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Advances in Materials Science
Metals and Ceramics Division
Triannual Progress Report
October 1979 through January 1980

Scientific Editor: John J. Truhan
General Editor: Kenneth M. Gordon

MASTER

March 31, 1980

**Lawrence
Livermore
Laboratory**

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Advances in Materials Science

Metals and Ceramics Division

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MAGNETIC FUSION ENERGY MATERIALS STUDIES*

SUPERCONDUCTOR DEVELOPMENT

Introduction

Lawrence Livermore Laboratory has been sponsoring a superconductor development program in industry since 1974 to ensure that a Nb_3Sn superconductor able to meet the 12-T requirements of future mirror experiments will be available. We are monitoring the development of this superconductor.

The Nb_3Sn superconductor differs from NbTi in two important respects: first, Nb_3Sn is a strain-sensitive material that requires special handling and process design to prevent degradation of its superconducting properties. Second, the matrix around the Nb_3Sn must be bronze rather than high-purity copper; this means a conductor must be developed that can transfer the current from the superconductor to the stabilizing matrix in the event of a fault.

We are currently working with a commercial supplier to manufacture a Nb_3Sn superconductor for demonstration in the High Field Test Facility (HFTF). Successful operation of the HFTF will provide the experience needed to construct 12-T coils for future mirror experiments.

This Nb_3Sn superconductor is a compacted cable made by the following steps: niobium rods are loaded into holes drilled in a bronze (Cu:13-wt%-Sn) billet, and a nose and cap are welded onto the bronze to form an extrusion billet. This billet is extruded, drawn, and formed into a hexagonal rod. The rod is cut into short lengths and loaded into a second billet, which is extruded and drawn. The resulting rod is clad with a tantalum diffusion barrier and high-purity copper, after which it is reduced to wire by cold drawing. The wire is wound into a triplet cable, and six of these are then wound together. The resulting 18-strand cable is jacketed with additional copper, compacted, and formed into a rectangular cross section. This component, called the core, is then heat treated so that the tin from the bronze matrix reacts with the niobium filaments to form the Nb_3Sn superconductor. Finally, embossed copper strips are soldered to each side of the core to produce a fully stabilized conductor (Fig. 1).

Evaluation of Nb_3Sn Core Samples

We are evaluating finished samples of Nb_3Sn core made with various strand configurations. We have measured the critical current as 12 T for cores containing 18, 27, and 54 strands. One 18-strand core and one 27-strand core sample achieved the specified critical current using a 10^{-11} $\Omega\text{-cm}$ criterion for critical current. One 18-strand core and one 54-strand core met the specified critical current, but only when a 10^{-10} $\Omega\text{-cm}$ criterion was used. We believe that this higher resistance in the cable resulted from breaks in some of the strands at cross-overs; these breaks occurred either during compaction or subsequent drawing. To prevent this, our supplier (Airco) is annealing the cables during the compaction sequence, and we have found no broken strands in etched samples taken from lengths of conductor processed in this way. Metallographic examination in progress is evaluating the degree of strand-to-strand bonding after the final heat treatment.

*For more information, contact R. M. Scanlan (415-422-7002)

FIG. 1. Transverse section of Nb_3Sn superconductor. This cable was made by wrapping 18 strands of bronze–niobium–filament composite in a copper tube, shaping the tube into a rectangular cross section (4.65×9.47 mm), and then heat-treating this core piece to form Nb_3Sn at the bronze–niobium interfaces.

Compression Tests on the Core

We subjected samples of the HFTF core to compressive tests to determine the strength of the strand-to-strand interfaces. The present configuration of the core is a compacted cable that, after heat treatment to bond the strands together, should adequately simulate the actual conductor with respect to current transfer and in its ability to withstand a compressive load. We found that when we compressed (by bending) 5.4-by-11-mm samples of core on the 5.4-mm-wide side, the compacted cable withstood loads of 83 MPa; this pressure deformed the copper sheathing but failed to delaminate the strand-to-strand interfaces.

Stabilizer Cladding

The HFTF cladding is designed to provide both high conductivity and strength for the HFTF conductor. Consequently, a cladding fabrication procedure has been developed to impart about 50% cold work to the copper cladding. The mechanical and electrical properties of the cladding were measured at ambient temperature and at 4.2 K. The residual resistivity ratio was 100 ± 10 at 4.2 K. The yield strengths at 4.2 K were 290 MPa in the grooves and 269 MPa in the land areas so that loads at a 0.2% offset were 7209 N (grooves) and 8628 N (lands); the specification for the HFTF cladding requires a strength of 5075 N.

LASER FUSION ENERGY*

DAMAGE THRESHOLDS OF POLISHED GLASS SURFACES

The goal of our experiments for the LLL Laser Fusion Energy program is to increase the ability of polished glass surfaces to transmit high-energy laser pulses without being damaged. Such surfaces are more easily damaged than the bulk material. There is speculation that the polishing process damages the surface and introduces impurities—two postulated causes for the lower damage threshold of surfaces. In a previous experiment, in which a fresh surface of fused silica was exposed by fracturing rather than by polishing, we demonstrated that a surface can have a damage threshold as high as the bulk material. Adsorbed gas and surface layers of environmental contamination (such as water) are also suspected of lowering damage thresholds.

During this reporting period, we tested the damage threshold of the polished glass surfaces that we prepared last quarter. The test pieces were fused silica polished on a nylon lap with 99.9+%-pure CeO_2 and etched with ultra-pure hydrofluoric acid. All four tested surfaces showed surface-damage-threshold values above 20 J/cm^2 . These threshold values were considerably higher than those we found previously and are, for the first time, of a magnitude suitable for Nova applications. We plan to reproduce the same polishing technique on a pitch lap because we cannot currently produce optically-figured surfaces on nylon laps. We also plan to start polishing BK-7 surfaces, which will be much more difficult partly because the surface of the material is chemically active. We are very encouraged by the higher damage-threshold values obtained this reporting period using a pure polishing compound and an acid etch.

We were also able to determine the damage thresholds of fractured fused silica surfaces during this reporting period. One surface was fractured and tested in a high-vacuum chamber. The surface tested at about 40 J/cm^2 , but the experimental conditions were not as well defined as we would have liked. Another surface, fractured in air using moisture to produce a cleaner fracture, also tested at about 40 J/cm^2 . We hope soon to schedule a series of fracture experiments in our own test chamber so that we have more control of the experimental conditions and can better characterize the factors that influence the surface damage threshold value of fractured surfaces.

CHARACTERIZATION OF PLATINUM-COATED MICROSPHERES

Introduction

In October, it was discovered that a batch of platinum-coated glass microspheres, intended for use as laser fusion targets, had lost their high-pressure deuterium-tritium (D-T) fill. The loss apparently occurred either during the sputter-coating process or during storage.

These targets had been prepared using the following steps:

1. Hollow glass microspheres ($70 \mu\text{m}$ in diameter with $1\text{-}\mu\text{m}$ -thick walls) were filled with D-T mix at 400°C under 13.2 MPa for 14 to 28 h. At the end of the filling period, the temperature was allowed to drop to room temperature. The pressure was then released immediately without stepwise decompression.
2. The filled microspheres were sputter-coated with platinum about $5 \mu\text{m}$ thick using a sputtering stream of 95% argon and 5% oxygen. (The Target Coatings Group found empirically that oxygen doping gave a better coating.)

The coated filled targets were stored until needed.

An attempt was made to refill these platinum-coated microspheres. The experiment was of interest not only as a means of restoring the empty balls to a "useful" status but also as a supplement to cryogenic filling experiments currently underway in the target group. Coating cryogenically D-T-loaded microspheres with platinum is not possible using standard techniques because of the high temperatures generated by the sputtering process; platinum-coating the balls before cryogenic filling, however, would avoid this problem.

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Although standard conditions were used to refill the empty microspheres in the hydrogen-fill system, the balls that emerged from the system bore little resemblance to those that went in—the formerly smooth spherical surfaces were blistered and distorted. SEM examination of a cross section showed that the platinum layer, normally 80–90% dense and quite uniform, was extremely porous (“foamed”) and irregular (Fig. 2).

Current Progress

The literature^{1,2,3} and structural information provided by initial SEM studies suggested that as hydrogen (D-T) diffused inward during filling, it was trapped in the platinum. After filling, the sudden pressure release caused the instantaneous evolution of the occluded hydrogen and the formation of the porous structure. Oxygen present during sputtering and trapped within the platinum layer may also have contributed to the deterioration. It seems reasonable to postulate selective “occlusion” of hydrogen at oxygen-bearing sites and the subsequent Pt-catalyzed reaction between the two to form water vapor. When the filling pressure was released, rapid evolution of the water vapor would have been substantially more destructive than that of hydrogen. The oxygen present during sputtering may thus have profound effects on the structure of the platinum coating.

Because the literature suggested that water formed within the platinum layer, we are currently evaluating the processing parameters, especially oxygen doping, and are characterizing their effects on the coating structure. Most of our work is being conducted on flat sputtered platinum films about 5 μm thick. We chose flat films instead of coated balls because of the relative unavailability of microspheres and the inconvenient size and geometry of microspheres for most types of materials testing.

FIG. 2. (a) Cross section of normal platinum-coated laser targets. The outer platinum coating (white layer) is dense and about 5 μm thick; the glass microsphere (dark layer underlying Pt coating) is about 1 μm thick. (b) Cross section of microsphere after refilling attempt; the outer platinum coating has become porous and distorted. Both polished sections are shown in reflected light.

We divided our investigation into three phases. Phase A examines the effect of oxygen on the structure of sputtered platinum film. Three levels of oxygen doping are used: 0%, 5% (the level used currently), and 10%. The testing methods in progress are 1) thermogravimetric analysis (TGA) from 25 to 900°C, 2) oxygen analysis by vacuum fusion, 3) metallographic, optical, and SEM examination of sputtered-film cross sections, and 4) x-ray diffraction analysis for the presence of oxides and changes in the platinum lattice parameter. The TGA tests have been completed but were unsatisfactory because of unacceptable signal-to-noise ratios resulting from small sample size.

Phase B examines the effect of the hydrogen filling process on the sputtered-platinum structure. In this phase, platinum films will be exposed to standard fill conditions and then either rapidly or gradually decompressed to ambient pressure. We are currently using optical, SEM, and x-ray diffraction analysis to characterize the microstructure of films subjected to these two conditions.

Phase C addresses the correlation between the structure of Pt films and the actual microsphere coatings. We will characterize the degrees of crystallinity and preferred orientation using a Debye-Scherrer powder camera to conduct the x-ray analyses on sputtered platinum film and on uncoated and Pt-coated glass microspheres mounted on glue stems.

FABRICATION OF ADVANCED LASERS*

During this reporting period, we investigated the possibility of corrosion damage to a welded section of 304 stainless steel pipe exposed to halogen gases. Our main concern was to determine the condition of the metal after exposure to these potentially corrosive gases and to learn if 304 stainless steel could withstand such environments.

In the 5-in. pipe section studied, the welding process had induced a wide heat-affected zone in which the stainless steel exhibited a sensitized grain structure. The stainless steel had been exposed to fluorine gas at a partial pressure of 530 Pa with inert carrier gases for a total pressure of 186 kPa at 20 to 40°C for 260 h. Further, chlorine gas at a partial pressure of 530 Pa with HCl as carrier gas was used for 100 h of experimentation, again at 20 to 40°C. The gaseous environment was kept dry by maintaining a base pressure of 10^{-4} Pa to remove traces of atmospheric moisture. During operation, the halogen and carrier gases passed through a cold trap to remove water vapor and all other condensible impurities.

We examined the weld and surrounding areas metallographically. We found no indication of attack in either the weld, the heat-affected zone, or the parent metal. A literature check confirmed that dry F_2 or Cl_2 does not attack 304 stainless steel but that the gases are extremely corrosive when moisture is present; chromium-depleted regions are particularly susceptible. We recommend that great care be taken to insure dry operating conditions.

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

ALUMINUM-AIR BATTERY AND VEHICLE*

INTRODUCTION

The goal of the aluminum-air electric-vehicle program is to develop a commercially feasible general-purpose electric vehicle that has the range, acceleration, and rapid refueling capability of today's automobile. The aluminum-air power cell currently under study combines an extremely high energy-to-weight ratio with the ability to be refueled by the addition of reactants. By matching the performance of conventional automobiles, the electric vehicle will have the potential for significant market penetration and a proportionately large savings of petroleum. We estimate that technical success of the program will allow commercialization in the early 1990's of a vehicle with a purchase price, operating cost, and total energy consumption competitive with advanced automobiles using liquid fuels derived from coal.

The aluminum-air power cell operates as a fuel cell: aluminum plates and tap water are consumed to produce electricity and a reaction product (Fig. 3). The reaction product, hydrargillite [$\text{Al}(\text{OH})_3$], is an intermediate produced during the industrial refining of aluminum; thus it can be converted back to the metal without necessitating modification of existing metal-winning technology. During battery discharge, tap water distilled using waste heat serves as the battery reactant and is used to wash the hydrargillite; this washing maintains the hydrargillite product in a highly pure state—a requirement for economical recycling. The

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FIG. 3. Operation of the aluminum-air power cell: aluminum plates and tap water are consumed in the aluminum-air cell stack to produce electricity, heat, and a reaction product. The reaction product, hydrargillite, is washed continuously with tap water distilled using waste heat; this washing maintains the hydrargillite product in a highly pure state, as required for economical recycling. The hydrargillite is stored as a nonreactive semidry powder containing about 14% water, which allows significant simplification of the system design and increases the system reliability. The hydrargillite is periodically withdrawn from the vehicle at service stations for subsequent conversion to aluminum plates by the aluminum industry.

hydrargillite is stored as a nonreactive semidry powder that is periodically withdrawn from the vehicle at service stations for subsequent conversion to aluminum plates by the aluminum industry. Thus, a fixed quantity of aluminum provides a reusable energy link between any source of electricity and the vehicle.

A five-passenger vehicle would have a nominal range of 400 km set by the frequency of tap-water additions. Fresh aluminum plates would be added every 1600–3200 km, and hydrargillite would be withdrawn every 400–800 km.

Major portions of this program are carried out under subcontracts with private laboratories and consulting firms. We at LLL manage this effort and also maintain a sizable in-house effort in some limited but critical areas. This coordinated program is intended to promote and maintain a high level of scientific and engineering capability in the subcontract research. It is also our responsibility to design the power-cell, to foster its commercialization by promoting industrial participation, and to disseminate our results.

CURRENT PROGRESS

Our principal efforts during the last reporting period were development of large scale aluminum–air cells and studies of crystallizers. We continued investigations of the anodic dissolution of aluminum and achieved a more thorough understanding of the interrelation between electricity price and the energy consumption and unit-product cost of the aluminum industry.

Development of 1000-cm²-Anode Aluminum–Air Cells

The first large-scale Al–Air cells have been constructed and are being assembled for testing in early February. The large-scale cells reflect designs developed jointly by LLL and Lockheed Missiles and Space Company (Palo Alto)—the program's major subcontractor for hardware development.

Figure 4 shows a 1000-cm²-anode Al–Air research cell being built at Lockheed. This cell differs slightly from the one we are currently assembling in several minor details: 1) the large cells allow independent control over air pressure and electrolyte flow rate, 2) experimental ranges of 0–5 kA/m² in current density, and 3) a range of flow rates with $R_c = 200$ –900. Provisions are made for the simultaneous measurement of current, electrode potentials, and hydrogen-evolution rates from parasitic corrosion. We have procured a multi-channel recorder to continuously measure these parameters and additional parameters (temperatures, pressures, reference potentials) required for control and diagnostic purposes.

We are also designing a second generation of cells. These will be made from laminated layers of 1.6-mm-thick fiber-filled epoxy sheets (such as circuit-board materials) that have been punched and sheared to provide internal passageways for the electrolyte. The total thickness of these cells would be about 12 mm.

Development of a Bayer Crystallizer

A Bayer crystallizer is used to maintain the composition of the caustic–aluminate electrolyte by precipitating $\text{Al}(\text{OH})_3$ at the same rate that it is produced by the dissolving aluminum anodes. We have investigated the precipitation of $\text{Al}(\text{OH})_3$ in several crystallizers run under the anticipated operating conditions. These crystallizers contained about 25–50 wt% of hydrargillite seed in 4–6M NaOH supersaturated with $\text{Al}(\text{OH})_3$. Figure 5 shows a typical concentration decay after the addition of seed crystals. The decay rate was determined by measuring the conductivity of the solution.⁴

The rate constants determined from this decay curve indicated that a vehicular crystallizer containing 15 kg of $\text{Al}(\text{OH})_3$ could maintain a vehicular-battery electrolyte concentration of 3M $\text{Al}(\text{OH})_3$. In general, we found that rates of $\text{Al}(\text{OH})_3$ precipitation from 6M NaOH solutions did not agree with those obtained by extrapolation from published experimental data in the lower concentration range (3–4M NaOH). This observation indicated that it will be necessary to operate the cell in the lower caustic range.

ANALYSIS OF RX808-F ALUMINUM ALLOY

A new aluminum alloy, RX808-F, has been received from Reynolds and is being evaluated for use in developing large cells. This alloy contains 50 ppm Fe, 900 ppm Si, and somewhat elevated quantities of Ga

FIG. 4. Exploded view of a 1000-cm²-anode Al-Air research cell being built at Lockheed.

FIG. 5. Decay of $\text{Al}(\text{OH})_3$ concentration in an experimental crystallizer. Precipitation of $\text{Al}(\text{OH})_3$ followed the addition of hydrargillite seed to a solution of 4.05M NaOH and 2.5M $\text{Al}(\text{OH})_3$. Decay was monitored by measuring the conductivity of the solution. The decrease in aluminum concentration in this experiment correlated well with industrial data for the same process.

FIG. 6. Coulombic efficiency data for a new aluminum alloy, RX808-F (Al:50-ppm-Fe;900-ppm-Si;900-ppm-Ga), which is being evaluated for use in developing large cells. This alloy exhibits a unique negative-difference effect (constant efficiency above a critical density) in 4M and 6M NaOH and appears to be suitable for use in large cell development.

FIG. 7. Electrical consumption of Hall cells currently used to produce aluminum. The prebaked-anode cells were designed to operate economically using relatively expensive electricity (15–26 mills/kW·h) and to consume 13–14 kW·h/kg of aluminum. Using aluminum produced near the technical limit (about 11–12 kW·h/kg of aluminum), the aluminum-air electric vehicle would match the energy use of internal-combustion automobiles of equivalent performance and weight.

(900 ppm). We investigated dissolution of the alloy in 4M NaOH solutions containing 2.5M Al(OH)₃. Figure 6 gives coulombic efficiency data. This alloy exhibited a unique negative-difference effect (constant efficiency above a critical current density) in 4M and 6M NaOH. The alloy is nonetheless suitable for use in large-cell development.

ECONOMICS AND ENERGY USE ANALYSIS

Figure 7 shows the electrical consumption of Hall cells currently producing aluminum. The prebaked-anode cells were constructed within the last five years to operate economically using relatively expensive electricity (15–26 mils/kW·h) and were designed to consume 13–14 kW·h/kg of aluminum. We expect that the high costs of urban electricity (30–50 mils/kW·h) would mandate reducing this even further, ultimately approaching the technical limit of the process (11–12 kW·h/kg of aluminum). Using aluminum produced near this technical limit, the aluminum–air electric vehicle would match the energy use of automobiles of equivalent performance and weight that burn synthetic liquid fuels.

DESIGN AND ANALYSIS OF THE ALUMINUM–AIR POWER-CELL SYSTEM

We completed the design of the aluminum–air power cell system based on computer modeling of mass and enthalpy flows within the battery.⁵ In addition, the weights and volumes of battery components were calculated, and generalized equations to express battery weight and volume as linear combinations of total battery power and energy content were derived.⁶ We concluded that Al(OH)₃ is best processed in the vehicle into a water-washed product containing 14 wt% water. A 40-kW (peak), 70-kW·h battery would be adequate for the needs of a 1200-kg five-passenger vehicle. Such a battery system would weigh about 240 kg and occupy a volume of 0.44 m³.

GEOHERMAL RESEARCH*

INTRODUCTION

The Geothermal Research program at LLL 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 brine causes scaling and corrosion of the 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 materials of interest in the high-temperature leg are the production-well casing and the surface piping that leads to the steam-brine separators. We have two experiments in progress to characterize the corrosion performance of well-casing and piping materials.

LOCALIZED CORROSION OF SURFACE-PIPING MATERIALS

The main concern with piping materials is their susceptibility to localized corrosion. Sections of the 10-in.-diam pipe at the San Diego Gas and Electric Company facility have shown severe attack at elbows and other locations where, presumably, pieces of lead sulfide scale are dislodged, which exposes the underlying steel to attack. We have observed that alloy steels containing up to 9% chromium and 0.5 to 1% molybdenum suffer much less corrosion in hypersaline brines (including brine that has been acidified to reduce the scaling rate). However, these Cr-Mo alloy steels do show some susceptibility to localized attack in the form of shallow pits.

To determine if pitting would limit use of these steels in geothermal applications, we wished to establish the time dependence of this pitting penetration. We began an experiment in June 1979 in which five spools were exposed to geothermal brine and steam; each spool contained nine commercial carbon- and alloy-steel coupons. Beginning one month after emplacement, one spool was removed each month and analyzed. The fifth spool was removed on January 22, 1980, but has not yet been analyzed; we expect that these upcoming results will agree with the results already obtained.

The data obtained for the third and fourth spools confirmed the trends suggested by the results from the first and second spools. The alloy steels are significantly more corrosion-resistant than the carbon steels. The carbon steels suffered high corrosion rates (in excess of 50 mils/year) and were attacked in a "mesa-canyon" pattern. These steels would be impractical for long term use, because the actual penetration rate is much higher than the overall corrosion rate indicates. On the other hand, the alloy steels showed low corrosion rates and only a slight vulnerability to localized corrosion. These steels would thus be suitable for piping and pressure vessels containing geothermal fluid. The costs of these alloy steels, relative to that of carbon steel, range from 2 times for 0.5Mo steel to about 3.2 times for 9Cr-1Mo steel. Thus the good materials performance of the alloy steels indicates that they are cost effective.

Prior experience indicated that carbon steels were marginally suitable materials for containing unmodified geothermal fluid. The piping (ASTM A106 Grade B) was made thicker to compensate for corrosion. With regard to material failure, it was felt that the high-temperature high-pressure carbon-steel piping would leak copiously before rupturing catastrophically, thus providing adequate warning. Also, the pipe-wall thickness was tested ultrasonically at periodic intervals.

The initial concern with the low- to intermediate-alloy steels (containing Mo [ASTM A 204] or Cr and Mo [ASTM A 387]) was pitting with perforation (or possible rupture) of the pipe and resulting loss of fluid. The high salinity of the brine coupled with scaling deposits create conditions favoring localized corrosion in many materials. Therefore, we undertook our experiment, in part, to survey the localized-corrosion

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tendency of the alloy steels. The results indicated that the alloy steels have only a slight tendency to pit; more importantly, the pits that do form grow in a lateral direction so that penetration of the pipe wall is not anticipated.

The corrosion rate appears to decrease with time, but this effect was not as pronounced as expected. Possibly, very high corrosion rates occurred initially (within the first week) until the scale covered the surface and offered some degree of protection. Corrosion still occurred because the principal scale component (PbS) and the principal corrosion products (Fe_3O_4 and FeS) are semiconductors, which allow transport of electrons. The corrosion-product layer forms on the steel and is covered in turn by the scale layer. Because these layers are porous, the solution has access to all surfaces. The data suggest that a steady-state reaction rate is established shortly after the initial exposure and that corrosion proceeds in a more or less steady-state manner. On the basis of these observations, a corrosion allowance for piping can be readily specified.

OIL SHALE RESEARCH*

INTRODUCTION

The Oil Shale program at LLL involves an *in situ* process for extracting crude oil from the western United States shale deposits. X-ray diffraction studies are being used to characterize the mineralogy of the raw shales and to determine what chemical products form when these minerals are heated.

CURRENT ACTIVITIES

Analysis of Raw Shale Used in the L-4 Retort Run

We conducted x-ray diffraction analyses on four samples of shale used in the L-4 run. This large retort run explored the feasibility of retorting at high rates (≥ 3 m/d). The charge consisted of two grades of Tract C-a shale; the grade change occurred at the mid-height of the bed. Temperature was controlled by varying the steam and air flow rates.

The shale specimens were pulverized and carefully blended to yield uniform and representative test samples. All four samples contained major amounts of dolomite and quartz, lesser amounts of calcite and analcime, small amounts of albite and microcline (sodium and potassium feldspars, respectively), and a trace of illite (an aluminosilicate clay). The presence of both albite and microcline in the samples had been seen only rarely in LLL retort samples analyzed previously.

The grade of oil shale has a very noticeable effect on the diffraction patterns. Quartz and calcite are markedly more abundant in the 46-gal/t samples than in the 24-gal/t samples. It should be noted that the diffraction patterns of microcline and the buddingtonite (ammonium feldspar, $\text{NH}_4\text{AlSi}_3\text{O}_8 \cdot 1/2 \text{H}_2\text{O}$) are quite similar. Because of this similarity, microcline could mask the presence of some amount of buddingtonite in these samples.

The diffraction patterns were obtained using our recently developed, automated x-ray system. This system features computer control of the diffractometer, storage of intensity-vs-angle data on a floppy disk, and in-lab computer analysis of the data. The computer analysis allows data smoothing, background subtraction, peak location, and operates through interactive graphics.

The presence of analcime can cause problems in the wet-chemical analyses of these shale. Some analcime dissolves during the acid leach during analyses, and the sodium and aluminum ions thereby liberated can be incorrectly attributed to the hydroxy-carbonate, dawsonite [a hydroxy carbonate, $\text{NaAl}(\text{CO}_3)(\text{OH})_2$].

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NUCLEAR WASTE MANAGEMENT*

INTRODUCTION

The Mineral Waste-Form program is evaluating and working to improve "Synroc" mineral ceramics,⁷ 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-equilibria 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. These studies will be conducted both in accelerated modes at high temperature and pressure and in long-term modes.

CURRENT PROGRESS

Synroc Development

We have studied the high-temperature processing parameters necessary to achieve equilibrium and preferential solid solution between radionuclides and specific synthetic minerals. Synroc minerals such as hollandite, zirconolite, and perovskite can accommodate these nuclides in their structures and are reported to offer superior leach resistance⁷. They are also reported to be thermodynamically stable with respect to other mineral phases that are expected to occur in defense-waste compositions processed at elevated temperatures.

We studied two methods of preparing mineral powder compositions. The first involves coprecipitation of metal salts dissolved in urea and decomposition of the salts to the oxides by calcination in air. The second involves grinding and mixing the oxides in a mortar and pestle. We have emphasized the first method because we expect to achieve more complete thermodynamic equilibrium through more intimate homogenization and smaller particle size. These factors should also improve the sintering and hot-pressing behavior, which will allow high-density mineral-waste forms to be processed at lower temperatures and pressures.

Small-scale hot pressing was conducted in a resistance-heated graphite die. We studied the behavior of three powders: M01 (Synroc B mixed oxides), U04 (urea coprecipitated Synroc B and 10 wt% simulated nuclear fission products), and U01 (urea coprecipitated hollandite, $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$). All three powders could be hot pressed at 1473 K and 13.8 MPa to > 99% of the theoretical density.

Hot pressing of M01 at 1473 K and 13.8 MPa yielded a density of 4.1 g/cm^3 and a porosity of 1.1%; hot pressing at 1573 K produced an almost identical density although grain-size development was about a factor of ten larger in the latter sample (Fig. 8). Several different crystalline phases in the size range of 5–50- μm range were apparent. Hot pressing at 1673 K produced conditions sufficiently reducing to convert almost the entire sample to the metal phase. X-ray diffraction and SEM results indicated that hollandite, zirconolite, and perovskite, and rutile were present in M01 samples.

The U04 powders were hot pressed at 1373, 1473, and 1573 K in both graphite and nickel liners. Nickel liners were used to explore the concept of both *in situ* encapsulation of radioactive waste and controlled oxygen fugacity. (For example, Ringwood⁷ recommended that an oxygen partial pressure over Ni/NiO for

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50 μm

FIG. 8. Synroc B. This sample of mixed oxides was hot pressed at 1573 K and 13.8 MPa for 1 h in graphite (M01HP3A, metallograph 9871).

10 μm

FIG. 9. Synroc C. This sample was prepared by urea coprecipitation and hot pressed at 1593 K and 13.8 MPa for 1 h in a nickel capsule (U04HP3A, metallograph 2088).

U. S. defense wastes high in Fe would insure that ferrous and ferric cations remain near the magnetite ratio for proper spinel mineral formation.) Figure 9 shows a U04 powder hot pressed in nickel at 1593 K. All major phases and radioactive-waste partitioning in those phases have been identified by electron microprobe analysis.

The U01 powders containing hollandite were hot pressed at 1473 K. The residual porosity of the sample was 1.7%, and at least two phases (hollandite and rutile) were apparent. Although we could achieve a single-phase hollandite using a 1:1:6 ratio of $\text{BaO}:\text{Al}_2\text{O}_3:\text{TiO}_2$ as the starting composition, we were unable to prepare single-phase hollandite if the TiO_2 was omitted.

Phase Equilibrium Studies of Synroc

We are working to learn the phase equilibria of Synroc as functions of calcination temperature, hot-pressing parameters (e.g., temperature, pressure, duration), composition, and starting conditions. During the last reporting period, we systematically evaluated the development of phases as a function of the calcination temperature.

X-ray diffraction measurements showed that calcination at 500 and 600°C yielded an almost completely amorphous product; calcination at 700°C yielded a largely single-phase, crystalline material that can be indexed on the basis of a cubic, pyrochlore-like structure. At higher temperatures, the pyrochlore structure disappeared as the Synroc B mineral structures appeared. No pyrochlore-type structure remained at calcination temperatures above 1100°C.

The diffraction lines of the pyrochlore phase were quite sharp, indicating a well-crystallized material of uniform composition. The change in lattice-constant of the pyrochlore phase undoubtedly represented changes (though uniform changes) in composition as the Synroc B minerals formed. The existence of a precursor pyrochlore phase may aid the successful fabrication of uniform and homogeneous Synroc products.

OFFICE OF BASIC ENERGY SCIENCES (OBES) RESEARCH

HOT-CORROSION*

Introduction

The hot-corrosion program is devoted to developing or 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. We are studying pure metals and binary alloys in simple controlled environments to develop a detailed theoretical model of the attack. We have used two major experimental techniques to date: thermogravimetric analysis (TGA) and electrochemical polarization in molten salts.

Current Progress

Previously, we have used TGA to study the behavior of 99.99% pure nickel in mixed atmospheres of CO_2 and SO_2 at 900°C .⁸ We reported that the parabolic and linear rate constants appeared to be functions of P_{S_2} , as shown in Fig. 10a. We reached this conclusion by plotting the rate constants of nickel oxidation as a function of the partial pressures of each species that could conceivably arise through decomposition or chemical reaction of a CO_2 - SO_2 mixture at 900°C . We found that the oxidation rate could be correlated only with P_{S_2} and P_{O_2} (Figs. 10a and 10b, respectively). A log-log plot of the oxidation rate appeared to be proportional to the sulfide concentration and inversely proportional to the oxygen concentration.

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FIG. 10. Reaction rate constants for the oxidation of nickel in a CO_2 - SO_2 atmosphere at 900°C as a function of (a) the partial pressure of S_2 and (b) the partial pressure of O_2 . The open circles represent rate constants determined in CO_2 - SO_2 atmospheres; solid circles give rate constants obtained in a CO_2 - SO_2 (65:35) atmosphere diluted with different amounts of argon. These data points show that the corrosion rate depends on the concentration of sulfur rather than of oxygen.

We then tried to determine whether the sulfur concentration was rate determining and whether the correlation for oxygen had real significance or was merely a function of P_{S_2} , i.e., as the sulfur concentration increased, maintenance of the equilibrium thermodynamic mixture of the gases present required formation of sulfur oxides, which decreased the oxygen concentration. To answer this question, we used TGA to measure the rates of nickel oxidation in three environments in which a CO_2 - SO_2 gas mixture of fixed proportions was diluted 5:1, 50:1, and 500:1 with purified argon. When these rate constants were plotted on Figs. 10a and 10b, the P_{S_2} data agreed very well with that obtained previously whereas the P_{O_2} data did not. This confirmed our expectation that sulfur is the rate-determining species and that the oxygen correlation was an artifact of the experiment.

Recent metallographic analysis indicated that the amount of nickel sulfide in the mixed nickel-oxide/nickel-sulfide corrosion scale increased as the sulfur concentration increased (Fig. 11). Furthermore, we observed a morphology change at about $P_{S_2} = -9.5$, the point of a discontinuous change of the rate constant. Presumably, at sulfur concentrations less than this value, the growth of nickel sulfide is inhibited by the presence of nickel oxide; above this value, the nickel oxide is increasingly unstable, and nickel sulfide forms without restrictions. This increase in the volume fraction of nickel sulfide in the corrosion scale as P_{S_2} increases is consistent with a transport-controlled interpretation of hot corrosion. Parabolic behavior of the oxidation rate constant implies diffusion of the rate-determining species through scale since the diffusion rate increases exponentially with temperature.

Using the analysis of Fueki and Wagner,⁹ we noted that the diffusivities of nickel in nickel sulfide estimated from these data are about 10 times less than the values obtained by linear extrapolation of values measured at lower temperatures to our experimental temperature. The observed diffusivities of nickel through nickel oxide are at least 1000 times lower than our estimated value and cannot account for the high observed rate constants. These results support our interpretation that the rate-limiting mechanism in this case is the rate of diffusion of nickel cations through the nickel-sulfide scale.

FIG. 11. Volume fraction of nickel sulfide in the nickel-oxide/nickel-sulfide corrosion scale as a function of the partial pressure of S_2 . The discontinuity of the rate constant at -9.5 is presumably caused by the presence of nickel oxide; below this value, nickel oxide inhibits nickel sulfide growth; above this value, the nickel oxide becomes increasingly unstable, and nickel sulfide formation is unrestricted.

THERMOCHEMICAL CYCLES FOR HYDROGEN PRODUCTION*

We are developing thermochemical cycles to produce hydrogen from water. Hydrogen generated by such cycles would be a renewable resource independent of fossil fuels and could use heat from such energy sources as high-temperature gas-cooled fission reactors, magnetic-fusion reactors, or solar concentrators.

We are concentrating our effort on a detailed study of chemistry of the ZnSe cycle. Our objective is to develop a basic understanding of the thermochemistry, kinetics, and mechanisms of several complex reactions in the cycle.

The thermochemical cycle under study consists of a series of chemical reactions operated in a closed loop so that the only inputs are water and heat and the outputs are separate streams of hydrogen and oxygen. All other chemical reagents are recycled within the system. The major reaction steps in the cycle are:

We are currently studying Reaction (4).

Decomposition of Zinc Sulfate

Zinc sulfate is decomposed in the ZnSe thermochemical cycle to liberate oxygen and to regenerate SO_2 as a reducing agent. This is the most endothermic step in the reaction scheme 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 $\text{SO}_2\text{-O}_2$ gas mixture. These characteristics indicate that the decomposition reaction is complex and that it will require effort to optimize decomposition.

Our first emphasis in studying ZnSO_4 decomposition was to establish the thermodynamic equilibria of the compounds involved. We are unable to determine the high-temperature properties of ZnSO_4 from literature sources because the heat and mass-transfer characteristics of previous experimental designs were limited. Also, formation of an oxysulfate ($\text{ZnO} \cdot 2\text{ZnSO}_4$) and a phase transformation of ZnSO_4 at 1015 K cast additional doubt on the validity of extrapolations from lower-temperature data. To obtain our own data, we are using drop calorimetry to measure the high-temperature enthalpies of ZnSO_4 and $\text{ZnO} \cdot 2\text{ZnSO}_4$ and the enthalpy of the ZnSO_4 α -to- β phase transition.

We are also studying the kinetics of ZnSO_4 decomposition. We hope to experimentally determine favorable conditions under which the reaction proceeds by minimizing the kinetic barrier to decomposition. During the previous quarter, we began studies on the decomposition behavior of ZnSO_4 using tungsten-image furnaces as a heat source. Results of these studies indicated that the rate of decomposition of ZnSO_4 depended markedly on the rate of heating through the ZnSO_4 α - β crystalline transition at 1015 K. These experiments also suggested the direction that our tests must take to obtain quantitative kinetic information.

As part of an effort to further develop thermochemical cycles, we outlined a scheme in which ZnSO_4 is substituted for H_2SO_4 in the sulfate-decomposition step in H_2SO_4 -based cycles. This modification could be used to overcome many of the difficulties presently associated with sulfate decomposition in these cycles.

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Thermodynamic Study

A pin-hole leak developed in the capsule of our original ZnSO_4 calorimetry drops and necessitated repeating several of the data points. Last quarter we made four more calorimetry drops on a new capsule of ZnSO_4 . Although initial calculations of the new data compared well with our original data, closer comparison of the two data sets during curve fitting indicated a possible discrepancy between the two data sets. Further questions about the data were raised because modifications were made on the calorimeter by another user between our experiments. Also, the second series of data was obtained with a different furnace system that is normally used only with much higher temperature drops. For these reasons, we felt additional data was needed.

This reporting period, we converted the heating unit in the calorimeter back to the platinum-wound resistance furnace used in our initial studies. We also recalibrated the calorimeter block. We completed several ZnSO_4 drops, and our preliminary calculations indicated these results fit better with our second series of data than did the original series. A possible explanation for this is that a purer sample of ZnSO_4 was used in the second series of drops. Although the ZnSO_4 sample for the second series was analyzed before being sealed in the capsule (wet chemical analysis indicated 100% ZnSO_4), the first-series sample was analyzed only after the drops were completed. Because a pin-hole leak developed sometime during the original experiments, it is impossible to know the starting composition of that sample. Perhaps some of the original sample was converted to zinc oxysulfate during drying. This most recent series of drops used the same sample as was used in the second series of drops.

OPTICAL MATERIALS WITH REDUCED NONLINEAR EFFECTS*

Introduction

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 fluoride glasses have small predicted nonlinear-index coefficients, they 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 lasers. Our part in this effort is preparation and characterization of beryllium-based glasses and crystals.

Zinc chloride glasses hold interest for laser applications because a ZnCl_2 lattice containing Nd^{+3} should have broad fluorescence line widths and low laser gain. To support investigation of these glasses, we are attempting to prepare ZnCl_2 glasses doped with NdCl_3 .

Current Progress

We continued our efforts to prepare Nd-doped ZnCl glasses but were not successful. Although we prepared binary glasses of ZnCl_2 -KI with and without the addition of excess iodine, all attempts to prepare ZnCl_2 - NdCl_3 were unsuccessful because the NdCl_3 precipitated.

We explored new phases of BeF_2 and AlF_3 by extending the technique of using aqueous HF to precipitate the fluoride phase from the chloride phase. Treatment of a solution 2M in BeCl_2 and 1M in AlCl_3 with HF gave no fluoride precipitate, however; evaporation of the solution yielded a yellow-green gel. We plan no further work.

We prepared low-refractive-index glasses of BeF_2 - EuF_3 and BeF_2 - NaF - EuF_3 , and we will evaluate them in laser line-narrowing experiments.

We synthesized $\text{Na}_3\text{Li}_3\text{Al}_2\text{F}_{12}$ (cryolithionate) powder by fluorinating AlCl_3 , LiCl , and NaCl powders with aqueous HF. Powder-pattern data indicate a *cubic* garnet lattice ($a = 12.12 \text{ \AA}$).

Crystals of materials that have low indices of refraction have significantly higher thermal conductivities than the corresponding glasses. This factor permits higher repetitive pulsing rates, and we have readied our state-of-the-art crystal-growing equipment to grow Cr^{+3} -doped BeAl_2O_4 .

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FLUORESCENCE-LINE NARROWING OF AMORPHOUS SOLIDS*

Introduction

The objective of this project is to investigate local structure and interactions in glasses by applying laser techniques for fluorescence-line narrowing. This project has both experimental and theoretical parts. Experimentally, we measure the fluorescence-line-narrowing spectra; theoretically, we model glass structures using a Monte Carlo computer code. In addition, we compute the optical properties of the rare-earth ion in our simulated glass. This investigation is nearly complete for the Eu-doped BeF_2 glass.

Current Progress

We completed an extensive set of Monte Carlo computer simulations of Eu-doped BeF_2 glasses of different fictive temperatures, densities, and interionic potentials. We analyzed the equilibration and structure of these glasses using these results. Colored ball-and-stick models were drawn by computer using the ATOMLLL program.

We wrote a program that computes the energy levels of the ^7F term of Eu^{+3} in the simulated glasses. Full J-mixing of all seven manifolds is possible. The program uses a point-charge model of the crystal field, and, using only the second-order crystal field, we found very good agreement between the calculated and experimental optical properties (Fig. 12). Although we consider this calculation to be only representative and accept it with reservations because of the well-documented weaknesses of the point-charge model, we are encouraged by this good agreement and plan more accurate molecular-orbital calculations.

We have also made a unique analysis of the structure around the rare-earth atom and its effects on optical properties using a principal-axis transformation. We found that splitting of the $^7\text{F}_1$ manifold of Eu increases with increasing distortion of the moments of the ligand charge distribution.

We measured the fluorescence-line narrowed spectrum of the $^5\text{D}_0$ - $^7\text{F}_1$ transition of BeF_2 :0.05-wt%- EuF_3 at 30 K. To excite the Eu with a CMX-4 flashlamp-pumped dye laser, we used Rhodamine 6G dye in trifluoroethanol. Use of this solvent shifts the emission maximum of the dye to about 5800 Å, which roughly coincides with the absorption peak of the $^7\text{F}_0$ - $^5\text{D}_0$ transition of Eu in Be_2 glass. Because the signals are very weak, we used photon-counting detection to measure signal intensity. We found that, even at 30 K, ion-ion energy transfer is significant in the sample during the first 500 μs after excitation. Figure 13 shows the variation of the emissions as a function of laser excitation wavelength. Several spectra in Fig. 13 were used in Fig. 12.

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FIG. 12. Comparison of calculated distribution of energy levels and experimental spectra of Eu in BeF₂ glass. The smooth lines are the experimental spectra and are the same as in Fig. 13. The histograms are the calculated distribution of energy levels. The top two curves are the broad-band-excited spectra while the bottom two are line-narrowed spectra. For the FLN case, only sites with a given 5D_0 - 7F_0 energy difference were used for the histogram of 7F_1 levels. The histograms give only the distribution of energy levels, and the calculation is not intended to reproduce the relative intensities of the observed bands.

FIG. 13. Line-narrowed fluorescence spectrum of the $^5D_0 \rightarrow ^7F_1$ transition of trivalent Eu in BeF_2 glass as a function of laser excitation wavelength. For each curve, the subset of ions that is excited has a $^5D_0 \rightarrow ^7F_0$ energy difference that is resonant with the laser frequency. Variation in the positions of the three lines is caused by site-to-site variations in the energy levels and transition strengths.

RAPIDLY-QUENCHED MATERIALS*

Introduction

Very rapid cooling of metallic alloys produces "metallic glasses" that have 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 (10^5 – 10^6 K/s) to suppress the nucleation and growth of the crystalline phase.

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Of particular interest to us during this past reporting period has been the synthesis of high-specific-strength (σ_y/ρ) material. Because of its low density and relative high strength, beryllium is an obvious choice as one constituent in any high-specific-strength alloy.

Several techniques, such as melt-spinning, arc-hammering, and sputtering, are available to rapidly quench molten alloys. Most of the viable binary and ternary candidate alloys were investigated by melt-spinning, though a few samples were arc-hammered to take advantage of the higher quench rate of this technique. We have now shifted our efforts to sputtering as a means of synthesizing high-specific-strength material. In addition, we have started a series of experiments to stabilize β -Be (bcc) phases by either melt-spinning or arc-hammering. If β -Be can be stabilized at room temperature, then the increase in ductility should greatly benefit beryllium technology.

Current Progress

We found three ternary systems (Be-Sc-B, Be-Ti-B, and Be-Fe-B) having at least one composition that becomes amorphous on melt-spinning. These compositions are $\text{Be}_{40}\text{Sc}_{55}\text{B}_5$, $\text{Be}_{35}\text{Ti}_{60}\text{B}_5$, and $\text{Be}_{20}\text{Fe}_{70}\text{B}_{10}$, all of which could be rapidly quenched into glassy ribbons by melt-spinning. [The $\text{Be}_{40}\text{Sc}_{55}\text{B}_5$ alloy could only be quenched into completely glassy (95%) material by arc-hammering.] The mechanical properties of these alloys were measured or estimated. Because none of the specific strengths of these materials exceeded that of $\text{Be}_{30}\text{Ti}_{65}\text{B}_5$, which has the highest specific strength known, we decided to concentrate on sputtering as a technique to form high-specific-strength amorphous materials.

DIFFUSION IN SILICATE MINERALS*

The Geosciences Division of DOE Office of Basic Energy Sciences recently funded our proposed research on diffusion in silicate materials. We and the Earth Sciences Division at LLL will cooperate on this project.

Olivine [$(\text{Mg,Fe})_2\text{SiO}_4$] is a major constituent in the earth's mantle and has been studied previously at LLL. 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 plan to make these measurements in olivine and other silicates in the future. We will anneal iron-free olivine crystals in ^{18}O gas at about 1300°C and then measure the extent of ^{16}O - ^{18}O exchange by bombarding the specimen with protons to convert ^{18}O to ^{18}F , which emits positrons and can be quantified using photographic film. This technique allows us to handle the tracer as if it were radioactive.

We are also preparing to use atomic tracers to measure ionic transport in olivine crystals in an electric field—the so-called “Chemla Experiment.” From our results, we expect to gain specific information about the sequence of jumps made by an atom as it migrates through the crystal. This information will provide a solid basis for interpreting creep, chemical reactions, and order-disorder kinetics in olivine. We will use iron radiotracers first because they are easy to work with, and we also plan to investigate silicon and magnesium migration in olivine since data on their migration rates do not currently exist.

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MATERIAL RESEARCH NOTES

RESTORATION OF MECHANICAL PROPERTIES OF MACHINING-DAMAGED BERYLLIUM*

Machining damage can seriously degrade the mechanical properties of beryllium. We recently completed a study in which substantial machining damage was introduced in two different structural beryllium grades.¹⁰ During the last reporting period, annealing and surface etching were examined as two methods for relieving this damage.

We found that annealing at or above 700°C changed certain mechanical properties in both grades of beryllium (Fig. 14). The yield-point phenomenon disappeared, the 0.2%-yield and ultimate strengths decreased, and hardness decreased. The magnitude of these changes depended on the annealing temperature and the beryllium grade. Thus, it is important to monitor these mechanical properties of the sample if annealing is employed to eliminate the effects of machining damage.

We also found that chemical removal of only 25 to 50 μm of material would restore the original ultimate strength and ductility of extensively machining-damaged material (Fig. 15). The 0.2%-yield strength and, when present, the upper yield point were not noticeably affected by the presence of machining damage or by chemical etching.

We learned that both annealing and etching treatments could restore mechanical properties without completely removing all microscopic evidence of machining damage. This indicated that the deleterious effects of machining resulted from damage in the first 25 to 50 μm below the surface. Although twinning and microcracks are usually suggested as the critical factors in machining damage, residual stresses and a layer of textured material at the surface have also been suggested. We did not see microcracks other than those that may have resulted from folding or smearing of surface material by machining or polishing processes, and these microcracks were observed before and after the machined samples were annealed. Although annealing may eliminate internal cracks, it probably does not close surface cracks; therefore, since annealing restored the mechanical properties, it was not the presence of surface microcracks that caused the degradation of mechanical properties observed in machined samples.

Microhardness surveys of machined specimens showed that, before annealing, the microhardness of the 100- to 150- μm -thick layer near the surface was much greater than that of the remainder of the sample (Fig. 16). Annealing decreased the surface microhardness of beryllium samples, and higher annealing temperatures had the greatest effect. We believe that in future studies, changes in microhardness can be used to follow the annealing and aging processes and correlated with changes in microstructure and tensile properties.

Although twins have been shown to act as substantial stress concentrators, we noted twinned microstructures at the surface of tensile specimens that exhibited optimum mechanical properties. Although the density of twins was not high in such cases, this observation demonstrates that twinning by itself does not necessarily degrade mechanical properties of beryllium.

The mechanical working of beryllium can easily produce strong textures. For example, rolling beryllium sheet can quickly produce a (0001) texture that is four to ten times greater than would occur randomly. If machining beryllium produced an equivalent situation, a basal surface texture could be produced in which the prism planes tend to be approximately perpendicular to the tensile axis—a surface layer ideally oriented for prism-plane cleavage. Our study indicated that, on the basis of the optical appearance of the microstructure, the very hard surface layer, and the response of surface regions to annealing, the surface layer of our samples was highly worked.

This evidence suggests that a strain-hardened and textured surface layer may be the basic cause of degraded mechanical properties in machining-damaged beryllium. If so, simple metallography and tensile tests alone cannot indicate the optimum annealing times and temperatures. Also, surface microhardness might be used in some situations to ascertain the extent of machining damage. Although this latter test is not a non-destructive test and risks initiating microcracks at the indent, it does avoid cutting up the entire sample to remove metallographic samples.

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FIG. 14. Effects of different annealing temperatures on the mechanical properties of machining-damaged samples of (a) 1319A beryllium and (b) S200E beryllium. Samples were treated for 1 h.

FIG. 15. Effects of chemical etching on the mechanical properties of machining-damaged samples of (a) 1319A beryllium and (b) S200E beryllium.

FIG. 16. Effects of different annealing temperatures on the microhardness of machining-damaged samples of (a) 1319A beryllium and (b) S200E beryllium.

SIZE DISTRIBUTION OF AEROSOL FLYASH PARTICULATES*

We are analyzing the size distribution of aerosol flyash particulates collected by two types of cascade impactors installed at the Huntington Canyon and Hunter power plants (HU01) in Utah. By determining these particle-size distributions, we will be able to more accurately correlate elemental composition with particle size. This work is sponsored by DOE through the Environmental Sciences Division at LLL.

During the last reporting period, we analyzed particles taken from the 8-stage Washington Mark III and the 12-stage Washington Mark V impactors. The Mark V was operated in the "low pressure" mode. In this mode, the backup filter and several stages above it are operated at reduced pressure, which allows these stages to collect more submicron-size particles than would be obtained under normal pressure conditions.

Particles were prepared for analysis by dispersion in hexane using a bath sonicator and filtration through 0.1- μm Nuclepore filters. The number-size distributions were obtained from scanning electron micrographs (SEM) using the Zeiss particle analyzer. In extrapolating number distributions to mass distributions, two magnifications were used in most cases to better assess the large-particle contribution.

As expected, the median particle diameter decreased with increasing stage number. In the case of the Mark III, however, the diameters of particles taken from stages 1 and 8 deviated from this general observation. Stage 1 particles were smaller than expected, which we have seen before; the separation capabilities of the first stage of an impactor stage is generally less sharp than the successive stages. Stage 8, which is a Nuclepore backup filter, exhibited a bimodal distribution as a result of particle deflection and re-entrainment. Mass distributions for stages 6 and 7 also show significant deflection from higher stages.

In the case of the Mark V, the additional four stages allowed us to obtain five particle fractions in the submicron range compared to only two from the Mark III. We were unable to determine distribution parameters for stage 12 (a Fluoropore filter) using our analytical method. Direct SEM inspection indicated that the largest particles were about 1 μm in diameter, but the fiber matrix and binder prevented accurate sizing of particles less than 0.5 μm . Stage 11 provided a particle fraction having a size range normally collected only on backup filters; the distribution had a single mode and was uncontaminated by the large particles usually found on other backup filters.

RADIATION-INDUCED CORROSION IN STEAM GENERATORS†

Many steam generators in pressurized water reactors (PWR) have suffered a corrosion-related problem called tube denting. The PWR steam generator is a tube-and-shell heat exchanger between the primary water, which is heated by the nuclear core, and the secondary water, which is converted to steam and drives the turbine. The corrosion problem occurs in the gap between the carbon steel support plates and Inconel 600 tubes that contain the primary water. Exposure of the tube support plate to the secondary water causes some corrosion of the steel, and the voluminous corrosion product (Fe_3O_4) expands against the Inconel 600 tubing. Eventually, constriction of the tubing restricts flow and, if a large number of tubes are plugged, the reactor must be shut down.

The nuclear power industry has investigated different aspects of this problem. Our involvement concerned the possible effects that radiation from the primary water system might have on the corrosion process. We evaluated previously published reports on this radiation effect and other related aspects of the tube denting problem for the Electric Power Research Institute and concluded the following:

- Gamma and beta radiation can penetrate the Inconel 600 tube wall from the primary water side to the secondary water side. The source of radiation in the primary side is ^{16}N , and the total radiation flow to the secondary side is estimated at 2.4×10^{13} eV/g-sec.

- The radiation does not affect the solid constituents (steel, Inconel 600, Fe_3O_4) but does influence reactions of species in the secondary water. For example, the secondary water system in a PWR is intentionally alkalized and deoxygenated by adding NH_3 and N_2H_4 , respectively. Also, ionic species appear unintentionally in several forms: as residual impurities in the make-up water, as leakage from the condenser cooling water, or as soluble corrosion products from components in the secondary loop.

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● Radiation probably oxidizes some iron present in the secondary water system from ferrous ions to ferric ions. Because of the alkaline pH (about 9), the ferric ions precipitate as the hydroxide. Also, a small amount of hydrogen gas is produced by the radiolysis of the secondary water.

The relatively small amounts of solid iron products and hydrogen gas are insignificant with respect to the amounts of these materials formed by the ordinary corrosion processes in the water. Therefore, we concluded that radiation does not significantly contribute to the tube denting problem. Solutions to this problem, therefore, must be directed toward selecting better materials or reducing the corrosion of carbon steel by improving water treatment.

SINTERING OF COVALENT SOLIDS*

Introduction

Most metallic and non-metallic fine-particle-size powders can be sintered to nearly the theoretical density when heated to about 75% of their melting point. One group of solids, however, cannot be densified by the conventional sintering process, i.e., without using high pressure and/or adding impurities. This group includes such technologically important solids as Si_3N_4 , B_4C , SiC , AlN , Si , and Ge ; these materials are uniquely identified because they are all covalently bonded. Several hypotheses, which involve both kinetic and thermodynamic factors, have been suggested to explain their non-sinterability, but the underlying cause of this peculiar behavior remains unclear.

We are studying the sintering of covalent solids and have selected Ge as a model system. Most of the properties of Ge have been well-documented, including some of the important mass-transport coefficients. If we elucidate the reasons for the non-sinterability of Ge , then that knowledge can undoubtedly be applied to understanding the other covalent compounds.

Matter can be transported in solids at temperatures below the melting point by several mechanisms: bulk diffusion, surface diffusion, grain-boundary diffusion, and evaporation-condensation. Equations have been derived for model systems, such as sphere-to-sphere or sphere-to-plate transport, by which the mechanism can be distinguished:

$$\frac{x}{r} = Kt^{1/3} \quad \text{evaporation—condensation} \quad (1)$$

$$\frac{x}{r} = Kt^{1/7} \quad \text{surface diffusion} \quad (2)$$

$$\frac{x}{r} = Kt^{1/6} \quad \text{grain-boundary diffusion} \quad (3)$$

$$\frac{x}{r} = Kt^{1/5} \quad \text{bulk diffusion} \quad (4)$$

where

x is the radius of the neck,
 r is the radius of the particle,
 K is a constant containing the diffusion coefficient,
 t is time.

Equations (1) and (2) are non-densifying mechanisms.

We selected the sphere-plate model to study the sintering of Ge .

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Current Progress

Germanium microspheres (100–200 μm in diameter) were fabricated by impinging a molten jet of Ge onto a spinning copper wheel. After the spheres were riffled and sized, they were placed in a Ge crucible. [The crucible was formed by hot-pressing a Ge ring onto a polished (100) or (110) surface of a single crystal plate.] Different crucibles containing 10 to 50 microspheres were annealed at 850°C for 2 to 100 h under either hydrogen, argon, or vacuum. After removal from the furnace, the microspheres were carefully fractured from the crucible surface, and the neck radius (x) was measured. We collected x/r -vs-time data in this manner.

Our initial runs were made in hydrogen to remove the oxide layer, but we discovered that the hydrogen reacted with Ge to form a volatile species that transported through the vapor phase. Nodules and numerous fine needles at the neck surface indicated this type of transport. We thus used argon in all subsequent experiments except one that was conducted in vacuum. Even though there was a large scatter of the data, a plot of $\log(x/r)$ vs $\log t$ gave a slope of about 1/3, which suggested material transport by evaporation–condensation. Because the vapor pressure of Ge is very low at 850°C, we concluded that there must be enough water vapor to act as the vehicle for transport.

The calculated neck size at selected times at 850°C (assuming that all the mechanisms were operating simultaneously) were reasonably close to the average experimentally measured neck size. As with most other solids, surface diffusion seemed to predominate at the initial stage of sintering. To date, the sintering behavior of Ge has not differed from that of other metallic or inorganic solids.

We plan to grind some Ge boules into a fine powder in a ball mill. After leaching these powders to remove any iron introduced from the steel balls, the powders will be cold-pressed and annealed in an argon or vacuum environment. We will follow the progress of sintering or densification by measuring the surface areas and the sample dimensions.

PRESENTATIONS

S. A. Brawer	Monte Carlo Studies of Rare Earth Doped Beryllium Fluoride Glass	Invited talk. Rochester, NY, October 8, 1979
S. A. Brawer		Invited talk. Univ. Park, PA, October 9, 1979
S. A. Brawer		Invited talk. Stanford Univ., November 1, 1979
C. F. Cline	Application of Metallic Glasses	Invited lecture and chairman. Electrochemical Society, Los Angeles, Symposium on Amorphous Metals and Films, Oct. 14-16, 1979
		Invited lecture and co-chairman. The Metals Research Society Annual Meeting, Cambridge, MA, Nov. 26-30, 1979.
C. F. Cline	Properties and Fabrication of Glassy Metal Alloys	Invited lecture. Sandia Lab Albuquerque, NM October 19, 1979
C. F. Cline	High Rate Consolidation of Metallic Glasses and Ceramics	Invited lecture. Oak Ridge National Laboratory, January 22, 1979
J. F. Cooper	Materials Problems in the Development of the Aluminum-Air Electric Vehicle Battery	Materials and Processing Congress, Fall 1979 Meeting of the American Society of Metals, Chicago, IL, November 13-15, 1979

J. F. Cooper	Metal-Air Batteries	DOE Battery and Electrochemical Contractors' Conference, December 10-12, 1979, Washington, DC
J. F. Cooper E. Behrin	Aluminum-Air Electric Vehicle Research and Development Program	Program Review Livermore, November 26, 1979
W. R. Holman	CVD Tungsten/Rhenium at LLL	(CMB6), October 18, 1979
J. B. Holt D. M. Makowiecki	Sintering of Germanium	Joint Fall Meeting of the Basic Science and Nuclear Divisions, The American Ceramic Society, New Orleans, LA, October 14-17, 1979
R. W. Hopper	Composition Distribution in Multicomponent Glasses in Nonuniform Temperature Fields	American Ceramic Society, Bedford, PA, October 10-12, 1979
R. W. Hopper	Mechanical Properties of Metallic Glasses	156th Meeting of the Electrochemical Society, Los Angeles, October 15-16, 1979
P. K. Hosmer	Solar Furnace Decomposition Studies of ZnSO_4	Users Association Solar Fuels Workshop, Albuquerque, NM, November 28-29, 1979
D. M. Makowiecki R. Naylor L. M. Jones J. B. Holt	Surface Self-Diffusion on Germanium	Joint Fall Meeting of the Basic Science and Nuclear Divisions, The American Ceramic Society, New Orleans, LA, October 14-17, 1979

R. M. Scanlan
J. E. Johnston
P. A. Waide

Manufacturing and Quality
Assurance for the MFTF
Superconductor

8th Symposium on
Engineering Prob-
lems of Fusion
Research, San
Francisco, CA,
November 13-16,
1979

J. J. Truhan
T. Jeys
R. P. Kershaw

Polarization of Nickel in Molten
Sodium Sulfate

156th Meeting of
the Electrochemical
Society, Los
Angeles, CA,
October 14-19, 1979

PUBLICATIONS

S. A. Brawer	The Glass Transition in BeF_2 : A Monte Carlo Study	UCRL-83524
S. A. Brawer M. Weber	Relation Between Structure and Spectroscopy for Monte-Carlo Simulated Rare-Earth-Doped BeF_2 Glass	UCRL-83682 Abstract
S. A. Brawer M. Weber	Monte Carlo Study of the Structure of Rare-Earth-Doped BeF_2 Glass	UCRL-83683 Abstract
S. A. Brawer M. Weber	Theoretical Study of the Structure and Optical Properties of Rare-Earth Doped BeF_2 Glass	UCRL-83803
C. F. Cline E. A. Kramer W. L. Johnson W. M. Keck	The Effects of Neutron Irradiation on a Super-Conducting Metallic Glass	Appl. Phys. Lett. 35(10), 1979
J. F. Cooper	Weight and Volume Estimates for Aluminum-Air Batteries Designed for Electric Vehicle Applications	UCRL-83881
D. N. Cornish H. L. Harrison A. M. Jewell R. L. Leber A. R. Rosdahl R. M. Scanlan J. B. Zbasnik	Progress on Lawrence Livermore Laboratory's Superconducting High Field Test Facility	To be published in the Proceedings of the 8th Symposium on Engineering Problems of Fusion Research, 1980
P. T. Cottrell W. D. Ludemann R. D. McCright	Computer Modeling of Nuclear Waste Storage Canister Corrosion	
J. E. Hanafee	Effect of Annealing and Etching on Machining Damage in Structural Beryllium	UCRL-83303 In print September 1979
J. E. Hanafee	Contribution to "Technology Forecast '80"	<i>Metal Progress</i> , p. 50-51 January 1980
C. L. Hoenig R. A. Otto	Hot Pressing and Sintering Studies of Ceramic Waste Forms	UCRL-83655 Abstract

C. L. Hoenig R. Lim R. Elson R. A. Otto C. A. Slettevold	Powder Preparation for Ceramic Waste Form Synthesis by Means of Urea Coprecipitation	UCRL-83657 Abstract
C. L. Hoenig W. Durham W. Steete W. Beiriger J. Tewhey	Phase Equilibria and Radwaste Element Partitioning in Synroc Waste Forms for U.S. Defense Waste	UCRL-83658 Abstract
R. W. Hopper	Ductile Failure Via a Homogeneous Strain Field	UCRL-83408
P. K. Hosmer O. H. Krikorian	The High Temperature Enthalpy of Zinc Sulfate and Zinc Oxy-Sulfate	UCRL-83719 Abstract
P. K. Hosmer O. H. Krikorian	Solar Furnace Decomposition Studies of ZnSO_4	UCRL-83634
O. H. Krikorian P. K. Hosmer	The Utilization of ZnSO_4 Decomposition in Thermochemical Hydrogen Cycles	UCRL-83540 Abstract
O. H. Krikorian	Materials Problems in Production Transport, and Storage of Hydrogen	UCRL-83771
O. H. Krikorian	Project Status Report: Materials Development for Thermochemical Cycles Period: September 1979	UCID-17835-79-9
W. D. Ludemann L. Abrego R. D. McCright	Corrosion Studies on Retrievable Spent Fuel Containers: A Progress Report	UCID-17917
R. M. Scanlan	Superconducting Materials	To be published in Annual Review of Materials Science 10, 1980
R. M. Scanlan J. E. Johnston P. A. Waide B. Z. Zeitlin G. B. Smith C. T. Nelson	Manufacture and Quality Assurance for the MFTF Superconductor	To be published in the Proceedings of the 8th Symposium on Engineering Problems of Fusion Research, 1980

C. Spencer
E. Adam
E. Gregory
W. Marancik
P. Sanger
R. Scanlan
D. Cornish

Fabrication and Testing of the
Nb₃Sn Superconductor for HFTF
(High Field Test Facility)

To be published in the Proceedings
of the 8th Symposium on Engineer-
ing Problems of Fusion Research,
1980

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L. M. Wagner

Fabrication of Thin Be Windows for
X-Ray Applications

UCRL-83767

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