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MASTER

Advances in Materials Science
Metals and Ceramics Division
Triannual Progress Report
June through September 1980

Scientific Editors: J. J. Truhan
and R. W. Hopper
General Editor: K. M. Gordon

October 28, 1980

**Lawrence
Livermore
Laboratory**

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*Magnetic Fusion Engineering Division

†Materials Fabrication Division

‡Materials Engineering Division

**K Division

Glossary

AISI	American Iron and Steel Institute.
API	American Petroleum Institute.
ARRADCOM	Army Armament Research and Development Command.
AlN	aluminum nitride.
Amzirc	copper-based alloy that is precipitate hardened with zirconium.
ASTM	American Society for Testing and Materials.
EC	erosion/corrosion.
EXAF	extended x-ray absorption fine structure.
FMIT	Fusion Materials Irradiation Test.
HE	high explosive.
KGRA	known geothermal resource area.
MZC	copper-based alloy containing 1 to 2 wt% Mg, Zr, and Cr.
NEP	Nuclear Explosives Program.
PTP	potassium trihydrogen pyrophosphate.
PVC	polyvinyl chloride.
PM	planar magnetron.
RTNS-II	rotating-target neutron source II.
SEM	scanning electron microscope.
TATB	1,3,5-triamino-2,4,6-trinitrobenzene.
TEM	transmission electron microscopy.
TGA	thermogravimetric analysis.

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Magnetic fusion energy program

Effect of strain on the cubic-to-tetragonal transformation in Nb_3Sn *

When Nb_3Sn is cooled below 45 K, it undergoes a martensitic transformation from a cubic to a tetragonal form. We are currently using x-ray diffraction to determine if mechanical strain affects the temperature of this transformation.

We conducted these x-ray diffraction studies in a cryostat cooled with liquid helium. A heater allowed us to vary the temperature from 10 K to well above the transformation temperature. A strain gauge was mounted on the sample (a thin ribbon of Nb_3Sn) that was, in turn, placed on a vise-like arrangement made of either copper or indium. This vise could be opened from outside the cryostat to provide the both compressive and tensile strains on the foil.

We monitored the x-ray diffraction peak height and peak width of the 116 reflection as a function of both strain and temperature. The 116 reflection undergoes an appreciable increase in diffracted intensity and sharpening in width as the cubic-to-tetragonal transformation occurs. These data indicated that the phase-transformation temperature increases approximately linearly with increasing compressive strains and that the amount of material transformed to the tetragonal phase increases with increasing compressive strains.

Measuring *in situ* creep under 14-MeV neutron irradiation†

Reactor experiments have shown that neutrons produced in a fission reactor have deleterious effects on internal reactor materials. Because fusion reactors will generate greater numbers of high-energy neutrons, a given neutron flux will cause even more severe radiation damage.

No fusion reactors are currently in operation, so radiation experiments with high-energy neutrons must be conducted using accelerator-based neutron sources. At present, two such sources are available to us: the Be (d,n) source at the University of California at Davis and the T (d,n) rotating-target neutron source II (RTNS-II) at LLNL. The Be (d,n) source produces a broad spectrum of high-energy neutrons ($4 \text{ MeV} < E < 14 \text{ MeV}$) from a deuteron stripping reaction, and RTNS-II generates monoenergetic 14-MeV neutrons from the T (d,n) fusion reaction. Maximum neutron flux from the Davis source is about $10^{17} \text{ n/m}^2 \cdot \text{s}$ ($E > 1 \text{ MeV}$), and maximum neutron flux from the RTNS-II is about $10^{17} \text{ n/m}^2 \cdot \text{s}$ ($E = 14 \text{ MeV}$). These flux levels are 10 to 20 times lower than those anticipated in a fusion power reactor. Studies of damage caused by high fluxes of high-energy neutrons cannot be made until early 1984 when the Fusion Materials Irradiation Test (FMIT) facility is completed at Richland, Washington. The predicted peak flux in FMIT is $10^{19} \text{ n/m}^2 \cdot \text{s}$. Until then, we will use the relatively low-flux, high-energy neutron sources to investigate the nature of high-energy neutron damage to materials of interest in the MFE program.

*For more information, contact R. M. Scanlan (415-422-7051).

†For more information, contact W. L. Barmore (415-422-7092).

We wish to determine the major effect of three variables—14-MeV neutron flux, stress, and temperature—on the creep-strain rate and to correlate these factors with creep mechanisms that have been developed to explain creep under lower-energy reactor-neutron irradiation. These results are being used in developing predictive models to explain creep under high-energy neutron irradiation.

During this reporting period, we ran an initial creep test at the RTNS-II on annealed polycrystalline niobium at 550 and 600°C and under stresses of nearly 120 MPa. In this very complex, fully-instrumented *in situ* creep experiment, we produced pronounced perturbations in creep behavior at 550°C by quickly cycling the 14-MeV neutron beam on and off the highly-stressed specimen. At a fluence of 6×10^{16} n/cm², deformation rates increased abruptly (by about 400%) when the beam was flashed on the specimen, and they decreased by the same amount when the beam was removed. These results were consistent with *in situ* creep results obtained at the Be (d,n) source at U.C. Davis.^{1,2} We found that, by precisely regulating target rotation and beam current, we could carry out creep studies at less than 10% of the typical RTNS-II flux, thus providing a wide range of flux variation during creep testing.

We ran a second RTNS-II creep test on niobium at 500 to 600°C under about 120 MPa axial stress. This test was interrupted at a fluence of about 2×10^{16} n/cm² when a strain-measuring transducer failed. This test will be restarted and continued, but preliminary results were compatible with creep results previously noted under 14-MeV neutron irradiation.

Niobium creep under 14-MeV neutron irradiation can be described by the dislocation climb-glide, rate-controlling mechanism.^{3,4} It is assumed that creep is a two-step series process in which 1) dislocations on crystallographic slip planes glide in individual grains and 2) edge dislocations climb around radiation-produced depleted zones (cascade regions) that act as barriers to slip. Either step may be rate controlling during irradiation.

Neutron irradiation produces many Frenkel defects in the displacement-damage regions of the crystallographic lattice. Because of their higher mobility, atoms displaced by neutrons into the interstices of the lattice apparently escape cascade regions in much greater numbers than vacancies, thus raising their concentration in the undamaged matrix volume. This affects the creep rate in opposing ways: the vacancy-rich depleted zones act as obstacles that impede dislocation motion on glide planes, whereas the excess interstitials interact with dislocations, causing the rate of dislocation climb at barriers to exceed that of the climb rate resulting from thermal creep. As the size and density of depleted zones increases with prolonged irradiation, the transient creep rate gradually decreases until a quasi-steady state creep rate is produced. A steady state creep region should result when the density of depleted zones has reached saturation level in the microstructure, and annealing at this juncture causes further damage to disappear as rapidly as it is produced.

Target fabrication for RTNS-II*

The RTNS-II at LLNL produces an intense neutron flux that is used to study neutron damage in fusion-reactor materials. The target assembly for the RTNS-II (Fig. 1) is coated with tritium-loaded titanium. When a deuteron beam is directed on the target, neutrons are produced by the reaction between deuterons and the tritium. Because this reaction causes intense local heating of the target, rotation and internal water-cooling are used to distribute and remove the heat. The targets used are 23 and 50 cm in diameter. They are rotated at about 5000 rpm, and the stresses on the large targets are greater than on the small targets.

The procedure used to make the targets has been described previously.¹ We encountered difficulties in making targets able to withstand experimental conditions, especially the 50-cm-diam targets. After bonding and forming, the 23- and 50-cm-diam targets are pressure-tested by hydraulically pressurizing the internal water channels to 3.5 and 17 MPa, respectively. Although most of the small targets survived the pressure test, most of the large targets failed.

During this reporting period, our primary objective was to optimize the bonding parameters for target production. Our secondary objective was to pursue other fabrication methods.

*For more information, contact W. D. Ludemann (415-422-7485).

Fig. 1. Target assembly for the RTNS-II. A deuteron beam is directed on the target (which is coated with tritium-loaded titanium), and reaction between deuterons and the tritium produces neutrons. Because this reaction causes intense local heating, the target is rotated at about 5000 rpm to distribute the heat and cooling water is circulated inside the target to remove the heat.

The bonding parameters under our control are 1) temperature, 2) pressure, 3) time at temperature and pressure, and 4) interfacial barriers and bonding aids. Higher temperatures accelerate interfacial contact by flow and diffusion and increase interdiffusion between the bonding and the copper substrate. Therefore, the temperature needs to be relatively high for good interfacial contact and yet low enough so that unequal diffusion rates do not leave a plane of voids near the bond.

Higher pressures accelerate interfacial contact by flow and close voids or prevent their formation. An adverse effect of excessively high pressure is collapse of the channels.

Longer times allow more flow and diffusion to take place. Time, however, is not easily varied during autoclave bonding; the sluggishness of heating and cooling precludes short bonding times while the economic desire to complete a bonding run in one shift precludes long bonding times.

The presence of interfacial barriers and bonding aids have varied effects. The following procedural changes were suggested:

- Reducing the thickness of the gold layer. The primary purpose of the gold interlayer is to prevent oxidation of the copper surfaces, which could be accomplished using a thinner gold layer. With less gold, less Au-Cu interdiffusion occurs, thus reducing the extent of void formation.

- Introducing a diffusion barrier. A diffusion barrier between the gold and copper reduces the amount of interdiffusion and hence void formation. One choice is nickel, which has been used successfully in other applications.

- Using a different bonding aid. Silver can be substituted for gold. In many cases, silver-silver bonds can be made at lower temperatures than can gold-gold bonds, especially in the absence of relative motion between the faying surfaces. The interdiffusion of silver and copper is less than that of gold and copper.

We are preparing 13-cm-diam test coupons to evaluate the effects of varying the bonding parameters discussed above. The test pieces have been machined and channels have been etched. Test coatings are being electroplated onto the faying surfaces, and crush tests are in progress.

We have also investigated making targets by electroforming, which is a very promising alternate to the autoclave bonding process used currently to make RTNS-II targets. Water-cooling channels are etched in a copper-alloy base plate and filled with wax. Silver powder is rubbed into the wax to make it electrically conductive, and copper is then electroplated over the face of the plate. The wax is melted and the channels flushed with a solvent. No more than 0.5 mm of electrodeposited copper is required to withstand hydrostatic proof testing. We have successfully cold-formed electroformed blanks into target shapes.

The electroformed rotating targets will require some redesign, mainly as a result of the marginal strength of the target substrate. A copper-base substrate is needed to provide good heat transfer, but because pure copper is not strong enough, alloys are used to provide the required strength. Choosing an alloy involves a trade-off between increased mechanical strength and lowered thermal conductivity. Amzirc and MZC are the two alloys now used for bonding targets. For 2.0-mm-thick bonded targets, they both are acceptably stiff so that target deflection during rotation is not too great.

Electroforming involves plating relatively soft copper onto an Amzirc or MZC substrate; less than 0.5 mm of plating is sufficient to contain the water pressure while the target is rotated. The 1.0-mm-thick baseplate is not stiff enough, however. To alleviate this shortcoming, we believe an electroplated nickel reinforcement or a graphite-fiber-reinforced composite should greatly reduce the stresses on the target. Another possibility would be using a stronger copper alloy for the base.

Laser fusion energy program

Chemical stripping of optical coatings*

Reworking a damaged or defective polarizer or an aspherical lens coating is both expensive and time consuming. A process that strips the coating from the substrate without requiring polishing would allow the coating vendor to correct bad coatings quickly and save the cost of repolishing.

During this reporting period, we completed our coating removal work.⁵ We used a solution of ammonium sulfate in concentrated sulfuric acid at 280–300°C to remove TiO_2 and SiO_2 coatings from BK-7 glass (a borosilicate-based glass). Because our procedure does not damage the polished substrate surface, no repolishing is required before recoating, thus saving both the time and expense otherwise required to rework a damaged or defective polarizer or aspheric lens. We stripped coatings from about 40 8-in.-diameter Shiva debris shields that had defective coatings, most of which were damaged by laser beams. Our results indicated that the laser damage on most of these parts extended beneath the coatings we can remove, which means that these parts require repolishing before recoating. However, coatings of undamaged parts can be removed very cleanly using our process.

When we examined the stripped debris shields, we observed that:

- No apparent TiO_2 coating residue is left on the surface.
- The remaining half-wave SiO_2 barrier layer usually appears to have many “pinholes” or a cloudy “Milky Way” appearance. The shields are usable despite this cosmetic defect, however.
- The solid matter implanted by the laser target is not removed when the TiO_2 layer is stripped away.

*For more information, contact T. M. Quick (415-422-8005).

- Laser damage is removed sometimes but not at other times. Further stripping to remove the SiO₂ layer still leaves laser damage on the surface at the coating-substrate interface.
- The acid process appears to enhance scratches and sleeks (very small scratches) on the substrate. This may result from the effects of heat as much as the acid. Surface defects also tend to be hidden by the polishing process and "fall out" during the cleaning-coating process.
- The process appears to work satisfactorily at 300°C. At lower temperatures, some residue is left on the surface.

Laser-glass polishing studies*

We studied polishing techniques and surface features to understand and improve the surface-damage threshold of bare polished surfaces. During this reporting period, we concentrated on polishing fused silica, which is being planned for use in the Nova lasers. However, to meet the Nova design requirements, the damage-threshold level of uncoated polished fused silica must exceed 20 J/cm². Recently, we successfully met these requirements; a pitch-polished fused silica surface (polished using our improved technique) attained a damage-threshold value of 26 J/cm². We are currently extending our polishing studies to BK-7 glass, which is more difficult to work with because the surface of this material is chemically active.

Table 1 summarizes our fused silica results. Our improved technique involves polishing an undamaged surface with a pure polishing compound (99.9+% CeO₂) and etching with ultrapure hydrofluoric acid. We started using purified CeO₂ as our polishing compound after we analyzed commonly used polishing compounds and found them highly contaminated with numerous elements.⁵ We added the ultrapure HF etching step to remove a portion of the surface layer that every polished surface appears to have. This surface layer is about 0.1 to 0.5 μm thick and has been both physically disturbed and chemically contaminated by the polishing process. Finally, we observe that a fused silica surface that has sustained previous laser damage, even if repolished, will not achieve the same high damage threshold value as a previously undamaged surface. Apparently, laser damage penetrates much more deeply into a fused silica surface than we have yet been able to detect. We hope further study will help us understand this damage phenomenon.

*For more information, contact T. M. Quick (415-422-8005).

Table 1. Damage-threshold values obtained for fused silica and BK-7 glasses prepared using the improved polishing technique.

Sample material	Polishing lap	Previous surface damage	Surface age (days)	Damage threshold value (J/cm ²)
Fused silica	Pitch	No	*	26 ^b
Fused silica	Nylon	No	*	20-25
Fused silica	Pitch	Yes	*	16-18
Fused silica	Nylon	Yes	*	14-17
BK-7	Nylon	No	60	39 ^b
BK-7	Nylon	No	1	28 ^b
BK-7	Pitch	No	30	17 ^b

*Not applicable.

^bOne experiment.

We are extending our polishing studies to BK-7 glass so that we can continue to improve our polishing technique. Preliminary BK-7 results are shown in Table 1. Our objective is to better understand the effect of polishing on surface-damage-threshold values and, as a result, improve the damage-threshold values of the optical materials being developed for the Laser Program.

Aluminum-air battery and vehicle research*

The aluminum-air battery is an advanced power source that combines high energy and high power-to-weight ratios with the capability of being rapidly recharged by adding two reactants: tap water and aluminum plates. These characteristics have made the aluminum-air battery a potential power source for a general-purpose electric vehicle having the range, acceleration, and refuelability of today's automobile. The technical success of this program would offer the nation the option of commercializing an electric vehicle that has the utility of the automobile and a cost and energy consumption comparable to advanced automobiles using synthetic liquid fuels derived from coal.⁶

An aluminum-air battery has two major components: a galvanic-cell stack and a crystallizer. A number of small auxiliary units—pumps, motors, condensers—are also required for battery operation. In the galvanic-cell stack, aluminum plates, water, and atmospheric oxygen are consumed to produce electrical energy and a dissolved reaction product, an aluminate complex. The crystallizer decomposes this aluminate complex to form a granular product, hydrargillite. This material, which is an intermediate feedstock of the aluminum industry, is periodically withdrawn from the battery for recycling into new plates at centralized industrial sites. Thus, there is no net consumption of aluminum, and a fixed quantity provides a reusable energy link between vehicles and sites of electric power generation.

The vehicle is being designed for plate additions at intervals of 1600-4800 km of travel; the vehicle range is determined by the frequency of water additions (400-600 km). When water is added, accumulated hydrargillite is withdrawn. By allowing long intervals between plate additions, the flexibility of refueling schedules will permit the vehicle to be used before the fledgling fuels-distribution network has become widely established. Once the network is in place, the frequency of plate additions can be optimized for maximum economy.

The overall chemical reaction of the battery is

The chemical basis of the crystallizer,⁷ the electrochemical behavior of the cell,⁸ and the engineering design of the battery⁹ have recently been reported. The design and analysis of the vehicle¹⁰ and a comprehensive study of the cost and energy balance of the transportation system¹¹ have also been published.

During this reporting period, we made significant advances in four areas: 1) development of cost-effective alloys for use in the vehicle, 2) successful scale-up of the aluminum-air cell to the 0.1-m²-anode size, and 3) integration of the crystallizer and galvanic-cell systems into a compatible unit.

Development of cost-effective alloys for use in electric vehicles

The "baseline" alloy used in the development and testing of cell hardware is Reynolds Alloy (RX808). This alloy is produced by adding gallium and magnesium to very pure aluminum (99.99+%).

*For more information, contact J. F. Cooper (415-422-7168).

Economic competitiveness requires that the vehicle fuel-plate alloy be produced directly from the single-step reduction of alumina using conventional Hall processes. The aluminum produced by this refining method does contain impurities, and these impurities increase the parasitic corrosion rate of the metal through the reduction of water on the anode surface. Iron present as an impurity is known to have this effect.

We found that the corrosion rates (current densities) of various alloys containing 400 ppm iron (a level consistent with the Hall process) and alloys produced from high purity stock when gallium was added differed insignificantly (Fig. 2). We learned that the heat treatment of the material and its effect on the segregation of impurities within the grain structure were more significant than the levels of iron impurities (50–400 ppm).

Fig. 2. Dependence of parasitic corrosion-current density on iron concentration in alloy. The current was measured at electrode potentials of -1.5 V vs Hg/HgO. The data points for a given iron concentration refer to samples prepared using different heat treatments and cold-working procedures. Alloys containing 300 ppm iron can be produced directly in a Hall cell without further refining.

Testing of 0.1-m² aluminum–air cells

We improved the air distribution on the air-cathode by using a porous carbon diffuser, and we decreased the resistance of the current collector by spot-welding the air-electrode screen to a metallic current collector. As a result of these improvements, the cell was discharged at current densities above 5.5 kA/m².

Below 2 kA/m^2 , cell voltage exceeded that obtained with the same pair of electrodes on the 25-cm^2 scale. Approximately 90% of the peak power density obtained with the 25-cm^2 cells was reached in the large cells. The anode polarization curve was found to be essentially independent of scale for these two sizes. Thus, we concluded that the anode electrochemical behavior was amenable to scaleup.

Use of a hydrargillite crystallizer to control electrolyte composition

During this research period, we used a hydrargillite crystallizer to stabilize the composition of the electrolyte flowing through a discharging 0.1-m^2 aluminum-air cell. Electrolyte of 9 l (total volume) was circulated through a cell discharging at a constant current of 180 A. A portion of this electrolyte was diverted through a fluidized bed (flow rate, $2.5 \text{ cm}^2/\text{s}$) containing $\text{Al}(\text{OH})_3$ seed granules (0.72 kg). By measuring the aluminate concentration in the cell and crystallizer, we determined that the rate of aluminum dissolution in the cell equaled the rate of $\text{Al}(\text{OH})_3$ precipitation in the crystallizer as the $\text{Al}(\text{OH})_3$ concentration in the cell reached a steady state (Fig. 3).

Fig. 3. Stabilization of aluminate concentration by use of a crystallizer. The 0.1-m^2 anode aluminum-air cell was discharged at 300 A into a small volume of electrolyte (9 l) for 95 min. The rise in aluminate concentration (at 100 min) stopped when the electrolyte was exchanged between the crystallizer and the cell. When dissolution of aluminum from the anode cleared (at 240 min), the electrolyte composition returned to equilibrium levels.

Using the crystallizer to stabilize the concentration of aluminate in the electrolyte of a 0.1-m² aluminum-air cell constitutes the major milestone of the last year. This milestone establishes the inherent compatibility of the processes taking place within a crystallizer and galvanic cell operating on a significant scale (0.1-m² anodes) and within the range of operating conditions anticipated for vehicular applications.

Geothermal research*

Corrosion of materials for well casings

The Geothermal Research program at LLNL is aimed at harnessing the total flow of the hot, hypersaline brines available from the Salton Sea field in southern California. A central problem encountered in tapping this enormous geothermal energy resource is that the brine causes scaling and corrosion of turbines, piping, and other equipment. To help minimize this problem, we are studying general corrosion, erosion-assisted corrosion, and stress corrosion of these materials. Currently, our principal concern is assessing the corrosion resistance of materials in the high-temperature leg of a double-stage flashed-steam electricity-generating system. The material of interest in the high-temperature leg is the production-well casing.

We recently completed a study of the corrosion performance of well-casing materials. We simultaneously exposed 20 different grades of steel to geothermal well fluid to compare the performance of low- to intermediate-alloy steels with carbon steel. We compared samples of American Petroleum Institute (API) grades of steel, which are used satisfactorily in the less-corrosive environments of oil wells and thus meet only mechanical specifications, to AISI and ASTM alloy steels, which meet strict composition specifications. We also heat treated short lengths of API J-55 and N-80 samples to simulate the different microstructure that might result during fabrication of these steels into tubular products. The heat treatments included austenization followed by air cooling, austenization followed by furnace cooling, spheroidization, and oil quench plus tempering.

A 550-m-long string of 1-1/4-in.-diam pipe samples was prepared. The string consisted of 74 sections, each 6 to 9 m long, arranged so that each of the 20 steel specimens was exposed at different zones of depth in the well. During well operation, the point of flashing varies with the flow rate and moves downward when the brine flow is shut off. (The temperature increases with depth.) Thus, the environment to which the steel specimens were exposed changed with depth and time. During periods of nonoperation, some stratification of chemical species occurs in the stagnant brine; as a result, we believe that the fluid becomes more corrosive at greater depths.

The sections of tubing were joined with J-55 couplings, which introduced a possible galvanic effect between the dissimilar tubes and couplings. However, because of the number of different steels tested, galvanic effects were inevitable regardless of the coupling material, and other materials were unavailable within a reasonable delivery time. Since the J-55 coupling was expected to be sacrificial, the important question became whether the coupling cathodically protected the test material.

The pipe string was emplaced in Magmamax I well for five months, during which period the well flowed about two-thirds of the time. Before the pipe string was withdrawn, a section of J-55 corroded through and about 150 m of the string fell to the bottom of the well; we recovered about 115 m of this section 2-1/2 months later.

Analysis of the corrosion performance of the string is underway. During the last reporting period, we visually inspected each section for perforations and deep penetrations. Generally, corroded areas were easily detected because the voluminous corrosion products had ruptured the lead sulfide scale. These ruptures formed tubercles that apparently continued to grow. The corrosion was nearly always localized. Large areas

*For more information, contact R. D. McCright (415-422-7051).

of surface were covered with scale but intact and free from significant corrosion. Even on the steels that suffered the most severe corrosion attack, most of the surface area remained intact, but where corrosion had begun, attack was extensive.

We have ranked the materials into three performance categories (Table 2). The first list is of the sections recovered in the initial retrieval operation in February 1980; 380 m of tubing exposed for six months were recovered in this operation. The second list comprises the coupling sections also retrieved at this time. The third list contains the sections exposed for eight months and recovered during the second retrieval operation in April 1980. One reason for ranking the materials in three separate lists was that the sections removed after six months of exposure were generally more corroded than those removed after eight months of exposure—despite the shorter exposure time. The sections exposed for six months were subjected to conditions of brine alternating with steam and brine, depending on the position of the flash point in the well. In contrast, the lower sections that fell to the bottom of the well were presumably immersed in liquid during most of their

Table 2. Rankings of materials exposed to Magmamax I well fluid.

Six-month exposure ^a	Eight-month exposure ^b	Pup-joint materials ^c	Category description
ASTM A 335-P9 ASTM A 335-P7 ASTM A 335-P11	ASTM A 335-P1 ASTM A 335-P2	None	Best performance. Showed no perforations, no appreciable penetration anywhere in the string.
ASTM A 335-P22 ASTM A 335-P2 ASTM A 335-P11	ASTM A 519-1018	J-55 Q and T N-80 AC N-80 FC N-80 Sph N-80 Q and T	Some corrosion pustules present that could rupture scales, which indicated some corrosion penetration in the tube wall. The penetration is believed shallow.
ASTM A 106 B	None	J-55 FC	Patches of considerable corrosion with evidently significant penetration in the tube wall.
ASTM A 335-P5 API N-80	API N-80	J-55 AC ^d J-55 Sph	Considerable corrosion, evident penetration, and one to five perforated areas in a 6-m section.
ASTM A 335-P1 API J-55 API C-75	ASTM A 106 B API C-75 API J-55 ^e	None	Worst performance. Considerable corrosion, evident penetration, and more than five perforated areas in a 6-m section.

^aMaterials exposed six months in upper and middle zones of well (surface to 400 m).

^bMaterials exposed eight months in lower zone of well (below 400 m). At some time during the exposure period, these sections fell to the bottom of the well. Not all sections were recovered so the listing here is not complete.

^cSpecially heat-treated pieces of J-55 and N-80. Q and T = quenched and tempered; AC = air cooled; FC = furnace cooled; Sph = spherodized.

^dPerforations were observed.

^ePerformance was judged from the appearance of the collars and recovered pup joints.

exposure. The changing environment appeared to be the more aggressive condition. Scale layers were thickest in the "middle zone" of the string (roughly 180 to 400 m), but this thick scale showed poor adherence and evidently provided little protection against corrosion. We ranked the coupling joint materials separately because they were included in the "string" to compare different heat treatments on corrosion performance.

Our rankings of materials in Table 2 were based on the samples that suffered the worst corrosion. We did this because even the most corroded samples contained large areas that were either intact or just lightly corroded. We thus concluded that the downwell corrosion of steels is localized in nature. This localized corrosion behavior suggests that the basis of attack lies in either inhomogeneities in the metal or in the environment (which includes the scale layer).

Inhomogeneities in the metal include compositional and microstructural variations from point to point. The presence and distribution of inclusions are probably important factors, since galvanic differences between the inclusions (e.g., MnS) and the matrix produce local currents. The traditional view on initiation of steel corrosion in acidic environments is that the carbide phase (cementite) behaves as a local cathode and the ferrite phase acts as a local anode. When sulfide inclusions are present in the steel, H_2S can sometimes be detected during the corrosion process. Formation of H_2S could be part of the anodic reaction (dissolution of the sulfide by acids generated by hydrolysis of the corrosion products). When inclusions are present as bands or stringers, an easy dissolution path exists in the metal to initiate localized attack. In geothermal environments, propagation of localized attack is favored because scale formation and precipitation of insoluble corrosion products create crevice-like conditions on the surface. The semiconducting properties of PbS and the electronic conducting properties of Fe_3O_4 mean that local anodes and cathodes can operate at considerable distances from one another.

The microstructure and interstitial composition of the steel are therefore important factors in their corrosion resistance in geothermal environments. All other considerations being the same, a "cleaner" steel should perform better than one containing many sulfide inclusions. Melting and fabrication processes can also affect corrosion performance in that they affect the distribution of inclusions.

The rankings of materials in Table 2 indicate that adding molybdenum and chromium as alloying elements usually increases the corrosion resistance. Even API N-80 and C-75 steels contain small amounts of chromium and molybdenum (to increase the hardenability), and we found that these steels suffered less attack than J-55. In chloride environments, molybdenum reduces pitting and crevice corrosion in both austenitic and ferritic stainless steels. Molybdenum may also be effective in alloy steels containing less than 12% chromium, although the mechanism by which molybdenum protects steel is not well characterized. As molybdenum itself has a high activation energy for dissolution (i.e., low exchange-current density), it may impart this property to the steel. Still, we were surprised that the presence of 0.5 to 1 wt% molybdenum had such a large beneficial effect. Higher chromium concentrations were probably also beneficial in corrosion protection of alloy steels, since chromium would be expected to favor oxide formation on the steel and promote some degree of passivation.

Inhomogeneity in the environment is a further point in the discussion of the mechanism for initiation of localized corrosion. Elemental sulfur, like oxygen, can initiate corrosion at sites where the sequestered solution does not mix freely with the bulk solution (e.g., crevices under scale deposits). Geothermal brines contain mixtures of sulfides and sulfates, and, presumably, free sulfur is also present. As in oxygen-cell corrosion, surfaces shielded from the bulk environment develop a local environment that is deficient in sulfur, higher in chloride ion, and lower in pH. Metal dissolution (anodic reaction) is favored in these shielded locations, whereas the cathodic reaction (reduction of S to S^{2-}) is favored elsewhere. In the cathodic regions, the metal surface is protected. A sulfur differential-concentration cell does not provide a complete explanation for the downwell corrosion mechanism because such a mechanism suggests that all materials corrode at the same rate, since the corrosion rate is controlled by the rate at which sulfur diffuses to the surface.

Metallurgical factors obviously have an important influence on the corrosion rate, and the corrosion initiation mechanism in geothermal brines probably involves metallurgical as well as environmental factors. Environmental factors apparently create crevice conditions under a rather porous and, in places, poorly adhering scale, and the more highly alloyed materials better resist corrosion in the locally acidic regions under the scale. We found that corrosion is usually most severe in the middle zone (180–400 m) where the scale layer

is thickest (1.0–1.3 mm) and less uniform than other locations. We think that flashing of brine to steam occurs in this zone. The scale-formation rate increases in the flash zone because CO_2 released from the brine causes local alkalization, which favors precipitation of PbS . Further, heat lost to vaporization may decrease the local temperature and increase the rate of scale precipitation. Nonuniform thicknesses of the scale layer and poor adherence may result from movement of the flash zone up and down the well so that the scale layer forms discontinuously. Scale layers thus formed seem to offer little corrosion protection.

The effect of coupling different steel alloys together using couplers made of API J-55 is another factor affecting our results. Our initial inspection of the exposed "string" sections and collars indicated that some galvanic corrosion did occur. We were primarily concerned, however, that the collars may have cathodically protected adjoining sections, thereby reducing the corrosion damage from what would have occurred without collars. The corrosion potential between the different materials tested, however, is not great—the maximum measured difference was 50 mV between carbon steel and a Fe:9-wt%-Cr;1-wt%-Mo alloy steel. Thus, the driving force appears inadequate to sustain significant cathodic protection. A further argument against cathodic protection of the alloy steels is that, had a significant degree of cathodic protection occurred, the collars should be completely consumed. This was not observed.

Though we cannot prove whether or not cathodic protection was significant by the above arguments, the region nearest the anode was expected to be the most protected, and the fact that the alloy steels corroded near the collars suggests that cathodic protection was not operating.

Our 6-month experiment showed that in hypersaline geothermal brines such as those found in the Salton Sea KGRA, API casing and tubing steels exposed to production-well conditions perforate in less than six months. Improved performance can be obtained using ASTM grades of carbon steel and particularly using grades containing at least 0.75 wt% chromium and 1 wt% molybdenum. The performance improvement may be attributable to both the addition of more corrosion-resistant alloying elements and to control of impurities (such as sulfide inclusions) that act as sites to initiate localized corrosion.

We plan to investigate the microstructure of exposed sections and compare them with historical samples taken from unexposed sections and from unexposed stock. We feel it is important to study the scale/corrosion product interaction to explain localized corrosion initiation. By examining selected metallographic sections, we hope to quantitatively assess the corrosion penetration as functions of well depth and alloy content.

Nuclear waste management*

Synroc development

The Mineral Waste-Form program is evaluating and working to improve "Synroc" mineral ceramics,¹² which are proposed as suitable host materials for the long-term storage of nuclear wastes from U. S. defense programs. The Synroc process immobilizes high-level radioactive wastes as dilute solid solutions in the constituent minerals of a synthetic rock made from mixtures of oxides, principally TiO_2 , BaO , ZrO_2 , Al_2O_3 , and CaO .

The program includes the following areas of investigation:

- Study of powder-coprecipitation techniques used to synthesize Synroc systems containing specific radionuclides.
- Phase-equilibrium studies to determine the most thermodynamically stable and leach-resistant mineral-ceramic waste form for the diverse compositions of defense wastes.
- Processing studies to optimize high-temperature fabrication methods for producing phase-equilibrated, high-strength, high-density products suitable for long-term storage.
- Aqueous-leaching studies to determine the behavior of various host minerals and to compare these behaviors with those of other potential waste forms, such as glass.

*For more information, contact C. L. Hoenig (415-422-8004).

We have previously described^{13,14} the preliminary hot-pressing conditions used for Synroc B, Synroc C, and hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$). Synroc B is the basic synthetic-mineral composition without radioactive material; Synroc C is Synroc B combined with 10 wt% simulated commercial nuclear waste.¹⁵

The Synroc C compositions we previously studied contained only seven elements added in order to simulate commercial-waste (U, Cs, Sr, Gd, Ce, Y and Lu). During this reporting period, we studied PW-4B-7, a more complete and complex simulation of true commercial waste (Table 3). Table 4 lists the Synroc composition we adopted to study PW-4B-7 waste.¹⁴

This simulated waste, prepared by Battelle Pacific Northwest Laboratories, was supplied in two forms: a calcined oxide powder and a liquid nitrate solution. We limited the simulated waste to 10% of the Synroc composition to insure dilute solid solution of the waste elements in the basic Synroc mineral phases.

Table 3. Composition of simulated commercial nuclear waste PW-4B-7.^a

Oxide	wt%
Nonradioactive components	
Cr_2O_3	0.85
Fe_2O_3	3.72
NiO	0.34
CdO	0.24
P_2O_5	1.65
Rb_2O	0.87
Y_2O_3	1.47
La_2O_3	3.64
Pr_6O_{11}	3.64
Nd_2O_3	11.50
Pm_2O_3	0.31
Sm_2O_3	2.27
MoO_3	15.70
Ru_2O_3	7.31
Rh_2O_3	1.22
PdO	3.64
Ag_2O	0.22
TeO_2	1.77
BaO	3.85
ZrO_2	12.17
Radioactive components	
Cs_2O	7.08
SrO	2.61
CeO_2	8.18
Gd_2O_3	0.33
UO_2	4.94
	100.00

^aRare earth oxides make up 30.36% of the PW-4B-7 waste. For information concerning PW-4B-7, contact J. M. Rusin, Battelle Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352.

Table 4. Synroc C composition.

Basic three-phase Synroc ^a		Synroc C	
Constituent	Oxide (wt%)	Constituent	Waste form (wt%)
TiO ₂	59.2	Basic Synroc	80.0
CaO	15.9	PW-4B-7	10.0
ZrO ₂	11.4	Ni powder	3.0
BaO	7.2	TiO ₂	4.0
Al ₂ O ₃	6.0	Al ₂ O ₃	3.0
	100.0		100.0

^a Approximately 40% hollandite, 35% zirconolite, and 25% perovskite.

One major concern of ours is the behavior of the molybdenum present in commercial waste. If molybdate (MoO₃) is not fully reduced to metal, cesium molybdates can form that have poor leach resistance. Because of this problem, redox control is very important during calcination and hot pressing to insure molybdate reduction. To meet this goal, we performed final calcination in dry hydrogen at 800 to 900°C, and we added a small amount of nickel powder to the calcined powder before it was hot pressed.

The Synroc starting materials were TiO₂ (as anatase), ZrO₂, Al(OH)₃, and barium and calcium carbonates. The addition of acidic liquid PW-4B-7 decomposed the carbonates and yielded a slurry for wet ball milling and mixing. After milling, the slurry was spray dried to insure maximum homogeneity before calcination.

X-ray diffraction of calcined powders showed formation only of perovskite and zirconolite at 800°C but indicated formation of complete three-phase mineral (hollandite, perovskite, and zirconolite) at 900°C. Chemical analyses of powders calcined at 900°C showed no loss of cesium by volatilization.

These samples were hot pressed at 1100 and 1200°C in both graphite and nickel capsules to densities exceeding 97% theoretical. X-ray analyses of hot pressed samples indicated good mineral formation of all Synroc phases. We made metallographic and electron microprobe analyses only on samples hot pressed at 1200°C because the grains on 1100°C samples were too small (< 1 μm) for individual phase analysis.

Our results showed that, within the limits of detectability, all of the molybdate was reduced to molybdenum, which alloyed with the nickel powder in the matrix. We consider this to be an ideal situation for immobilizing molybdenum in Synroc C. We also measured the relative concentrations of radwaste elements in the respective Synroc phases (Table 5). The cesium partitioned predominantly into hollandite (as expected)

Table 5. Electron microprobe analysis of relative partitioning of radioactive-waste elements in Synroc C.^a

Oxide	Hollandite		Zirconolite		Perovskite	
	Graphite	Nickel	Graphite	Nickel	Graphite	Nickel
SrO	b	0.1	b	b	b	b
Cs ₂ O	2.0	0.9	0.3	0.5	0.6	0.4
Ce ₂ O ₃	c	0.9	b	b	1.9	2.5
Nd ₂ O ₃	c	b	0.4	0.2	1.6	1.9
Gd ₂ O ₃	b	b	0.1	c	0.5	4.5
UO ₂	0.1	b	0.4	0.6	0.8	0.8

^a Hot pressed in graphite and nickel capsules at 1200°C.

^b Below detectable limits.

^c Not analyzed.

when both the graphite and nickel capsules were used. However, some cesium was found in both zirconolite and perovskite, and distribution into these phases was apparently enhanced by using a nickel capsule during hot pressing. The rare earth oxides partitioned into both the zirconolite and perovskite phases with perovskite acting as the dominant host. Urania (UO_2) partitioned into both zirconolite and perovskite in nearly equal concentrations. Neither UO_2 nor rare earths were noticeably affected by the use of graphite or nickel capsules.

Office of Basic Energy Sciences (OBES) research

Hot corrosion project*

Quantitative models of hot corrosion

The hot corrosion project is developing and extending current quantitative models of hot corrosion, which is defined as high-temperature attack of metals exposed to a multi-oxidant system. Hot corrosion is usually associated with sulfidation and molten-salt attack, and it is observed in gas turbines and coal-conversion systems. To develop a detailed theoretical model of the attack, we are studying pure metals and binary alloys in simple controlled environments. We have used two major experimental techniques to date: thermogravimetric analysis (TGA) and electrochemical polarization in molten salts. To aid in the development of quantitative hot corrosion models, we are also determining the thermodynamic properties of chromium sulfide phases that are important in the corrosion process.

During this reporting period, we continued preparing Ni-Cr alloy specimens to be used for TGA and electrochemical polarization in molten sodium sulfate. We finished preparing most of the samples (including sectioning and lapping for several compositions), and the remaining compositions should be completed shortly. We also plotted the results for the constant-potential polarization runs in oxygenated sodium sulfate and compared our results with results previously obtained for polarization runs that were deoxygenated using an argon purge.¹⁶

Sample Preparation

We improved our alloy casting procedure,¹⁴ in which the alloys were arc-melted in a crucible, to produce homogeneous castings largely free of pores. Two changes accounted for most of the improvement. First, we added a small radiation furnace to preheat the mold before casting (Fig. 4). By using proper insulation, we were able to preheat the copper mold to temperatures over 500°C. Because the hot mold slows solidification of the melt, gases dissolved in the melt are able to diffuse out. Second, we decreased the argon pressure in the chamber to about 30 kPa (0.3 atm). This vacuum is sufficient to maintain a stable arc but reduces the tendency of the melt to trap argon during agitation in the crucible. Although the arc-melting time probably has little effect on pore formation, we limit the arc time to 90 s to obtain consistent castings from sample to sample.

We also improved our thermomechanical processing and can produce specimens containing very large grains, thus lessening the effect of grain boundaries, which artificially accelerate oxidation. First, we machined the specimens to a smaller diameter before cold working them to the desired size by swaging. Because cold working introduces nucleation sites, decreasing the extent of cold working produces fewer sites, thus allowing recrystallized grains to grow larger during the heat treatment. (We decreased the percentage of area reduction from 13% to less than 5%.) Second, we increased our heat-treating temperature from about 1200°C to 1300°C, which is only about 45°C below the eutectic temperature for the Ni-Cr system and represents the maximum maintainable temperature in that furnace. We also increased the heat-treating time from

*For more information, contact J. J. Truhan (415-422-6925).

Fig. 4. Small radiant heater, located in the arc-furnace chamber, is used to preheat the copper-casting mold. This system can achieve a mold temperature greater than 500°C. The crucible in which the alloy sample is arc-melted is not shown.

1 h to 24 h. This thermomechanical cycle produces from two to three grains in the 11-mm-diameter rod. Samples of two compositions have been cut from the heat-treated rods, lapped, and await attachment of platinum leads by electron beam welding.

Constant-potential polarization

We also studied hot corrosion during molten salt attack of Cr-Ni alloys using constant-potential polarization. We found that obtaining reliable scale-thickness measurements for specimens polarized in oxygenated sodium sulfate was more difficult than when the sodium sulfate was deoxygenated during the experiment by an argon purge. This unreliability may result from faster NiO formation (caused by the increased

oxygen activity of the melt), which in turn forms a less-stable NiO scale that is subject to spalling. Figure 5 shows that after passivation, the oxidation rate in the oxygenated molten salt increases in comparison to the deoxygenated case as the scan proceeds in the noble direction. This enhanced oxidation rate corresponds to the increase in oxygen activity in the melt. Figure 6, which shows the scale growth as a function of time, supports this argument. At rest potential, the scale growth, although initially slower than that observed in the deoxygenated condition, proceeds at a more rapid rate after about 90 min. Although no external potential is applied in this case, localized cell formation could easily polarize areas into the transpassive region and enhance the oxidation rate if the specimen is left in the melt long enough. Spalling of the NiO scale after a critical thickness is reached could further increase the number of local cells on the surface.

Although the potentiokinetic polarization scan and potentiostatic polarization apparently agreed well for arbitrary lengths of time, the lack of reproducibility of a scale-thickness measurement led us to conclude that potentiostatic polarization is a tool useful only in determining scale chemistry and morphology; kinetic information cannot be obtained reliably by measuring a mechanically unstable scale *ex situ*.

Fig. 5. The potentiokinetic polarization of nickel in molten sodium sulfate at 900°C shows a higher rate of attack for the oxygenated salt because of faster nickel oxide formation.

Fig. 6. The nickel oxide scale growth on nickel in molten sodium sulfate is enhanced after about 90 min for the oxygenated salt. This result is analogous to the potentiokinetic polarization behavior shown in Fig. 5.

In further work with the Ni-Cr system, we plan to correlate the active-passive behavior in anodic polarization with specimen composition and compare these results in turn with sodium sulfate-coated specimens in flowing gas systems (by TGA). We will make potentiostatic runs to determine the scale composition and morphology and again compare these results to scale formation in a TGA experiment.

Thermodynamics of sulfides in hot corrosion

The corrosion of metals and metal alloys by sulfidation produces undesirable effects in many of the high-temperature processes involved in energy conversion. High-chromium-iron and high-chromium-nickel alloys promise the best resistance to sulfidation, although relatively little thermodynamic information is available to develop these alloys. To provide protection from sulfur attack, we need to understand the sulfidation process and, in particular, the role played by chromium. We especially need data on the thermodynamics of chromium sulfide formation in order to calculate the driving force for diffusional transport, to develop equilibrium diagrams, and to understand the reaction mechanisms.

Our goals are to determine the equilibrium sulfide phases in Fe-Ni-Cr-Al-S systems, measure the thermodynamic properties of key phases, and calculate the phase behavior as a function of gas and alloy compositions.

During this reporting period, we prepared enough Cr_2S_3 for measuring its enthalpy (using a drop calorimeter) and for producing the lower sulfides— Cr_3S_4 , Cr_5S_6 , Cr_7S_8 , and CrS —whose enthalpies we will also measure. We have prepared small quantities of all these lower sulfides except CrS , which is currently being produced. X-ray diffraction analyses have indicated that our preparations are single-phase compounds.

Thermochemical cycles for hydrogen production*

We are investigating thermochemical cycles to produce hydrogen from water. In these cycles, the only inputs are water and heat, and the products are separate streams of hydrogen and oxygen; all other chemical reagents are recycled within the system. Hydrogen generated by these cycles is a renewable resource not dependent on fossil fuels, and this process could use heat from such energy sources as high-temperature gas-cooled fission reactors, magnetic-fusion reactors, or solar concentrators. We are directing our current effort toward developing a family of cycles that utilizes the decomposition of ZnSO_4 as the high-temperature step and toward a hybrid LiH cycle. Our objective is to develop a basic understanding of the thermochemistry, kinetics, and mechanisms of several complex reactions in the cycle.

Through the use of the ZnSO_4 -subcycle, many of the problems associated with H_2SO_4 -based thermochemical cycles¹⁷ can be avoided (e.g., special materials for heat exchangers used to concentrate and evaporate H_2SO_4 solutions and to decompose SO_3 vapor can be eliminated). This subcycle replaces the high-temperature oxygen-producing steps in the H_2SO_4 -based cycles according to the following reactions:

The hydrogen-producing step is not described here but can be represented by several existing thermochemical cycles that use SO_2 as a reducing agent to produce H_2SO_4 in addition to hydrogen. We are currently studying Reaction 4.

The second cycle we have examined is a hybrid LiH cycle that combines electrochemical and thermochemical steps. The reactions in this cycle are:

We are developing an electrolyte-membrane system for Reactions 5 through 7.

*For more information, contact O. Krikorian (415-422-8076).

Decomposition of zinc sulfate

Zinc sulfate is decomposed in the ZnSO_4 subcycle to liberate oxygen and to regenerate SO_2 as a reducing agent. This is the most endothermic step in the cycle and requires temperatures of about 1200 K. Even at these high temperatures, the reaction is hindered kinetically and produces SO_3 rather than the thermodynamically favored SO_2 - O_2 gas mixture. These characteristics indicate that the decomposition reaction is complex and that it will require effort to optimize decomposition.

Our work during this reporting period was directed toward developing a technique to study the kinetic behavior of ZnSO_4 decomposition. Our previous method using tungsten-image lamps as a heat source met with several difficulties such as inaccurate temperature measurement and undefined temperature profiles during sample exposure.¹⁸ This method did, however, allow us to demonstrate that rapid heating of ZnSO_4 particles through their α -to- β phase transition at 1015 K accelerates the decomposition rate because of particle fracturing. We also saw evidence that ZnO catalyzes the decomposition.

We also tried a second technique for decomposing ZnSO_4 using a resistance furnace equipped with a quartz reaction chamber.¹³ The approach met with difficulties in measuring the gas evolution rate, probably as a result of SO_3 reacting with the system walls. We are currently trying to identify the source of the problem so we can correct it. We are also evaluating the advantages of switching to a transpiration experiment, which would allow us to obtain data on a dynamic rather than static system.

LiH hybrid cycle

Previous experiments by Behr *et al.* on the LiH hybrid cycle¹⁹ were based on an electrolytic cell using a fused NaOH-based electrolyte operating at 600 to 700 K. Atomic hydrogen forms at the cathode membrane, diffuses through the membrane, and reacts with molten lithium on the other side to form lithium hydride, which remains in solution. The hydrogen can be recovered at higher temperatures using conditions under which the lithium is not significantly volatile. The most serious problem in this cycle is electrolyte attack of the metal membrane separating the electrolyte from the molten lithium. We believe that a nearly neutral or even acidic electrolyte would be more compatible with cathode-membrane materials.

During the previous reporting period, we approached the electrolyte-membrane problem by testing the behavior of metaboric acid at temperatures between 520 and 670 K. Unfortunately, the viscous and glassy qualities of this material make it an unacceptable electrolyte. During the present reporting period, we evaluated several other molten salts, including potassium thiocyanate, citric acid, phosphoric acid, and several partially neutralized phosphoric acid salts. The most promising of these materials was potassium trihydrogen pyrophosphate (PTP), which has the approximate formula $\text{KH}_3\text{P}_2\text{O}_7$. This material melts at about 400 K and is stable to at least 620 K. It has good electrical conductivity and is receptive to the addition of steam for hydrolysis. We also attempted to prepare phosphate salts less acidic than PTP, but we could not obtain stable melts of these salts.

After identifying an acceptable molten salt to serve as an electrolyte, we still needed to identify compatible membrane materials. Although phosphoric acid is extremely corrosive at these temperatures, we suspected that PTP would be much less reactive. We ran short-term corrosion studies using strips of niobium, tantalum, vanadium, titanium, and platinum in both unpolarized and cathodically polarized states to establish which materials could resist PTP. Titanium and vanadium were severely corroded, but both niobium and tantalum exhibited considerable resistance to the PTP, especially when cathodically polarized. Although tantalum is embrittled by the hydrogen formed during hydrolysis, we believe that, when tantalum is used with the lithium depolarizer, the lithium will scavenge enough hydrogen to reduce embrittlement significantly.

We set up an electrolysis test cell using a niobium membrane, a platinum anode, and PTP in a quartz vessel.¹⁴ Polarization curves indicated that 2.9 to 3.0 V were needed for a current density of 300 mA/cm² without the lithium depolarizer. Behr's¹⁹ original work on the LiH cell using a molten sodium hydroxide electrolyte with a silver-coated titanium membrane required only 1.3 V for a similar current density without lithium. The difference in polarization behavior can be explained in large part by the higher resistivity and

thickness of the electrolyte layer for PTP than for NaOH. Additional factors for the energy difference include Behr's higher reaction temperatures (670 vs 520 K) and different cell dimensions and configurations.

We have not yet made any measurements using lithium as a depolarizer.

Optical materials with reduced nonlinear effects*

The development of high-power lasers, principally for fusion research, places increasingly stringent requirements on the properties of transparent optical materials. The electrical fields associated with such laser beams are so intense that higher-order, nonlinear terms in the polarizability of the material become important. This program studies the effects of these nonlinear terms and searches for ways to circumvent or surmount the problems they cause.

One of the effects of interest is self-focusing by nonlinear contributions to the refractive index of a glass. Because the predicted nonlinear index coefficients of fluoride glasses are small, these glasses are the most promising candidates for both passive components (such as lenses and windows) and active components (such as the laser-amplifier and Faraday-rotation media) in high-power laser systems. Our part in this effort is preparation and characterization of beryllium-based glasses and crystals.

Crystallization of BeF₂ glass

During this reporting period, we heated a rectangular sample of pure BeF₂ glass under a nitrogen atmosphere at 500°C for 500 h to crystallize it in the β -BeF₂ temperature region. We then lowered the sample temperature very slowly through the β -to- α BeF₂ transition. This gave large grains (1 to 2 mm in diam) of BeF₂ that were isomorphous with α quartz. Each grain appeared to be a single crystal. (We made no attempt to determine if dauphine twinning, which occurs in quartz when heat-treated in this way, had taken place.) During crystallization, the sample retained its original size and shape but developed large internal voids that decreased the density of the sample by an estimated 20%. This result is consistent with the density difference between α -BeF₂ (2.304 g/cm³, measured by x-ray diffraction) and BeF₂ glass (1.987 g/cm³).

X-ray diffraction analysis of the polycrystalline surface of the sample showed a high degree of preferred orientation. The two perpendicular faces of the sample were predominantly {100} and {102} planes, respectively. The analysis also showed that there were impurities at the grain boundaries and that some BeO was present. Reflectance measurements were made on a polished section of the sample containing areas one grain or less thick.

We cast samples of BeF₂ glass doped with NdF₃ containing 0.1, 1.0, and 4.0 mol% NdF₃ and ground them into disks of various thicknesses. These samples were needed for extended x-ray absorption fine structure (EXAF) studies to determine the position of neodymium edges in the glass. We also made BeF₂ glasses containing 0.5 and 2.0 mol% GdF₃ and will characterize them optically.

Fluorescence-line narrowing of amorphous solids†

We are investigating local structure and interactions in glasses by applying laser techniques for fluorescence-line narrowing. This project has both experimental and theoretical parts. Theoretically, we model glass structures using computer codes; experimentally, we measure the fluorescence-line-narrowing spectra. In addition, we compute the optical properties of the rare-earth ion in our simulated glass.

During the previous reporting period, we wrote computer programs using the molecular dynamics technique to simulate rare-earth-doped BeF₂ and alkali beryllate glasses. The molecular dynamics technique computes the motion of ions in phase space by integrating Newton's equations of motion numerically. The temperature is fixed by first giving the ions a Maxwellian velocity distribution. The code then calculates average velocities over the covered phase space. The molecular dynamics approach offers two advantages over Monte Carlo methods: time-dependent properties can be determined, and a faster equilibration is usually obtained in a given amount of computing time.

*For more information, contact C. F. Cline (415-422-8021).

†For more information, contact S. A. Braver (415-423-1011).

During the last reporting period, we simulated several rare-earth doped NaF-BeF₂ glasses and made several interesting observations:

The coordination number of *all* cations (Na, Be, rare earth) increases as the Na:Be concentration ratio increases.

- The coordination spheres of the rare earth cations become more ordered as the Na:Be concentration ratio increases; this agrees qualitatively with spectroscopic measurements.

Time-dependent motions show the same quasi-periodic motions (which are associated with defect sites) as described for Monte Carlo simulations elsewhere.²⁰

Rapidly quenched materials*

Very rapid cooling of metallic alloys produces "metallic glasses" having unique physical and chemical properties not possessed by the corresponding crystalline forms. These amorphous solids are prepared by quenching compositions near the eutectic composition at very rapid rates (10⁵-10⁸ K/s) to suppress the nucleation and growth of the crystalline phase.

Our past work has concentrated on the synthesis of amorphous or "glassy" beryllium-containing binary and ternary alloys. During this reporting period, we investigated the supersaturation of aluminum with beryllium and other metals using the rapid-quench technique. Aluminum alloys are attractive materials for structural applications because they offer relative high strength, high elastic modulus, and low density.

We previously reported our large extension of the solid solubility of beryllium in aluminum.¹⁴ According to x-ray diffraction analyses, we extended the solubility limit, usually only 0.07 to 0.10 at.% at equilibrium at 600°C, to at least 15 at.%. However, lattice parameter and Vickers hardness measurements indicated that "clustering" may occur well before that limit. To assess this possibility, we examined the foils using TEM. Preliminary investigation of foils containing 1 and 5 at.% showed heavy concentrations of dislocation loops but no visible clusters. In contrast, small spherical precipitates were readily visible in the samples containing 10 at.% beryllium. These precipitates were about 400 Å in diameter and evenly scattered through the grains. (Their small size prevented identification by electron diffraction.) Because there is no intermediate compound in the Al-Be binary system, we concluded that the clusters are pure beryllium or beryllium containing aluminum in solid solution. These observations from the TEM photographs verified the conclusions based on the value of the lattice constant and Vickers hardness plots.

We also discovered an interesting solid-solution extension of iron and silicon in aluminum that showed some unusually high hardness values. Consequently, we are evaluating the mechanical properties of Al₈₀Fe₅Si₁₅ to determine its utility as a structural material.

We arc-hammered several Al₈₀Fe₅Si₁₅ and Al₈₀Cu₅Si₁₅ samples into thin foils to examine their propensity to form amorphous materials. In all instances, however, x-ray diffraction showed crystalline structures. The Al₈₀Cu₅Si₁₅ alloy consisted of several phases, but the Al₈₀Fe₅Si₁₅ foil showed only the α fcc structure of aluminum, suggesting that iron and silicon were in solid solution. Even though the supersaturation of aluminum with various elements by rapid-quench techniques has been well studied, we have found no reference to the addition of both iron and silicon to aluminum. The Vickers hardness of the Al₈₀Fe₅Si₁₅ foil was 400 kg/mm², which is an unusually high value compared to other aluminum alloys. Even with this particular composition, there may be small "clusters" not observed by x-ray diffraction.

A series of samples were arc-hammered to examine further the solid-solution extension of other elements in aluminum. These samples included the following: Al₈₀Si₁₅B₅, Al₈₅Si₁₀B₅, Al₈₅Be₁₀B₅, Al₉₀Be₅Be₅, and Al₉₅B₅. The first three compositions in this list were crystalline and contained second phases in each case. The x-ray pattern of the Al₉₀Be₅B₅ foil was identified as the familiar α phase of aluminum, suggesting complete solid solution. The Al₉₅B₅ foil contained trace amounts of an unknown second phase. These are only preliminary results since most of our effort is directed toward the interesting Al₈₀Fe₅Si₁₅ alloy.

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Diffusion in silicate minerals*

We are working to obtain good measurements of atomic diffusion in selected silicate minerals. These data should help us understand a variety of geological processes such as mantle creep and continental drift, diffusion of radionuclides from radioactive waste disposal sites, and ore formation. The Geosciences Division of DOE Office of Basic Energy Sciences is supporting our research on diffusion in silicate materials. We are cooperating with the Earth Sciences Division at LLNL on this project.

We directed our initial studies to olivine, $[(\text{Mg},\text{Fe})_2\text{SiO}_4]$, which is a major constituent in the earth's mantle and has been studied previously at LLNL. Although good measurements of the electrical conductivity, the iron and oxygen bulk diffusion, and creep of olivines have been measured, oxygen diffusion in grain boundaries and dislocations has not.

We are studying the diffusion of ^{18}O into olivine at high temperatures. We monitor the paths of diffusion by bombarding the specimen with 2.8-MeV protons to convert ^{18}O to ^{18}F , which emits positrons and can be quantified using photographic film. This autoradiographic technique allows us to handle the tracer as if it were radioactive.

During the last two reporting periods, we annealed specimens in ^{13}O gas at 1350°C and obtained other specimens run in ^{18}O . Both types of specimens were activated in the LLNL Tandem accelerator and Van de Graaff generator. The activation experiments showed grain-boundary diffusion of oxygen, and although we hope to detect dislocation diffusion, we have been unable to do so yet. We are analyzing our data to obtain a value for the grain-boundary diffusion coefficient, but this preliminary value may be subject to later revision since our activation procedure is not yet perfected and the beam is not sufficiently homogeneous to assure uniform activation.

Chemistry Research Resources

Metallic alloy glasses†

The objective of the metallic alloy glass project is to use rapid quenching techniques to produce new materials (mainly alloy glasses) and to determine their properties. The general direction of our work is guided by potential applications of these techniques in the Nuclear Explosives Program (NEP).

We evaluated the thermal properties of Mo-Ru-B-Al glass ribbons, prepared as described previously.¹⁴ X-ray diffraction showed no crystallization in the ribbons on heating to 1000 K, and calorimetry showed no thermal events in this temperature range. Annealing for one minute at 850 K caused complete loss of ductility, although only a partial loss of ductility was observed at 800 K; bend strength did not deteriorate. Because this alloy ribbon exhibited these favorable thermal characteristics, we expect that by further optimizing the composition, we can prepare metal-matrix composites reinforced with ductile, high-strength alloy-glass ribbons.

We also prepared sputtered Mo-Ru-B glasses. Transmission electron microscopy is underway to verify the noncrystalline structure indicated by x-ray diffraction. These alloys exhibit good bend ductility in a specimen about $5\text{ }\mu\text{m}$ thick, which is remarkable for a sputtered alloy glass. We are currently preparing thicker specimens to be machined into targets for studies of hydrodynamic instabilities in shock-loaded materials.

Explosive compaction of ceramic powders**

We are investigating the methods of producing ceramic objects by the explosive compaction of aluminum nitride (AlN) powders. Most nitrides and carbides (e.g., AlN, SiN, SiC, etc.) offer outstanding

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strengths but are difficult to fabricate into shapes useful in engineering applications. We believe explosive compaction may prove to be an alternative to sintering as a fabrication process.

Our study is divided into three general areas: fabrication, characterization, and modeling. Work in these areas is proceeding concurrently.

Fabrication

We are pursuing two approaches for compacting AlN powders: implosion using high explosives (HE) and compaction of disks using projectiles fired from high-pressure gas guns.

A preliminary series of implosion shots was fired to evaluate the suitability of using small-diameter tubes. The shots were successful. The preliminary series consisted of four shots at nominal pressures of 2, 3, 4, and 5 GPa. The AlN powder was packed into steel tubes threaded into the base of a PVC canister, and the steel capsules were vacuum sealed and evacuated before compaction. The detonation velocity was measured with standard self-shorting pins. This arrangement worked well. Although there was some concern that a steady state detonation would be difficult to obtain over the length of such short capsules, this proved not to be the case, and all the samples were fairly uniformly compressed along their length.

Examination of cross sections revealed expected trends in the macrostructures of the samples. Those fired at 2, 3.1, and 3.8 GPa were "under compacted" and a soft core of undensified material remained on axis. The sample fired at 5.6 GPa, however, showed noticeable cracking and was apparently overdriven. These observations were confirmed quantitatively by the density profiles obtained radiographically. These data showed that the densities of under-compacted materials decreased smoothly toward the axis. Qualitatively, a high-pressure pulse proceeded farther into the powder before rarefaction from the explosive caught up to it and rapidly released the pressure. The result was a soft core of decreasing diameter. The density-profile data for the over-compacted specimen was also interesting—there was a moderate decrease in the density near the axis, presumably caused by cracking. Farther from the axis, the density remained constant except near the outer edge, where an observed increase in the density may have resulted from a measurement error.

At a sufficiently high pressure, nearly uniform density was expected in over-compacted samples (i.e. nearly 100% compacted) except near the center where cracking would produce variation in the measured density. The quality of our density data was good, although there was a systematic error in the absolute density determinations. Although an attempt is underway to eliminate this error using a standard piece of hot-pressed AlN of known density, we will continue to calculate the measured average density, compare it with the known average density, and scale accordingly.

We also fired a series of shots to begin mapping out the behavior of dynamically compacted AlN in pressure-time duration space. All six shots were fired at the same nominal pressure (5 GPa) using the same explosive. The ID of the PVC canister, however, was varied so that the explosive thickness ranged from 6 to 32 mm, which changed the duration of the pressure pulse. For this series, the pulse shape and impulse will be calculated. It is hoped that in future series the pressure-time profile can be measured. The two shots having the least amounts of explosive (6 and 13 mm, respectively) detonated at 4 rather than 5 GPa. We suspect that this was related to the thinness of the explosive layer and the resulting rarefaction behavior. Nevertheless, these specimens showed a remarkable amount of compression. Even with only 6 mm of explosive, the average density was 81% of theoretical, although the material was obviously under-compacted. The remaining four samples were all within 10% of the nominal pressure and were compacted to densities between 90 and 94%. The highest pressure (5.4 GPa) also had the largest quantity of explosive and predictably over-compacted the AlN powder. Density measurements on this series are currently underway.

The compaction "map" requires that the pulse duration at a given pressure be specified. By specifying a certain duration at a given pressure, the necessary powder loading to achieve a desired result is fixed; how the pressure and time are practically obtained may then be of less concern although pulse shape may be important. This approach avoids using the traditional explosive-mass-to-powder-mass ratio (E/M), which is an ambiguous quantity that depends on the type of explosive, the properties of the cladding material, and the properties of the containment medium. The correct definition of duration must be tied to the total impulse, but the variable used here has not been chosen yet.

Our initial experiments indicated that the "window" for satisfactory compaction may be very narrow, requiring that the pressure deviate no more than perhaps 1 to 2%. Achieving such a tolerance may be very difficult, requiring not only careful packing of the explosive to maintain uniform density but careful preparation of the explosive itself.

Explosive compaction of a cylindrical capsule of powder has a serious drawback, however: the converging shock wave and its concomitant effects threaten the mechanical integrity of the sample and introduce radial variations in the microstructure. Although these effects can be mitigated by matching shock dissipation to the rate of convergence, it is more advantageous to use projectiles fired from high-pressure gas guns because the impact velocity (and hence the pressure) can be closely measured and controlled.

Our initial design for compaction experiments using a gas gun was simple. The powder to be compacted was held in place in the compaction chamber by a thin plate made of the same material as the projectile. Our experiments used a 2.5-in. gas gun, which fires a 240-g Lexan projectile using helium. The maximum velocity attained in test firings was 450 m/s, but certification to a higher breech pressure will allow velocities of about 600 m/s. The Lexan projectile has dual advantages of low density (1.2 g/cm^3) and low shock speed compared to metals (2 vs 5 km/s, respectively). In our initial experiments using a projectile velocity of 260 m/s, we compressed a coarse aluminum metal powder from an initial bulk density of 46% to a final density of 94%. The consolidated piece was much like an aluminum casting. An attempt to compact copper powder (initially at 69% density) at 316 m/s distorted the compaction cup so much that it could not be disassembled; the powder, however, was uncompacted. Apparently, the initial density was too high and transmitted the shock with less dissipation, thereby preventing powder-particle velocities high enough to yield interparticle welding. The use of mild steel for the compaction cup was, in addition, a poor choice. A new fixture is presently being made from 4340 steel. The experiment will be repeated with a coarser copper powder. Although we doubt that AlN can be driven to high density with this gun, these experiments serve as a development tool on which experiments for larger guns can be efficiently developed and tested.

Characterization

Transmission electron microscopy (TEM) examination of materials revealed a "mottled" intergranular phase in the compacted AlN. Our prime objective was to determine if this material was crystalline or amorphous. The regions were small, about $0.1 \mu\text{m}$ across, so that conventional selected-area diffraction with the 500-Å beam available on present instruments gave ambiguous information. Certain areas of the specimen containing large amounts of the mottled phase, however, showed a polycrystalline diffraction pattern which matched that of AlN, suggesting that at least some of the material was crystalline. This observation was corroborated by results obtained on a different TEM by Dahmen at the Lawrence Berkeley National Laboratory. The mottled region showed a spotty ring pattern characteristic of a polycrystal whereas the obviously crystalline grains flanking the mottled region showed distinct spot patterns. We plan further work with the STEM, which has a much smaller 200-Å beam.

Photographs made using the scanning electron microscope (SEM) showed that the grain morphology of the compacted material was substantially the same as that of the starting powder; the fine $0.1\text{-}\mu\text{m}$ grain size was preserved. This was in contrast to hot-pressed material, which developed $1\text{-}\mu\text{m}$ grains in 1 h at 1700°C . There was some indication of localized melting, particularly near the axis of the specimens.

Modeling

We demonstrated the capabilities of the two-dimensional hydrocode HULL to model HE compaction of powders, both for explosive compaction in a cylindrical geometry and for projectile compaction. We are working to correlate the measured density profile with our calculations and to derive a workable and realistic model for compaction of AlN.

Surface self-diffusion on silicon and germanium*

We concentrated our efforts on measuring the surface self-diffusion on silicon because it is more readily available as a high-purity single crystal and because we have greater expertise in the photoetching techniques on silicon. We were also able to prepare a very good 3-mm-square mask with a 2-mm-wavelength pattern.

We resolved two major technical problems during this reporting period. We significantly reduced the contribution of evaporation-condensation to changes in surface morphology and eliminated the nonlinear response of the laser-diffraction technique. As a result, we are observing changes in the laser diffraction patterns resulting from surface self-diffusion on silicon.

Chemistry and Materials Science research

Preparation of special isotopically enriched foils†

We have been attempting to prepare special isotopically enriched foils for nuclear physics experiments that study the scattering of 500-MeV electrons from selected nuclei. To be useful in these experiments, the thin foils must be able to withstand the electron beam. In the past, we prepared 80- μ m-thick foils of Be^{17}O and Be^{18}O , and we recently prepared foils containing ^{29}Si and ^{30}Si . We first tried using SiO_2 as a carrier material for the silicon isotopes but were unsuccessful because silica undergoes several phase changes when heated from room temperature to its melting point. In many cases, our hot-pressed specimens cracked, and those that appeared satisfactory deteriorated rapidly in the beam. We obtained our best results when we used very finely ground silica, but failures still occurred. In these cases, failure may have been caused by adsorbed moisture, even though we kept our raw materials covered with an organic liquid before hot pressing.

Recently we prepared silicon carbide by reacting silica and a measured amount of graphite powder in the hot press at 1910°C:

The product appeared dense, hard, stable, and fairly strong—even in thin foils. These samples have not yet been irradiated in scattering experiments.

Diffusion bonding of stainless steel using silver**

We used planar magnetron (PM) sputtering to coat lapped 316 stainless steel surfaces for diffusion bonding at 225°C and 100 MPa for 15 min. The PM sputtering technique has proven itself to be less complex and more reliable than the hot-hollow-cathode technique used in earlier studies. Bond strengths approaching the yield strength (280 MPa) of the annealed 316 stainless steel were achieved with 1.0- μ m-thick PM-sputtered silver coatings. Bond strengths of nearly 210 MPa were achieved using the joining process and 0.3 μ m of silver on each lapped 316 stainless steel surface.

Such high bond strengths were only recorded for specimens that failed in the silver layer and not at the silver-stainless steel interface. Although specimens coated with 0.3 and 1.0- μ m-thick layers of silver failed

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at the silver layer, the appearance of the fracture surface for the thin ($0.3\ \mu\text{m}$) specimens was not the classic ductile-dimple failure mode observed for the more thickly coated ($1.0\ \mu\text{m}$) specimens (Fig. 7).

We were not as successful in preparing high-strength bonds with the $0.3\text{-}\mu\text{m}$ -thick silver coatings. Failure occurred more frequently at the silver-stainless steel interface with the thinner silver coatings. The predominant failure mode (Fig. 8) is best described as a combination of the odd-looking ductile failure shown

Fig. 7. Failure modes observed in silver coatings on 316 stainless steel tensile bars. The thinly coated ($0.3\ \mu\text{m}$) specimens (a) did not fail by the classic ductile-dimple mode that was observed for the more thickly coated ($1.0\ \mu\text{m}$) specimens (b).

Fig. 8. Failure modes observed for 316 stainless steel tensile bars joined with a layer of silver $0.3\ \mu\text{m}$ thick. This micrograph shows failure at the silver-stainless steel interface and in the silver layer.

in Fig. 7a and failure at the silver-stainless steel interface. Bond strengths averaged about 120 MPa for specimens that displayed this combination of failure modes. We currently have no reasonable explanations for either the unusual ductile failure in the silver or the greater incidence of silver-stainless steel interface failure observed using the stainless steel specimens bonded with the 0.3- μ m-thick silver coatings.

High-temperature x-ray diffraction of TATB*

We studied the high-temperature behavior of TATB (1,3,5-triamino-2,4,6-trinitrobenzene) using our hot-stage diffractometer. First, we made a diffraction scan at room temperature; then we raised the temperature to 120°C and took a number of diffraction scans over a 24-h period. Finally, we made another room-temperature scan after the heat treatment for comparison purposes.

We made the following observations:

- TATB seemed to show no permanent changes after cooling to room temperature.
- No major changes in the diffraction patterns occurred after 24 h at 120°C, indicating that TATB suffered no serious degradation under these conditions.
- The patterns taken at room temperature and at 120°C showed relatively large shifts of the 002 and 004 peaks and relatively little shifts of all the other peaks. This indicated that thermal expansion was highly anisotropic and that the largest expansion was along the c axis.

We calculated that the thermal expansion coefficient from the shift of the 004 line was $\alpha_{001} = 206 \times 10^{-6}/^{\circ}\text{C}$. This is a large value, but may not be unusual for this family of compounds. The other coefficients were near zero. (To obtain the complete expansion tensor, we will have to measure many d-values and refine the unit-cell parameters.)

This anisotropic expansion could mean that compacted TATB might deteriorate if it undergoes thermal cycling while in storage. If the compact is composed of randomly oriented grains, the differential thermal expansion could weaken the grain boundaries and cause the compact to disintegrate.

X-ray diffraction analysis of volcanic ash[†]

During this reporting period, we analyzed volcanic ash from fallout areas near Mt. St. Helens. Analyses were conducted on untreated ash samples and samples separated on the basis of density and chemical properties. We examined ash from four different locations and developed semi-quantitative standard curves to determine the amount of quartz (in wt%) in quartz-cristobalite mixtures as a part of the LLNL characterization effort. As a part of a round-robin analysis conducted by NIOSH with several other laboratories, four ash samples of unknown composition were quantitatively analyzed for quartz and cristobalite. This analysis required a separate set of quartz and cristobalite standards and a corresponding set of new calibration curves to permit the quantitative x-ray analysis to be made in the presence of other noninterfering minerals. We reported our results to NIOSH; the compilation of the round-robin results will allow us to evaluate our analysis techniques with respect to those of other laboratories.

Mechanisms of hot-flow multiphase erosion/corrosion**

The purpose of this program is to determine the dominant mechanisms that operate in erosion/corrosion (EC) environments, primarily gun-barrel EC. Using a specially designed laser system, we are simulating the material response in reactive environments similar to those encountered in gun barrels. We

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hope to develop meaningful mathematical treatments of EC reactions so that material response can be accurately predicted. We will also evaluate the role of refractory coatings in different gun-barrel materials. This work is part of the ARRADCOM project and is funded by the Army Research Office.

Previous research used pulsed-laser experiments to evaluate AISI 4340 steel (a commonly used gun-barrel material) and tungsten-clad steel. A special pressure chamber was designed and constructed so that specimens could be struck with laser beams at different pressures in controlled reactive environments. We used a laser-beam pulse lasting 660 μ sec on the AISI 4340 specimens. It produced surface melting and cratering at energies of 44 J and greater; the surface damage increased monotonically as the number of laser pulses increased. Metallographic examinations revealed that a white etching layer formed in the damaged area, and the layer appeared to be separated into three distinctly different layers. Similar white etching layers have been found in eroded gun barrels; this indicated that our laser system probably could simulate gun-barrel response.

The tungsten clad specimens were previously coated by chemical vapor deposition, and an intermediate layer of nickel was deposited on the AISI 4340 specimens to improve adhesion of the tungsten. The tungsten coatings were about 250 μ m thick, and the intermediate coating thickness on different specimens varied from about 2 to 10 μ m. When the specimens were exposed to the laser beam, the extent of damage in the tungsten layer noticeably decreased as the thickness of the intermediate nickel layer increased.

During this reporting period, the pressure chamber of the laser system was completed, and the data acquisition system was substantially upgraded to facilitate computerized processing of the collected data.

As a preliminary test of the pressure chamber system, we examined a series of AISI 4340 specimens in air and in argon. The responses in the two different environments were dramatically different. Specimens exposed to the laser beam in air normally emitted a large incandescent vapor plume when the beam energy was sufficient to melt and vaporize the sample; plume formation is recorded photographically during a laser impact. Specimens tested in air also formed a dark film, assumed to be an oxide. The film appeared continuous near the periphery of the exposed area and in regions associated with the lower energies of the inhomogeneous beam, but it was discontinuous near the melted areas where the beam intensity was greatest. A network of microcracks observed in the continuous portions of the film may be of significance in EC mechanisms. Perhaps one of our most significant observations was that the pitting occurring extensively in the melted regions appeared to be associated with preferential response of inclusions. This could be a significant EC mechanism.

In contrast to the specimens exposed to the laser beam in air, most of the specimens exposed in argon did not emit vapor plumes. The surface damage and cratering was much less severe than that in the specimens tested in air, and the exposed areas were bright and not discolored. A few specimens did emit very faint vapor plumes, but the surfaces of these specimens were also slightly discolored. The discoloration indicates that a contaminant such as air or water vapor was present. When the surfaces of the specimens were examined at high magnifications, both optically and in the SEM, martensitic relief was observed in the heavily melted regions. A fine cellular structure also was found to be superimposed on the martensitic structure in these areas. Although the origin of the cellular structure is unknown, it could be related to impurities or contamination. These observations are considered significant since surface reactions and the related structural response of the surface are considered to be important aspects of EC mechanisms. Again, we observed preferential response of inclusions.

We considered the noticeably different response of the specimens tested in air, argon, and contaminated argon to indicate that specimen response in the laser system is extremely sensitive to the environment despite the relatively short duration of the laser pulses. We found this highly encouraging because it demonstrates that impacting specimens with brief laser pulses in controlled environments is a valid experimental technique for simulating gun-barrel EC.

Model materials

Because EC mechanism involves both chemical and mechanical reactions and because these reactions are extremely difficult to detect in standard gun-barrel materials such as AISI 4340 steel (which have very complex microstructures), we chose Fe:3-wt%-Si as a model material to analyze these reactions. The

mechanical response or plastic deformation behavior of Fe:3-wt%-Si has been well characterized in metallurgical research. Its primary attribute is that it has excellent etch-pitting response for revealing the dislocation substructure, and this enables the dislocation structure generated during plastic deformation to be readily detected. In many cases, correlations of etch-pitting response with known amounts of plastic deformation can permit reasonable quantitative analyses of the extent of plastic strain in etch-pitted specimens. This will greatly facilitate the analysis of plastic deformation that occurs during laser pulsing, and it will be of particular value in determining how deformation may be modified by the presence of a reactive environment. Using Fe:3-wt%-Si should also prove invaluable in studies of how coatings exposed to laser beams behave and how coatings may modify the response of a substrate during EC.

The success of this program requires that we properly isolate and identify the material parameters that dictate EC response. These material parameters are difficult to isolate unless they can be controlled in a systematic manner. We plan to approach this problem using materials having different physical and chemical properties. We will then correlate variations in EC reactions and response with the appropriate variations in the properties. Good reproducibility of the laser system will be required for this phase of the program.

Theoretical considerations

The successful culmination of this program must include meaningful mathematical treatments of the various damage mechanisms that operate. Although the role of plastic deformation in EC is not currently understood, we consider it an important aspect of gun-barrel EC. Therefore, we initiated a survey of the field of dislocation dynamics to determine plausible approaches for modeling plastic-deformation response during EC. The classic Johnston-Gilman relation appears to be most amenable for this application. However, this treatment requires modification for the transient response that occurs during EC, and careful correlation with the laser experiments is necessary to determine the modifications imposed by a reactive environment. If the laser system can yield the appropriate quantitative data, this treatment promises to be an extremely stimulating aspect of this program.

We are also evaluating the way we treat reaction-rate data from the laser experiments. The kinetics of the carburizing, nitriding, and oxidizing reactions suspected to occur during gun-barrel EC are usually studied under steady state isothermal conditions, and reaction-rate constants obtained from these experiments are rigorously applicable only under identical conditions. Because both the thermal and pressure pulses that occur in gun barrels are highly transient, the equilibrium-kinetics approach does not strictly apply. The possibility does exist, however, that equilibrium reaction-rate data may serve as a useful first-order approximation in estimating instantaneous reaction-rate kinetics, and we will explore this. We will also attempt to deduce an empirical or effective reaction-rate constant from the laser experiments, which the dislocation-dynamics treatment requires in order to account for composition fluctuations during EC pulses.

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Presentations

R. D. McCright	Review of LLNL Downwell Corrosion Testing	Invited talk. Committee on Well Casings and Drill Pipe, sponsored by DOE Division of Geothermal Energy and Brookhaven National Laboratory, Salt Lake City, UT, Sept 8, 1980
T. M. Quick	Improved Damage Thresholds for Shiva/Nova	Fusion Research Associate Director's Briefing, Livermore, CA, July 1980
G. W. Smith	Crystallographic Studies of the Mineral Waste-form, Synroc	American Crystallographic Association Summer Meeting, Calgary, Alberta, Canada, Aug. 17-22, 1980

Publications

R. D. McCright	Localized Corrosion of Steels in Geothermal Steam/Brine Mixtures	<i>Proc. Geothermal Resources Council Meeting</i> , Salt Lake City, UT, Sept. 9-11, 1980