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Informal Report

TESTING OF PROTECTIVE COATINGS IN HYDROGEN

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Abstract

A series of tests of protective coatings on carbon-carbon substrates were performed. The tests involved exposure of the coated material to hydrogen at high temperatures, the examination of the coatings by scanning electron microscopy and the measurement of weight losses. The coatings included Re, TaHfC, TaC and NbC, with thicknesses of the order of 20-60 μm .

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TESTING OF PROTECTIVE COATINGS IN HYDROGEN*

1. Introduction

The problem of erosion of carbon by hydrogen at high temperatures has been known for a long time. The rate of erosion is expected to be dependent on the type of carbon, the temperature, and probably the pressure and flow rate of the gas. Protective coatings which are unreactive in hydrogen are expected to reduce the rate of removal of carbon, by interposing a diffusion barrier between the reactive gas and the substrate. The success of this strategy depends on (a) the continuity and structural integrity of the coating at the temperature of the test and (b) the diffusion rates of the reacting species and reaction products through the coatings. Since there are many different forms of carbon, and the coatings can be prepared with a variety of compositions and microstructures, it is essential to carry out empirical determinations of the effectiveness of a given composite structure in the context of its intended use.

In the present study, coated pellets of 3-D carbon-carbon were woven from Hercules AS-4 fiber and densified with Ashland A-70 petroleum pitch to a density of 1.93. After densification, samples were heated to 2500 °C. and coated. Coated samples were tested in hydrogen at two different temperatures. The pellets each had three holes drilled through them to test the integrity of coatings within penetrations. Four types of coating were tested, including Re, TaHfC, TaC and NbC. The deposition conditions used in the preparation of the coatings were not available, but presumably could be repeated if necessary.

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2. Procedures

Each specimen was examined under the scanning electron microscope (SEM) prior to testing. Samples with significant flaws in the coatings (i.e., missing patches larger than 1 or 2 grains) were not tested further. To remove possible volatile contaminants, each sample was weighed, baked for 10 minutes at 1000 °C in a tube furnace under flowing argon, and weighed again. No significant weight loss was observed at this stage. Each sample was then mounted in a NbC-coated graphite crucible placed in a similarly coated graphite susceptor cup as shown in Fig. 1. The assembly was mounted on a boron nitride pedestal in a quartz tube located inside the coil of an rf induction heater. The specimen was brought up to the test temperature in a flowing inert atmosphere. Then hydrogen was allowed to flow through the susceptor and crucible for a specified time, at the end of which the flow was switched back to argon or helium and the heating was terminated. After the test, the sample was again weighed and examined under the SEM.

Figure 1. Diagram of induction furnace assembly

3. Results

3.1 General Observations

Typically, the coefficient of thermal expansion (CTE) of the coatings is greater than that of the carbon-carbon substrate. Since the coatings are deposited at elevated temperatures, they shrink and crack on cooling to room temperature. These cracks are evident in the SEM images of the as-received samples, even at low magnification. Sometimes they roughly follow the boundaries of bundles of fibers in the substrate. Usually, they occur at grain boundaries rather than cutting across individual grains of the coating. It is expected (though not easy to observe directly) that during the heating cycle the cracks close up, sealing off the underlying material from the surrounding atmosphere. If the test temperature is higher than the deposition temperature of the coating, compressive strains may buckle the surface and cause parts of the coating to flake off.

3.2. Re Coatings

The microstructure of the Re coatings is shown at two different magnifications in Figures 2 and 3. The grains are shaped like hexagonal barnacles, having sharp angles and edges protruding out from the substrate surface. This structure scatters visible light in a non-specular way, resulting in the dark grey appearance of the coatings. After testing for 2 minutes in hydrogen at 2300 K, there was no major change in the appearance of the coating, as shown in Fig. 4. There was, however, an easily measurable weight loss of 1.0 ± 0.2 mg, representing about 0.3% of the carbon substrate weight. If one sets an arbitrary criterion of 1% C weight loss as the limit one can tolerate in a particular application, and if a linear extrapolation is assumed, the useful life of the coated part is about 6 minutes at this temperature, pressure and flow rate of hydrogen.

A second Re-coated sample was tested in hydrogen at 2800 ± 50 K, but no data could be obtained on weight loss because the coating apparently melted during the heating cycle, brazing together the pellet and the NbC-coated crucible with a strong bond. This result was not very surprising, since the test temperature was higher than the Re-C eutectic temperature (2760 K), and some overshoot was possible during the heating cycle, which was manually controlled during these first tests. Nevertheless, the resulting strong bond between two pieces of carbon was interesting, and could be useful in certain applications.

Figure 2. Re-coated sample at low magnification (15X)

Figure 3. Re-coated sample at high magnification (5000X)

Figure 4. Re-coated sample after exposure to hydrogen at 2300 K for 2 minutes.(1000X)

3.3. TaHfC

Figure 5 shows the microstructure of one sample coated with TaHfC in its initial condition. The coating was again very rough in appearance, with a "cauliflower" texture, rather than faceted crystals. A test in hydrogen for 2 minutes at 2300 K caused a weight loss of about 1 % of the carbon, and a test of a second sample for 2 minutes at 2800 K resulted in a weight loss of 2 % of the carbon. This type of coating apparently does not afford much protection to the substrate. Perhaps a more impervious structure could be obtained with this composition if the deposition temperature were higher, or if a high temperature anneal were performed in an inert atmosphere to recrystallize the "cauliflower" material.

Figure 5. TaHfC coating microstructure (100X)

3.4. NbC

The NbC coatings consisted of flat, smooth grains with straight boundaries and a mirror-like appearance. An example is depicted in Fig. 6, which is typical of films grown or recrystallized at temperatures close to their melting points. As with all the coatings, thermal contraction cracks were evident at low magnification, and appeared to follow grain boundaries for the most part. In the first set of test conditions (2300 K for 2 minutes in H_2) there was no weight loss, within the precision of the measurement. Longer exposures will be necessary to determine whether there is a small rate of weight loss at this temperature. At the higher temperature (2800 K) the loss of carbon was 0.17 % after 2 minutes. Subsequent reheating of the same specimen resulted in a weight loss which increased roughly linearly with exposure time, as shown in Figure 7. Under these conditions, the coating can prolong the useful life of the substrate for half an hour.

Figure 6. NbC coating showing smooth, flat grains (100X)

Figure 7. Weight loss of NbC-coated sample after repeated exposure to H₂ at 2800 K

3.5. TaC

The TaC coatings were the most resistant to hydrogen of the set. As with all the other other coatings, some samples had major flaws when received (Fig. 8), and could not be meaningfully tested in hydrogen. Their microstructure showed the same smooth-grained appearance (Fig. 9) as the NbC coatings. The color as received was a yellowish tint. The weight loss was negligible after 2 minutes in hydrogen at both 2300 and 2800 K. There was little change in the appearance of the coating after heating, except for a few individual grains which disintegrated, leaving round holes which looked like burst bubbles (Fig. 10). Further testing of TaC samples should show some weight losses as the hydrogen penetrates at such weak points in the coating.

Figure 8. TaC coating with major flaws (1000X)

Figure 9. TaC coating microstructure (750X)

Figure 10. TaC after exposure to H₂ for 2 minutes at 2800 K(1000X)

4. Conclusion

The data obtained on coated samples indicate that, for samples in which the coating was good, i.e. no flaws, there was little or no weight loss in hydrogen for short exposures at 2300 K. The TaHfC coatings behaved the worst in these tests, but at this temperature even they would probably be acceptable. At 2800 K, only the NbC and TaC showed acceptable weight losses. Re coatings are reactive at these temperatures with the carbon substrate and should not be considered for further testing. A crucial point in all this is the initial coating integrity. All samples tested had reasonable integrity.

Testing of samples with uncoated areas is not recommended for several reasons. First, the reaction rate of hydrogen with carbon at these temperatures is quite rapid. Previous testing of uncoated carbon-carbon at 3050 K showed weight losses of almost 30 wt. % in 3 minutes.¹ This high rate of attack was also observed for vitreous carbon samples tested. The rate of attack in hydrogen is probably proportional to the exposed surface area so that in testing of samples with exposed carbon a surface area of exposed carbon would have to be estimated. This would be difficult to do especially at temperature. A second reason for not testing such material is related. It has been observed that when hydrogen attacks a carbon sample with a refractory coating, the carbon under the coating is attacked. This undercutting of the coating leads to spalling of the coating. Thus, weight losses in experiments in which pieces of coating are missing and which are prone to spalling would be hard to quantify in a way which would be meaningful for larger samples. In samples obtained from vendors, we have noted that the quality of coatings obtained is quite variable. On small samples it is certainly possible to obtain coatings with no major flaws. This would be required for a large-scale application and it would therefore be prudent to invest effort in the quality control on the coating process rather than obtain data on samples which are flawed.

¹R. Barletta, J. Adams, J. Svandrlík and J. R. Powell, Performance of Carbon-Based Hot Frit Substrates, I. Low Pressure Helium and Hydrogen Testing, LV-S-07-020-91 (April, 1991)

Finally, the data presented herein were obtained at one atmosphere and under low flow rate conditions. More data should be obtained to establish the flow rate and pressure dependence of the degradation process. Still, the data are useful from a screening standpoint since large numbers of samples can be tested quickly. Further, there is no reason to expect that a specimen which cannot survive these conditions would last in a high pressure, high flow rate environment. If further testing is desirable, it is recommended that samples from the same coating batch be first tested at low pressure at the desired temperature. Once data are evaluated at low pressure, samples can then be selected for high pressure, high flow rate testing.

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