Conf-830336--1

CONF-830336--1

DE83 009783

RECENT DEVELOPMENTS IN GRAPHITE*†

J. E. Cunningham
Oak Ridge National Laboratory

Significant progress has been made in advancing graphite science and technology in recent years, and this report highlights findings emanating from research performed in the field by Walter P. Eatherly and C. Raymond Kennedy. What has changed recently is the recognition that design flexibility and confidence in material behavior during service can both be improved within the range of present-day technology. As a result, there has been a steady drift away from specifying commercial grades of graphite to new ones especially designed and fabricated for nuclear and aerospace use. Although the evolution is far from complete, it is no longer governed by empirical procedures; our understanding of the material and its modes of failure has provided a firm base upon which to develop new or modified grades for the desired behavior. Examples are GraphNOL N3M grade for special duty service in nose cones for reentry vehicles, rocket engine throats, and flight control surfaces of military and civilian spacecraft as well as Grade H451, Grade H451-I, and Stackpole Grade 2020 for nuclear service.

Failure Criteria

With the initial introduction of fracture mechanics into the theory of solids, it has been obvious that graphite strengths are controlled by flaws. The quantification of these concepts has until recently eluded us by the very complexity of polycrystalline bulk graphite. In the past few years the picture has shifted considerably, due initially to developments in the aerospace applications of graphite. It is now possible to detect disparate flaws in these very high quality graphites by non-destructive techniques; quantify them in terms of both size and frequency of occurrence; and trace their influence directly into the mechanical strengths. These advances have been quickly applied to the nuclear graphites, although the picture is complicated both experimentally and theoretically by the coarser structure of the nuclear materials. With the acquisition of large data bases on the HTGR core graphites, the problem has yielded to statistical techniques. As a result, the gains in design safety factors attainable by improving the commercially available grades have become apparent and desirable both technically and economically.

New Nuclear Grades for Reactor Core Application

A case at point is the evolution of the HTGR core graphite from what was essentially an electrode grade to what is now a highly specialized nuclear material. In the early days of the Hanford gas-cooled reactors, the core graphite was simply a purified electrode graphite, the

*For presentation at the meeting of the Advisory Technical Awareness Council of the American Society for Metals, scheduled for Wednesday, March 16, 1983, in Cleveland, Ohio

†Research sponsored by the U. S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

well-known AGOT-types. The original material in the Ft. St. Vrain reactor was a similar material in every way, differing only in the replacement of raw materials by similar types as the availability of cokes shifted. The next step in the U. S. program was to develop a more radiation-resistant graphite. This was accomplished in large measure by avoiding the premature weakening of the AGOT-type materials due to their radiation-induced expansion in the preferred c-axis direction, specifically by controlling the anisotropy at the intragranular scale. The result was Grade H-451 produced by Great Lakes Carbon Corporation. Today this material is licensed for and in use at Ft. St. Vrain as the replacement graphite. Currently under development is an improved material, H451-I, wherein the intragranular morphology is retained to preserve the radiation behavior, but the fabrication techniques are altered to specifically shift the flaw pattern downward in both size and frequency. The ability to effect this shift has been demonstrated, the radiation behavior has been maintained, and an optimization program is in progress. Unless a surprise stands around the corner, a marked improvement in design allowables is anticipated.

Core Support Structures

A similar evolution is occurring in the core support graphite. Here the graphite grade of preference for the support post structure is Stackpole grade 2020. Radiation damage is not a factor; degradation by oxidation is the performance characteristic of concern. There is no evidence in either laboratory or Ft. St. Vrain experience to indicate that oxidation by water vapor in a gross sense is significant. However, in the regions of stress concentration, such as the Hertzian forces developed at the contact area between posts and seats, the picture is not so clear. Grade 2020 graphite is a much finer grained material than H-451 and relatively free of structural defects. Here, however, the flaws take the form of impurity particulates acting as the stress risers. Grade 2020 also has a much lower fracture surface energy (G_{IC}) than H-451, but this is more than compensated for by its smaller average flaw size as reflected by its much higher mean strength. Impurities are udesirable, not only as they affect mechanical properties, but also since they complicate the oxidation problem as possible catalytic agents. Currently, Stackpole is developing an improved 2020, not only by eliminating the particulate impurities, but by exerting tighter control over processing to further raise the design allowables.

Concurrently, an intensive study of oxidation is underway. At GA Technologies (GA), microbalance studies have been initiated to determine the coefficients in the Hinshelwood-Gatsby kinetic rate equation at one atmosphere total pressure. At both GA and Kerforschungsanlage Julich (KFA), high-pressure loops are now studying 2020 graphite to determine the effects of pressure on penetrating oxidation. Initial data indicate that the effect of high pressure is to decrease the in-depth oxidation in accordance with diffusion theory. An engineering-scale experiment at Oak Ridge National Laboratory (ORNL) is specifically studying oxidative effects in regions of Hertzian stress concentrations under accelerated reactor conditions. Finally, samples of PGX graphite are being exposed to the reactor atomosphere in Ft. St. Vrain. The initial round of those test coupons have been removed and indicate again only surface, not in-depth, oxidation has occurred and at the low rates predicted by extrapolating the laboratory measurements. It is anticipated the data base for the core post structure will be well established within the next two to three years from the viewpoint of both basic design and seismic accidents.

Development of GraphNOL N3M for Aerospace Application

This product is designed primarily for special-duty service in the aerospace and the nuclear power industries. It can withstand extreme conditions of thermal shock or stress such as those encountered when space vehicles reenter the earth's atmosphere, and can maintain structural integrity when subjected to intense bombardment by energetic neutrons. Consequently, its primary function is to serve as the main material of construction in the manufacture of nose cones for reentry vehicles, rocket engine throats, and flight control surfaces of military and civilian spacecraft as well as in the manufacture of the moderator and other components that must function free of radiation damage in fission and fusion energy devices.

The degree of improvement in operating performance is significant, and the sophisticated approach taken to achieve it unusual. Compared with hitherto available materials, GraphNOL has the capability to withstand thermal shock that is 50% more intense and survive bombardment by fast particles that are 30% more damaging. These increased material capabilities are realized by rational application of several theoretical concepts. Unique interparticle binding of carbon grains is achieved, for instance, by the exremely careful control of hydrogen bonding throughout the forming process. The high strain-to-failure performance results from superior bonding forces and from control of void texture in regard to both size and morphology as dictated by modern concepts of fracture mechanics. As a concomitant, the resulting sonic transparency permits identification of both inherent dispersed flaw field as well as disparate flaws introduced in the manufacture. This inspection technique itself represents a unique innovation to quality control in the processing of these critical components.

GraphNOL has some very exciting properties, and compared to other existing grades exhibits a 100% improvement in strain-to-failure performance, possesses a 50% improvement in thermal shock resistance and a 30% improvement in radiation damage resistance. These improvements are attained with no significant increase in cost or penalty to other properties. Of potentially greater significance is the ability to design with the material on the basis of fracture mechanics and with detailed knowledge of the flaw texture. This design capability rests on the material's sonic transparency and provides a design reliability heretofore unattainable.

Summary

Overall, the HTGR graphite situation is in excellent shape. In both of the critical requirements, fuel blocks and support structures, adequate graphites are at hand and improved grades are sufficiently far along in truncation. These improved design allowables should largely remove any restrictions on design imposed by various accident conditions.

In the aerospace field, GraphNOL N3M permits vehicle performance with confidence in trajectories unobtainable with any other existing material. For fusion energy applications, it is unique in that no other graphite can simultaneously withstand both extreme thermal shock and neutron damage. Hence, the material promises to create new markets as well as to offer a better candidate material for existing applications.

This is not to say additional work is not required. Data bases are still inadequate for establishing tolerance limits. We still lack adequate theoretical treatment of multiaxial stress states and fully defined failure criteria. The oxidation information on the support structure is incomplete, especially in regard to high pressure effects. But these are problems facing the graphite industry in general. Over the next few years, as these "details" are resolved for the nuclear industry, they will also be contributing to the entire field of graphite applications.