many questions remain. Some of these include the relationship between gelator structure in the gel and the crystal structure of pure gelator, the specific interaction between the solvent and gelator, the state or states of the solvent, and the factors that determine what solvents a given gelator will gel and how the material properties of the gel on a macroscopic scale will be influenced by the nano- and mesostructures of the gel.

Although our knowledge of gel structure is far from complete, the current results suggest several remarkable inferences may be made. If we assume that the cholesterol units in the current gelators stack in much the same way they form liquid crystals, we can imagine that the gelator "scaffolding" consists of stacks or columns which may have as their primary self-assembly element the cholesterol with the appended aromatics occurring more-or-less like "spokes" projecting from the columns. Interactions between stilbene or squaraines within the column may be difficult, but interactions between aromatic units in adjacent columns should be possible and may account for the weak indications of aggregation that are observed, especially for the stilbene gelators.

For the squaraines, where the tether is longer and more flexible, the degree of interaction between squaraines may be such that both intra- and intercolumnar interactions may take place. The observation that photoisomerization can occur for the gels of and that it reversibly destroys the gels supports the idea of a structure in which weak self-association of the trans-stilbene units is essential for gel formation but that the self-association is quite different from the crystal structure of gelator alone. These results are in agreement with those of other studies that indicate much of the solvent in the gel exists as a nonviscous fluid in pools or channels that are sufficiently large such that solutes dissolved in the solvent experience an environment very similar to that in the fluid alone. This does not preclude the likelihood that some of the solvent is associated with the gelator and that it may be an important component of the gelator scaffold. The fact that these gels organize into fibrous structures on the nano-, meso-, and macroscopic levels supports a concept wherein gelator columns (or a small bundle of columns) may be the unit element of gel formation and that there may be similar interactions occurring initially between columns, leading to the smallest fibrous strands entrapping solvents and to subsequent interactions between strands as progressively larger fibers are formed. It seems most reasonable that these proposed interactions may be largely due to self-assembly of the aromatic units or to a composite self-assembly process involving both the aromatic groups and some associated solvent molecules. The remarkable ability of the gels to exhibit, more-or-less simultaneously, glassy, fibrous, solid-like, and liquid-like behavior suggests their potential utility in a variety of advanced materials applications.

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