HIGH-TEMPERATURE CHEMISTRY OF MATERIALS: AN UPDATE

Advanced structural materials are gaining in importance to the Laboratory and the Department of Defense. In many applications of these materials, performance is limited by chemical reactions. After a brief introduction to advanced materials in general, progress in solving the materials chemistry problems discussed in an earlier article in the *Johns Hopkins APL Technical Digest* is described and new independent research and development efforts in advanced materials technology insertion are presented.

INTRODUCTION

In a 1986 article in the Technical Digest¹ I described initial calculations on some problems in the high-temperature chemistry of structural materials. This work continued²⁻⁸ under the support of APL's Independent Research and Development (IR&D) funds through the Aeronautics Department, while a transition was made to external support from the Office of Naval Research. Concurrently, the tools developed were inserted 9,10 into departmental programs from the Naval Surface Warfare Center (Materials Systems for Hypersonic Tactical Missiles), the Department of Energy (Aerospace Nuclear Safety Program), and the Army (Non-Nuclear Kill Radome Evaluation R&D). Related parallel efforts have also continued in APL's Research Center. 2,11-13 Meanwhile, the Department of Defense (DoD) has established several new materials-oriented programs, including the National AeroSpace Plane industrial consortium and the Defense Advanced Research Projects Agency's Advanced Submarine Technology Materials Program. Other programs from 1986, like the Air Force Ultra-High Temperature Materials Program, have gained momentum. In recognition of the increasing importance of materials, APL is now supporting a new interdepartmental IR&D effort with expanded scope, called Advanced Materials Technology Insertion.

After a brief introduction to advanced materials in general, I describe the further progress in solving the materials chemistry problems discussed in Ref. 1 and discuss the new IR&D areas of research.

ADVANCED MATERIALS AND THEIR IMPORTANCE

The materials of interest here are structural "composites," indicating that reinforcing particles, fibers, or single-crystal whiskers are built into a matrix phase. Coatings are also important, both on fibers and on exposed surfaces. The chemical constituents are often ceramics and refractory metal alloys (with high-melting oxides) and carbon. Such materials are increasingly used, or at least considered, in many systems important to APL. Examples include

1. Turbine rotors made of carbon fibers in a carbon matrix, with improved high-temperature strength that en-

ables higher jet engine temperatures and improved thrust.

- 2. Ceramic linings for combustion zones of diesel and Otto engines to improve fuel efficiency by permitting higher operating temperatures.
- 3. Composite, structural components that reduce the weight of modern tactical planes and could make possible greater depths for submarines and other underwater vehicles.
- 4. Ceramic coatings on the space shuttle and the National AeroSpace Plane for oxidation resistance.
- 5. Coatings for managing radar and sonar signatures. Thus, the payoff of advanced materials is improved performance. Their importance has been recognized in numerous recent strategic planning documents from DoD.

MATERIALS CHEMISTRY BACKGROUND

The effort we began in Ref. 1 focused on the hightemperature chemistry of advanced materials. This particular subject is important to DoD partly because the speed and range of air-breathing missiles are limited by the inability of traditional structural materials to withstand chemical attack by high-temperature oxygen in the air and in combustor gases. Both external leading edges and the liners of air-breathing combustors are subject to oxidation at high speeds. Free oxygen is present in the combustors of air-breathing engines because, unlike rocket engines, they run fuel-lean at peak efficiency, leaving oxygen in the combustion process. The combustor temperatures anticipated for advanced wide-area missile concepts and other high-speed ramjets are as high as 3000K. Thus, we need a better understanding of the hightemperature oxidation chemistry of materials to help guide the selection of new materials that are able to withstand temperatures up to 3000K in the presence of oxygen. Important candidate materials for the ramjet application include, for example, hafnium-based ceramics and alloys. Key aspects of the chemistry of these materials, and advanced materials in general, are the heat transfer and solid-phase diffusion processes that control the reaction rates involving oxygen and the numerous interacting condensed phases possible in composite materials

with coatings. We need estimates of the lifetimes of the candidate materials and a knowledge of which chemical species will form in given situations. Although experimental approaches are still safer, the effort needed to make measurements over a complete design envelope is often unreasonable. Our long-term goal, therefore, is to refine and develop a set of predictive, computational tools that use known and measurable data on fundamental chemical properties.

Much theoretical work exists on the chemistry of carbon oxidation, but less attention has been given to the newer, more complex materials. Carbon is uniquely simple since only one kind of atom is present in the solid phase and only gaseous oxides are formed (CO and CO₂). Advanced materials can also contain metals, which usually form at least one solid oxide (iron forms three, namely, FeO, Fe₂O₃, and Fe₃O₄), and ceramic compounds like silicon carbide.

A further complication is the difficulty in predicting the morphology of an oxide that forms on exposure to a hot, oxidizing gas. The formation of a compact oxide layer is advantageous, since the oxide is then interposed between the oxygen and the substrate, interfering with further oxidation. Other morphologies are also possible, however. Alloys can oxidize "internally," wherein disconnected particles of oxide form in depth. One component of an alloy may oxidize "selectively" while another may not. Under special conditions, dendritic oxide growth is possible. Oxide layers grow, often to a thickness of 10³ to 10⁶ molecules, through in-depth diffusion. Two extreme cases are copper and hafnium. Evidence indicates that copper atoms migrate through the oxide layer from the substrate to the exposed surface, where oxidation occurs. With hafnium, the oxygen dissolves in the oxide and migrates to the interior interface, where oxidation continues. The migration processes rely on the existence of imperfections in the otherwise regular oxide structure. These imperfections include vacancies, electron holes, and interstitial ions. In-depth migration results from concentration gradients and also from an electric field that establishes itself to ensure no net current. Thus, calculations of high-temperature oxidation chemistry require mathematical models of several processes and data that may need to be estimated at high temperatures.

The chemical reaction calculations are performed mostly with thermodynamics at high temperatures and by finite-rate chemical kinetics at lower temperatures. The rates of chemical reactions increase as temperature increases. A general rule for gas-phase reactions is as follows: since both "forward" and "reverse" reaction rates increase, the reactions go to "completion" more rapidly, at which point the forward and reverse rates are balanced, and a chemical equilibrium analysis is appropriate. The same rule applies to reactions involving a condensed phase, if the phase remains condensed. Many components like carbon, ceramics, and refractory metals used in advanced materials remain solid to very high temperatures. We have conducted a detailed analysis of the transition from finite-rate control to equilibrium control for carbon oxidation and found that the equilibrium calculations become accurate above approximately 1300°C, ⁴ depending on the particular rate coefficients for carbon, and because the oxygen is supplied by diffusion through a stagnation-flow gas boundary layer. Similar calculations must be carried out for the various component interactions and diffusion paths (including diffusion of dissolved species) possible in each advanced material of interest. Unfortunately, little experimental data are available on the necessary finite-rate chemical kinetic (Arrhenius) coefficients and the diffusion coefficients. Thus, we can only assume that carbon, ceramic, and high-melting metal systems reach (local) chemical equilibrium.

The required input for equilibrium calculations is the chemical thermodynamic properties of all or many of the species made from the elements present. We implicitly assume here that sufficient thermodynamic data will be available. A number of lengthy compilations have been written for simple, pure compounds; we have been using properties based on the Joint Army Navy Air Force tables. Some data are also available on more complex pure phases like intermetallics and compound oxides, and even solution phases like alloys and nonstoichiometric compounds. Much more data are needed, however, even at moderate temperatures. This represents an opportunity for APL to make a useful contribution, without a large start-up investment (at moderate temperatures), by establishing a capability to make calorimetric and vapor pressure measurements from which chemical thermodynamic properties may be derived.

Another approach to acquiring thermodynamic property data is to adjust the property values to give agreement between predicted and measured "overall" phase diagrams of the traditional form seen in textbooks and the literature. These diagrams show the equilibrium phases that are present for a given overall elemental composition. Unfortunately, many of these diagrams are unavailable for the higher temperatures. The number of elements involved in practical problems is usually at least three, and considering the large number of possible combinations of three elements, the number of possible ternary and especially quaternary phase diagrams is also large. Considering that the number of researchers in the field is small and decreasing, APL can contribute by establishing a capability to measure "pieces" of multicomponent phase diagrams, as required, at reasonable temperatures. Even limited solubility data are important, as is any information on the stability of new compounds. The measurements are not prohibitively difficult, except at the ultrahigh temperatures predicted for recent vehicles.

The following sections provide examples of our progress since publication of the earlier article in the *Technical Digest*. That article presented calculations of the diffusion-controlled rate of silicon oxidation to form silicon monoxide gas, the vapor pressure at a silicon-silicon dioxide interface, limits on the interface vapor pressures in hafnium-carbon-oxygen systems, and the rate of isothermal oxidation of hafnium carbide to form solid hafnium dioxide. Subsequent work² provided experimental confirmation of our hafnium carbide oxidation rate theory presented earlier. Other theories describe pro-

cesses that occur when a material is exposed to a hot oxidizing gas. Computational tools were developed to predict what chemical reactions can occur, assess material compatibility and volatility, estimate lifetimes, calculate the heat throughput, and predict conditions of chemical vapor deposition for manufacturing applications. The chemical processes include pressure buildup at interior interfaces, evaporation, oxidation to form gaseous oxides, oxidation to form solid oxides, "duplex" layer formation (defined below), internal oxidation, and multiple layer formation. Demonstration calculations were carried out on several practical systems, including Si-C-O, Ta-C-O, Hf-C-O, C-O, Fe-S-O, Ni-S-O, Fe-Si-O, Ni-Cr-O, Cu-Si-O, Ti-B-Cl-H, Fe-O, Zr-C-O, Teflon, and phase-change systems.

CHEMICAL OPTIONS

When a pure condensed (solid or liquid) phase is exposed to a flowing gas mixture, the phase can

1. Evaporate congruently

$$Si(1) = Si(g)$$

2. Evaporate incongruently

$$2SiO_2(1) = 2SiO(g) + O_2(g)$$

3. Form gaseous oxides

$$2C(s) + O_2(g) = 2CO(g)$$

4. Form smoke

$$Si(l) = Si(g)$$

 $Si(g) + O_2(g) = SiO_2(smoke)$

Here, the surface always retains its chemical identity despite the loss of mass, and no important role is played by the in-depth diffusion of dissolved gases. Other processes, however, are possible on exposure of the pure condensed phase; for example, the surface can also

1. Form a condensed oxide phase

$$2HfC(s) + 3O_2(g) = 2HfO_2(s) + 2CO(g)$$

2. Form multiple oxide layers

$$2Fe(s) + O_s(g) = 2FeO(s)$$

 $6FeO(s) + O_2(g) = 2Fe_3O_4(s)$
 $4Fe_3O_4(s) + O_2(g) = 6Fe_2O_3(s)$

3. Form a multicomponent (duplex) layer $3Fe(s) + SO_2(g) = 2FeO(s) + FeS(s)$

4. Form solution phases

$$2HfC(s) + xO_2 = 2HfCO_x$$

Here, the surface changes its chemical identity, and, in addition, the reaction rate and the process of in-depth heat transfer also would be influenced by the extra phases, which would be interposed between the original reactants.

Thus, the first question to be resolved concerns the range of gas compositions in which a given pure condensed phase at a given temperature can retain its chemical identity without forming a second condensed phase. We have defined new "flowing gas-phase diagrams" to address this question. We find that we can correctly anticipate the formation of a duplex FeO + FeS layer on Fe exposed to SO₂ and a duplex Ni₃S₂ + NiO layer on Ni exposed to SO₂. Details of the morphology due to in-depth diffusional processes or oxygen solubility limits are not predicted by this approach.

Where a pure condensed phase is changed by exposure to a gas mixture, we have developed several thermodynamic tools for calculating the chemistry at the possible condensed phase interfaces. These results constitute chemical boundary conditions on the governing differential equations of in-depth diffusion and heat transfer that, in principle, determine the morphology. Solution methods for these equations will require more research to develop, however. The tools are of more immediate use in interpreting observed morphologies and in estimating the chemical compatibility of adjacent phases in manmade composites.

The calculations of interface vapor pressures begun in Ref. 1 were automated and carried out for the silicon-carbon-oxygen (Si-C-O) system and the tantalum-carbon-oxygen (Ta-C-O) system. Silicon-based ceramics are used for oxidation protection on the space shuttle, while tantalum carbide ceramics, containing TaC and Ta₂C, block carbon diffusion and have been proposed for protecting carbon structural components. The vapor at interfaces evolves from chemical reactions that occur between the adjacent condensed phases, especially as temperature rises. The resulting pressure build-up can create bubbles, delaminations, and cracks. ¹⁵ An example of an interface reaction is

$$SiC(c) + 2SiO_2(c) = 3SiO(g) + CO(g)$$
, where c denotes condensed.

Figure 1 shows the total pressure of all the vapor species at three-way junctions possible in the Ta-C-O system as a function of temperature. Equivalently, the results also apply to two-way carbide-oxide interfaces with varying amounts of carbon and tantalum present. The amount of carbon is least and the amount of tantalum greatest for the high-temperature curve, while the amount of carbon is greatest and the amount of tantalum least for the low-temperature curve. We may conclude that a carbide-oxide interface can survive to much higher temperatures if the carbide is rich in metal and deficient in carbon. Similar results have been observed for Si-C-O and Hf-C-O systems. ¹

Alloys only rarely keep their original composition on exposure to heat or reacting gases, and predicting what new phases form and their morphology is especially tricky. Typically, the components at least evaporate at different rates (distillations of liquid solutions like alco-

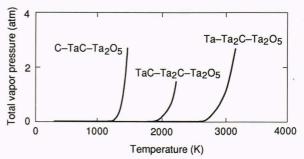


Figure 1. Vapor pressures in the Ta-C-O system. Each curve is labeled by the formula of one of three solids in mutual equilibrium with a vapor phase (containing several species) whose total pressure is given on the vertical axis. The pressure and composition of the vapor are unique at each temperature on each curve

hol and water take advantage of this fact). In addition, alloys can experience selective oxidation, in which one component is preferentially attacked, and internal oxidation, in which an oxide forms initially in-depth as disconnected particles.

In-depth diffusion of the alloy components is an important process for alloys. Some progress has been made toward obtaining qualitative estimates of the resulting morphology. Specifically, we have made calculations on several systems, including Fe–Si, Ni–Cr, and Cu–Si alloys.

Figure 2 shows the partial vapor pressures of O₂ in simultaneous equilibrium with Ni-Cr alloys and the oxides as indicated. This system provides an example of interoxide formation, a frequent process in alloy oxidation. Here the interoxide is NiCr₂O₄, sometimes written as NiO·Cr₂O₃. In general, the oxide that forms first on a given alloy has the lowest vapor pressure of O2. Suppose the chromium content is low enough for NiO(c) to form first, namely, $\log_{10} X_{Cr}$ is lower than -8.4. The formation of NiO(c) withdraws nickel from the alloy. Thus, while the NiO(c) is forming, the concentrations of O2 and chromium at the interior alloyoxide interface move along the NiO(c) curve toward the crossover, or case (a) in Figure 2. The distance moved depends on the outcome of the competition between inward diffusion of O2 through the oxide and outward diffusion of nickel through the alloy (see figure, upper right). The only oxide to form (selective oxidation) may be NiO(c). If the initial state is not too far from the crossover, however, NiCr₂O₄(c) can also form at the interior interface (internal oxidation). When NiCr₂O₄(c) forms first, the system follows case (b) in Figure 2, and NiO(c) can form internally if conditions are right. Therefore, there is a range of alloy compositions around the crossover where both oxides form. Similar arguments may be applied when Cr₂O₃ forms, as seen in case (c). Wagner reached similar conclusions for a general two-

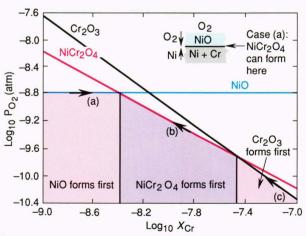


Figure 2. Partial pressures of O_2 (P_{O_2}) in equilibrium with Ni–Cr alloys and an oxide at 1373K with various number fractions ($X_{\rm Cr}$) of chromium in the alloy. For a complete discussion of this figure, refer to the text under "Materials Chemistry Background."

component alloy by different arguments. ¹⁶ Morphology options also have been discussed. ^{17,18} These approaches provide qualitative interpretations of the observations by Birks and Meier ¹⁴ on the Ni–Cr–O system; Cu–Si alloys may be analyzed similarly.

OVERALL PHASE DIAGRAMS

Phase diagrams of the traditional textbook form, or overall phase diagrams, show the phases that are present given the overall elemental number fractions of all the gas and condensed phases taken together. Quite often, the phase diagram needed has not been measured for a particular application, however. The immediate challenge becomes "calculating" the overall phase diagram from available data on fundamental thermodynamic properties. These calculations are an essential part of the calculations mentioned earlier in which thermodynamic property values are varied to give agreement with the pieces of phase diagrams that have been measured.

We have developed a new and advantageous method, using Ref. 3, for calculating overall phase diagrams. Figure 3 shows calculated conditions for titanium diboride (TiB₂) deposition from titanium-boron-chlorine-hydrogen (Ti-B-Cl-H) mixtures; TiB₂ has been proposed for use in the National AeroSpace Plane. Each line in Figure 3 separates a TiB₂ region (to the right) from a gas region (to the left). The axes are overall elemental number fractions.

PREDICTIONS OF CHEMICAL PROCESS RATES

In what follows, I describe some of our recent results on predicting the rates of chemical processes in materials. The morphology, which is assumed, has been obtained either from experimental observations or from calculations described in the preceding discussion.

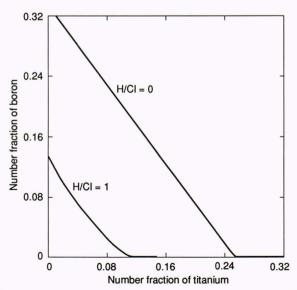


Figure 3. Calculations of part of the overall phase diagram of Ti-B-Cl-H systems at 1200K and 0.84 bar. Each curve separates a gaseous region (on the left) from a TiB₂ region (on the right).

Boundary-Layer-Controlled Ablation Rates of Pure Condensed Phases

When a pure condensed phase is known to retain its chemical identity on exposure to a flowing gas, and not to be influenced by diffusion of dissolved gases, then the next questions concern the actual rate of evaporation or reaction and the magnitude of the in-depth heat flux. These quantities are needed for the interpretation of test results and for design calculations where the basic issue is the lifetime of the condensed phase in specific gas environments.

If the surface temperature is expected to be high enough for local equilibrium conditions to prevail, the rate of mass loss may be calculated in terms of the surface temperature using chemical thermodynamics and a model of boundary layer diffusion. The results are directly applicable to the interpretation of furnace tests when the temperature is uniform throughout the furnace and, hence, the surface temperature is readily available. For applications when temperature gradients are present in the specimen, the calculated mass loss rate in terms of the (assumed) surface temperature becomes a boundary condition to be used in solving the governing equations for in-depth heat transfer, the solution of which fixes the complete temperature distribution in the condensed phase as well as the mass flux.

Figures 4 through 6 show some new calculations to describe the oxidation of C and the vaporization of HfO_2 in air. The *B*-number on the vertical axis is a degree of reaction, specifically, the mass of an exposed phase lost per unit mass of flowing gas, calculated with the condensed phase in excess. Thus, the *B*-number is a mass-based stoichiometric coefficient in the overall reaction between the condensed phase and the flowing gas.

Figures 4 and 5 show the increases in the degree of reaction of exposed carbon that occur with increases in temperature and oxygen pressure. The lower plateaus correspond to CO(g) formation, the second plateaus to $CO_2(g)$ formation, and the high-temperature rises to C(g) formation (sublimation). Figure 6 shows how $O_2(g)$ suppresses the evaporation of condensed HfO_2 .

The *B*-number may be used in lifetime predictions. It determines the mass loss flux \dot{m}'' (mass lost per unit area per unit time) when the chemical reactions are controlled by species diffusion through the boundary layer:

$$\dot{m}'' = \frac{\rho_{\rm g} D}{\Delta} B.$$

Here, $\rho_{\rm g}$ is the gas density, D is the common diffusivity of all the gas species, and Δ is the boundary layer thickness. This theory predicts that the mass flux becomes infinite when a material like carbon reaches its sublimation temperature. In practice, the flux is thermally controlled.

Thermally Controlled Ablation Rates of Pure Condensed Phases

The assumption of chemical equilibrium at the surface of a material undergoing heat transfer and ablation is val-

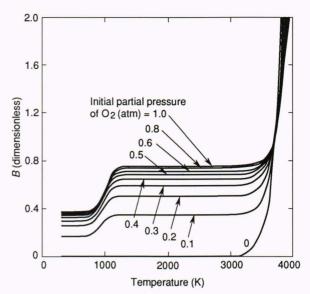


Figure 4. Dimensionless mass loss rates of carbon (graphite) in O_2 -He gas mixtures at 1 atm. The lower plateau corresponds to CO(g) formation, the higher plateau to $CO_2(g)$ formation, and the steep rise to C(g) formation or sublimation.

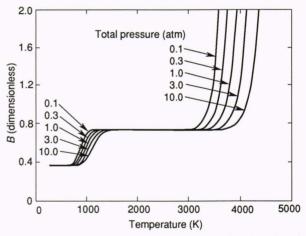


Figure 5. Dimensionless mass loss rates of carbon (graphite) in pure O_2 .

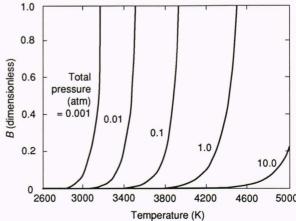


Figure 6. Dimensionless mass loss rates of HfO_2 exposed to air, which suppresses the evaporation process.

id when the temperature is high enough, but at lower temperatures the reaction rates are controlled by surface temperature through Arrhenius finite-rate reaction coefficients. We have published a finite-rate analysis4 of carbon heat transfer and ablation, controlled by the rate of $2C(c) + O_2(g) = 2CO(g)$. Other materials, like a Teflon infrared window, also irreversibly decompose at relatively low temperatures to form a gas mixture. For these materials, in-depth gasification is important, especially since the Arrhenius reaction rate coefficient is nonzero at the interior temperatures. Then the surface becomes an undefined mushy zone. We published a new calculation of Teflon ablation in the presence of forced convection,6 complementing our earlier calculations with radiant heating. 19 We also calculated both the recession speed and an effective surface temperature, improving and extending earlier results by Lengellé. 20

The rate of heat transfer controls the mass loss that occurs when a material melts and the liquid is continuously blown away, or when a material like carbon reaches its sublimation temperature and a process like boiling occurs. The mass flux is then given by

$$\dot{m}'' = \frac{F}{\Delta \hat{H}} ,$$

where F is the applied heat flux, and $\Delta \hat{H}$ is a heat of reaction per unit mass. We have extended the original calculation by Landau²¹ of the in-depth temperature distribution using a new and more efficient numerical method that applies a fixed spatial grid and does not require tracking the receding surface.⁸ This work offers more efficient solutions to similar two- and three-dimensional ablation problems.

As with diffusion, the rate of heat transfer in most structural materials is affected by density variations and phase changes that occur as temperature rises. In particular, the calculation of the in-depth temperature distribution is complicated by the unknown locations of the exposed surface and any interior interfaces. We have developed new numerical methods for solving this problem with a fixed spatial grid and no front tracking.^{7,8}

Rates of Solid Oxide Formation

When a protective oxide layer forms on a substrate, the rate of oxidation tends to be controlled by the rate of diffusion through the oxide layer. Specifically, the rate of diffusion in-depth tends to be slower than the rate of diffusion through the gas boundary layer. Thus, a common assumption is to neglect the gas boundary layer gradients, equating the gas concentrations at the surface to the free stream concentrations. We make this assumption here, but we are also working to assess better the competition between boundary layer and in-depth diffusion, especially at high temperature, where oxide evaporation becomes important.

Complicating the prediction of the rate of in-depth diffusion is the motion of the oxide layer that results when its volume differs from the volume of the substrate being replaced. My earlier article¹ presented an approximate solution of the in-depth diffusion equations and

an exact solution for single-layer oxidation of carbides. Despite the motion, the solution has the same "parabolic" form, which is found when swelling is neglected and the layer thickness is proportional to the square root of time. Predictions of the theory, using experimental diffusivities, are consistent with arc heater tests.2 Recently. Bargeron and co-workers advanced this work using a high-temperature furnace. ^{2,11-13} We are currently making calculations of the combined processes of indepth diffusion and heat transfer in a growing hafnium oxide layer and have found that the rate of oxidation is still parabolic, despite the heat flow, if the initial temperature of the hafnium carbide is uniform when first exposed to the hot oxidizing gas and if the surface temperature then jumps immediately to a constant higher value as oxidation begins.

EFFORTS IN ADVANCED MATERIALS TECHNOLOGY INSERTION

While work on high-temperature chemistry continues with good progress, APL's IR&D Committee has recommended, and the Executive Committee has endorsed, a broadened interdepartmental effort on advanced materials technology insertion. The objective is an increased ability to model, design, fabricate, and test materials in anticipation of the future needs of sponsors for technical evaluations and advice. Specific projects funded for 1990 concern

- Ceramics exposed to heat and chemically reactive gases.
- 2. Composites to protect satellites from nuclear radiation.
 - 3. Composites designed for submergence in the ocean.
- 4. Novel heat pipes and evaporator tubes to protect against heat.
- 5. Materials and structures made with electrorheological fluids to manage interactions with radar, sonar, shocks, vibrations, and bending moments. (These fluids were originally proposed solely for their rheological properties, which change in an applied electric field.)
- 6. Nondestructive evaluation of composites by analysis of interactions with ultrasound.

These projects all relate to interactions between materials and their environment.

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