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# SELECTED ADVANCES IN MATERIALS RESEARCH

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This report describes several notable findings emanating from materials research that should have a beneficial impact on technological advancement in the future. The impetus and support for the research came mainly from the Department of Energy and Department of Defense. Specifically, the report will deal with the specialty product GRAPHNOL, a new class of high-temperature brazing alloys for joining refractory components, gel-sphere-pac process for manufacture of nuclear fuel, and noble-metal fuel cladding for service in radioisotope thermoelectric generators designed to provide auxiliary power aboard spacecraft for planetary exploration.

## I. GRAPHNOL: An Improved Heat-Resistant Material

GRAPHNOL is a bulk graphite product developed for special-duty service in ballistic and other types of military missiles. The product serves the dual function of heat-sink and ablation-sublimation material and is unique in that it can withstand 100% greater strain before failure and thermal shock treatments 50% more severe than other available graphites. The material is polycrystalline and nearly isotropic. Moreover, it retains the other exceptional properties that make graphite a most versatile material, such as high strength-to-weight ratio, good thermal conductivity, ease of machineability, increasing strength with increasing temperature up to 2750°C, and useful strength above. The improvement in high-temperature performance has been achieved mainly through control of intergranular bonding and void geometry.

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Conventional graphites are normally produced by combining carbonized or graphitized filler materials with hydrocarbon binders derived from organic precursors. During subsequent heat treatment to produce the final aggregate body, the filler material undergoes essentially no dimensional change due to shrinkage, whereas the binder shrinks drastically as it is reduced from hydrocarbon to graphite form. As a result, the final product contains a network of angular voids that can be only partially "healed" by further heat treatment and impregnation. This pore morphology obviously weakens the overall structure.

The effect of pore morphology becomes particularly significant when stresses are generated internally by differential thermal expansion of neighboring crystallites. One example is crystallite growth in the *c*-direction during exposure to neutron radiation. Another example is crystallite expansion in the *c*-direction during thermal stress or shock. These adverse effects induced by preferred orientation of the crystallites can be overcome to a large degree by stengthening interparticle boundaries and reducing the tendency of micropores to act as stress risers. The desired structure, therefore, is monolithic with smaller and less angular voids that give rise to a less dominant pore texture than is usually present in coke structures.

In their product development work at ORNL, C. R. Kennedy and W. P. Eatherly actually followed an alternate approach. They used green coke taken directly from the coke drum to serve as filler material. This change in feed material offered two distinct advantages: (1) the chemical activity on the surface of the coke particles was high and contributed significantly to ease of bonding with the binder. (2) The volume shrinkage of the coke filler more closely matched the shrinkage characteristics of the binder during pyrolysis. However, several additional processing modifications were required before green coke feed material could be successfully used to yield a structurally sound product.

The new product, GRAPHNOL, is definitely superior to conventional graphites and exhibits a 50% improvement in resistance to thermal shock, nearly 100% improvement in fracture strain, 10% increase in thermal conductivity, and better flexure strength. The material is technically competitive at a fraction of the cost with most carbon-carbon fiber composite materials.

Among the existing and potential areas where this new technology might be applied with advantage are:

- radiation-resistant nuclear grades for moderator and reflector service in high-temperature gas-cooled reactors designed for electric power production by either the conventional steam cycle or a direct gas turbine and/or for the production of high-quality process heat for industrial use;
- materials with improved thermal shock and ablative properties for wing leading edges, nose cones, and structural members in aerospace vehicles;
- erosion-resistant materials for limiters and beam stops in Tokamaks designed to produce electrical power from fusion energy;
- electrodes based on coal derivatives and employing technology of this nature required by the ferrous metals industry for melting in electric arc furnaces; and
- high-strength to low-density parts for weight saving in the automobile industry.

## II. Brazing Alloys for Joining Graphite to Itself and Dissimilar Materials

A new class or family of high-temperature metal alloys has been formulated for joining graphite and dissimilar materials into an integral structure by brazing. The main function of the alloys is to join graphite to graphite, steel, alumina, and refractory metals, so that the desirable characteristics of each component part can be incorporated with advantage into the same engineering system. The resulting joint is structurally sound, durable, gastight, shock-resistant, and thermally stable over a wide temperature range.

Previous experience indicates that proper wetting of the nonmetallic substrate and obtaining the degree of flow required to secure a sound structure would be problem areas. Premetallizing the substrate was investigated and abandoned because the procedure required an extra costly step and limited the temperature at which the joint could be used. The researchers overcame these difficulties and produced a composite end product with excellent high-temperature mechanical properties and good corrosion resistance by judicious choice and combination of the right metallic elements in the correct proportion. Suitable alloys were found, in particular, in the titanium-chromium-vanadium and titanium-zirconium-germanium systems.

Many advanced energy-conversion concepts call for use of high-temperature heat exchangers tubed with nonmetallic materials to obtain greater thermodynamic efficiency. Graphite, silicon carbide, and other carbon products are potential candidates for fabrication of such tubes, because of their excellent characteristics and resistance to chemical attack. The joining of graphite tubes to provide a contiguous bond will be mandatory if optimum efficiency is to be realized. Hence, these new alloys should aid in the developmment and commercialization of advanced energy systems designed to operate at elevated temperatures.

## III. Gel-Sphere-Pac Fuel is Easier to Fabricate and Performs Better than Conventional Pelletized Fuel

A relatively new process has been developed by the Fuel Cycle Technology Group at ORNL for the manufacture of new and recycle fuel for service in nuclear power plants. The process involves the formation of dense, free-flowing microspheres and subsequent loading of spheres into metal containment tubes. The motivation for the development is severalfold and can be traced to the following considerations: the economic incentive to upgrade fuel burnup capability and thus reduce operating costs by increasing fuel residence time in the reactor, the keen desire to eliminate or greatly reduce exposure of operating personnel to radiation during processing of recycle fuel, and interest in proliferation-resistant nuclear fuel cycles to thwart terrorist activity and other unauthorized use.

The new fabrication technique, designated as the gel-sphere-pac process, offers several advantages and is equally suited for all types of nuclear fuel cycles. Simplified processing steps are one great advantage of the technique, particularly when applied to remotely operated processing facilities. Unlike fabrication of conventional pelletized fuel, no milling, pressing, or grinding operations are required; hence, dusting and the attendant time personnel are in contact with the fuel are eliminated. Nuclear fuel materials in aqueous solution or suspension are formed into spherical droplets, chemically and/or physically treated to form the desired ceramic substance, dried, and calcined. Spheres of selected sizes and/or compositions are blended and loaded into the cladding tubing with low-energy vibration aiding packing to the desired density. All fuel streams consist of either liquids or spherical particles, which can be easily conveyed within the plant in closed pipe systems.

Evidence from irradiation tests indicates that sphere-pac fuel has significant performance advantages over pelletized fuel. For instance, there is less chemical and mechanical interaction between fuel and cladding (fuel containment alloy). Reducing such interaction permits greater freedom of operation in the sense that the fuel can be brought to rated power faster, operated in load-following mode, and taken to higher burnup with less risk of failure. Furthermore, an increased fuel lifetime gives rise to improved resource utilization.

Results achieved to date have been most encouraging. Full-scale fuel components have been compacted to the densities required for both light-water reactor and fast breeder reactor applications. Several units are undergoing test in power plants being operated by the utilities. The technical information acquired thus far is currently being transferred to industry for commercial utilization.

## IV. New Noble-Metal Alloys Enhance Containment of Radioisotopic Heat Sources

A neat example and application of the use of radioactive decay heat is to provide auxiliary power aboard spacecraft designed for exploration of planetary space. The decay heat emitted from $^{238}PuO_2$ over a long period is of sufficient quality that it can be converted directly into electricity by use of thermoelectric generators. This feat was successfully accomplished to power instrumentation aboard the spacecraft used in the Pioneer and Viking missions. Similar radioisotopic-powered units, but of higher electrical output, are currently operating aboard Voyager I and Voyager II, which were launched in late summer of 1977 and which recently flew by and explored Jupiter. These space probes are presently en route to Saturn and Venus.

The isotopic heat source must be properly contained in suitable refractory alloys to safeguard the material during normal and accident or abortive conditions. The functional requirements of the fuel encapsulating alloy are indeed rather formidable, and, thus far, only the noble-metal alloys based on platinum, iridium, and rhodium possess the desired high-temperature characteristics. The heat source consists of an outer graphite impact shell, a fuel encapsulation shell of refractory alloy, and the isotopic fuel. These encapsulated heat sources are designed to normally operate at 1300°C and withstand excursions of a few minutes duration into the 1600 to 1800°C range due to aerodynamic heating on reentry. Calculations indicate that the fuel sphere assembly after reentry would impact earth at a velocity of about 90 m/s and be subject to temperatures in the range of 1200 to 1400°C. This even is followed by exposure to air or water until retrieved. Advanced designed for more difficult missions impose more severe requirements and call for the cladding alloy to withstand a peak temperature of 1900°C and higher rates of strain on impact. These harsh conditions and hostile environments eliminate conventional superalloys, such as were successfully used in the Appollo missions to the moon. Factors to be considered include service temperature, melting point, and chemical compatibility with both graphite and fuel. The multilayered refractory alloy structures, such as tantalum alloys clad with Pt—30 wt % Rh successfully used at lower temperature in the Pioneer and Viking space probes, would suffer impairment from oxygen embrittlement as well as incompatibility with graphite and fuel.

Two new alloys have been developed and qualified for heat source application. One is a platinum-based alloy (designated at Pt-3008) containing 30 wt % Rh and 8 wt % W. This alloy has a high melting point of 2000°C, adequate high-temperature strength, good oxidation resistance, and acceptable fabricability. The second alloy is Ir—0.3 wt % W doped with about 40 ppm each of thorium and aluminum. This alloy, designated as DOP-4 iridium, can withstand more severe service conditions than Pt-3008 by virtue of its greater strength and higher melting point in contact with graphite (>2200°C). The upper temperature limitation for continuous service, however, is 1400°C.

These advances in heat source design and construction are the result of a need to increase efficiency of conversion of heat to electrical energy. Emphasis must necessarily be placed on safe and reliable performance. That this is being accomplished is reflected in advances in fuel containment alloy, moving from the initial use of conventional superalloys through multilayers of refractory alloys to the noble refactory alloys.