

Methods for Improving the Oxidation Resistance
of Graphite

Ernst M. Goldstein, Materials Engineering Department
Martin Marietta Corporation
Orlando, Florida

If we talk about a material's oxidation resistance and its evaluation by testing methods, it must be understood that no standardized methods exist (or ever will exist) to measure accurately this chemical property. The reason is that countless test variables would have to be considered, all of which influence more or less the response of a candidate material to ablation. Such test parameters are, e.g., temperature employed, duration of a model at temperature, pressure, flow rates, oxidant type, purity and concentrations employed, specimen geometry, heating rates and type of heating used. Standardization of all these and many other parameters is virtually impossible. The oxidation resistance of a material is therefore a relative chemical property.

Oxidation tests referred to in this paper were carried out by the plasma arc technique with simulated dry air as the working gas and stagnation pressures slightly above one atm. The oxidation performance of the test models was evaluated by comparing specimen recession (which had to be symmetrical) and weight change with an arbitrarily selected standard, e.g. AGKSP graphite.

Three approaches are discernible to increase the oxidation resistance of graphite, viz. (1) transpiration cooling based on cooling of a model through the endothermic evaporation of an infiltrant, (2) composite technique, and (3) coating.

Transpiration cooling requires a porous graphite and an infiltrant non-reactive with the graphite. The former should have a high heat of evaporation and must not clog the pores of the material to be cooled, e.g. by decomposition products. Transpiration cooling is of limited interest to the aerospace industry because the evaporation of large amounts of infiltrant results in a deleterious ionization of a missile's boundary layer and uncontrolled weight changes during flight.

In the composite technique (a kind of coating in situ) an additive is admixed to the graphite. During ablation the additive oxidizes preferentially, forming a protective layer over the graphite. Typical additives of this kind are zirconium carbide and zirconium diboride, which form during oxidation a barrier layer of refractory zirconium dioxide. The synthesis of specimens of this type will be briefly explained. Results of experiments are presented which demonstrate that the oxidation resistance of graphite composites is indeed markedly improved (as compared to pure graphite) through various additives. During preparation of such graphite composites chemical reactions can occur in the graphitization step which have a profound effect on the composition of the model obtained. The limitations of the composite technique are discussed, e. g. the melting point of the oxide barrier layer formed, diffusion phenomena and chemical interactions between the barrier layer and the virgin graphite at the interface. Improvements could be expected from binary oxide layers due to their greater stability in the presence of graphite at elevated temperatures.

The third way to protect graphite from excessive oxidation is coating. An effective coating must be essentially non-porous, non-reactive with the substrate graphite, and have a high melting point and good oxidation resistance. In addition, coating and graphite must have a closely matching coefficient of thermal expansion. All these conditions are fulfilled to a degree by silicon carbide and iridium. SiC-coated graphite is good to about 1600-1800°C. At higher temperatures oxidation and finally dissociation of the SiC occurs. SiC-coated graphites are now commercially available. Ir-coated graphite (first investigated by Union Carbide) can be used up to 2110°C, higher than SiC-coated graphite. At this temperature a liquid Ir-C eutectic forms and the model fails. Since the melting point of pure Ir is 2450°C, the coating potentialities of this metal have not been fully exploited.

Various Ir coating processes will be reviewed, e. g. coating by vapor deposition, slurry dipping, fused salt electrolysis and plasma spraying. The high price of Ir and the limited supply of this noble metal in the Western Hemisphere (against large Ir ore occurrences in Russia) can be cited against the use of Ir in the aerospace industry. An extension of the applicability of Ir-coated graphite above the melting point of the Ir-C eutectic can be expected by (1) using high melting Ir alloys which do not form a low melting eutectic with carbon, (2) using a second, refractory coating on top of the Ir coating, (3) increasing the emissivity of the model, resulting in lower surface temperature through radiation, and (4) by some combination of these methods.