INFLUENCE OF CARBON POLYMORPHS ON ABLATION OF GRAPHITIC MATERIALS*

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Three nose tip models that were tested in the Air Force Flight Dynamics Laboratory 50 MW ablation test facility were studied with respect to their microstructure and for evidence of transformation of graphitic carbon to linear carbon forms. Two were 994 graphite and one was a GE 223 multidirectional carbon-carbon composite.

The sectioned nose tips were metallographically polished and ion-etched with xenon specifically for examination in the scanning electron microscope. A low-magnification overview of the cross-sectioned nose tip indicates that microstructural changes occurred near the ablated surface. The light areas in the micrographs indicate higher secondary electron emission and the presence of linear carbon polymorphs. These light areas occurred not only in bands across the top (ablated surface) of the specimen but also in depth. Higher magnification clearly shows the significant microstructural differences that existed for material 200 to 300 μm below the top surface. There is an absence of large pores and an indication of columnar structure, but this region still had the etched structure indicative of graphite basal alignment. Affected material occurring in bands to a depth of 500 μm had microstructural characteristics similar to that occurring at the surface.

The different carbon forms (e.g., graphite, diamond, lonsdaleite, and chaoite) have characteristic carbon negative ion spectra, as observed in the Ion Microprobe Mass Analyzer (IMMA), and the signal intensity ratio for C_2^-/C_6^- is the most diagnostic feature for the carbon forms [1]. The symbol C_x^- refers to a molecule for x carbon atoms with a single negative charge. The absolute C_6^- intensity for all the linear forms is at least three orders of magnitude greater than the C_6^- signal from graphite or graphite material. By means of the C_2^- and C_6^- signals, profiles can be obtained that show the distribution of the linear forms. Complete negative ion spectra can be obtained at particular points to obtain a rough measure of the extent of transformation, and in some cases, to identify the linear carbon form.

A general IMMA search over the nose tip sections revealed that some of the graphitic material transformed to the linear carbon forms and were in a thin layer at the top. Profiles of C_2^- and C_6^-, starting at the surface and extending axially down the section, indicate that the layer of extensive transformation was approximately 300 μm thick and that the concentration of the linear forms died away very rapidly beyond this depth, except for isolated regions at depths of about 400 to 500 μm. These profiles correspond to the micrographic result of banded microstructural regions. Complete negative ion spectra taken at selected points along the profile confirmed the results indicated by the C_2^-/C_6^- ratio. The profiles obtained on the 994 graphite and the GE carbon-carbon composite were essentially indistinguishable with regard to both distribution and identity of polymorphs. Also, the carbon-carbon composite fiber orientation had no effect on the transformation, and the matrix behaved the same way as the fibers.

A very limited electron diffraction study of samples taken from the nose tip showed that carbon XII was formed at the ablating surface, carbon VII and XI formed in the first 50-μm thick layer, and chaoite was formed ~200 μm below the surface. However, the nose tip was not quench-cooled; therefore, these may not be the carbon forms that existed while the nose tip was under test conditions.

Studies on the effect of quench-cooling carbon that was heated to ~3800 K by laser heating on carbon showed that, when a sample was allowed to cool by just turning off the laser, there existed a layer of linear polymorphs about 280 to 300-μm thick, similar to that found on the nose-tip sections. The average cooling rate involved here was ~2000°C/sec. If the sample was quenched (cooling rate ~30,000°C/sec), the linear forms were found to a depth of about 2400 μm, and there was evidence that the transformation was more extensive when the sample was at 3800 K. Since the nose tips showed normal behavior with regard to linear polymorph formation, there is good reason to believe that perhaps 1.5 to 2.4 mm of of the nose tip could be transformed under reentry conditions. The exact amount would, of course, depend on the temperature gradient in the nose tip.

There is some evidence that the rate of transformation is not the same for all forms of graphitic carbon. In a two-phase carbon, the filler appears to transform faster than the binder. Consequently, an analysis of the final slow-cooled nose tip gives very little insight into the course of events that occur in the carbon during the heating and cooling phases during reentry.

Reference

1. Stuckey, W. K. and Whittaker, A. G., "Identification of Carbon Allotropes by Ion Microprobe Mass Analysis," TP176, 10th Biennial Conference on Carbon, LeHigh University, 27 June - 2 July 1971.

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