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DEPOSITION AND MODIFICATION OF TANTALUM CARBIDE COATINGS ON GRAPHITE BY LASER INTERACTIONS*

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ABSTRACT

Graphite surfaces can be hardened and protected from erosion by hydrogen at high temperatures by refractory metal carbide coatings, which are usually prepared by chemical vapor deposition (CVD) or chemical vapor reaction (CVR) methods. These techniques rely on heating the substrate to a temperature where a volatile metal halide decomposes and reacts with either a hydrocarbon gas or with carbon from the substrate. For CVR techniques, deposition temperatures must be in excess of 2000° C in order to achieve favorable deposition kinetics. In an effort to lower the bulk substrate deposition temperature, the use of laser interactions with both the substrate and the metal halide deposition gas has been employed. Initial testing involved the use of a CO_2 laser to heat the surface of a graphite substrate and a KrF excimer laser to accomplish a photodecomposition of $TaCl_5$ gas near the substrate. The results of preliminary experiments using these techniques are described.

INTRODUCTION

The use of refractory carbide coatings for protecting materials from corrosive gases at high temperatures or to provide surface toughness is well established. Recently, we have become involved with the use of these materials for the protection of graphites and carbon-carbon composites from attack by hot hydrogen at high temperatures [1]. Typically, these coatings have been applied to the carbon substrate using either conventional chemical vapor deposition (CVD) or chemical vapor reaction (CVR) techniques. The latter process has proven quite effective in producing dense, adherent and protective coatings. In this process a metal halide vapor reacts with carbon in the substrate to produce the carbide. For a refractory carbide such as tantalum, the reaction is

$$TaCl_5 + C_{(substrate)} \rightarrow TaC + \frac{5}{2} Cl_2. \qquad (1)$$

This reaction typically occurs at temperatures in the range of 1700 to 2600 K, depending on the carbide with coating thicknesses on the order of 10 to 100 micrometers [2]. Since these coatings are produced at high temperatures, the grain size is quite large.

In an effort to reduce the overall substrate temperature as well as to provide a means to perform "spot repairs" for coatings, work has been initiated to develop an alternative coating method which could achieve the same grain morphology and coating stoichiometry as the CVR process. Thermochemical data [3,4] indicate that high surface temperatures are necessary for the carbide formation to proceed. Since the region of carbon diffusion is small, however, bulk heating of the substrate is not required. Thus, the use of surface heating of the carbon with an infrared laser was chosen. Further, experiments on the photo-assisted formation of TaO from $TaCl_5$ indicate the efficacy of UV photons in the photo-decomposition of the starting metal halide [5,6]. Given these considerations, a coating process in which the metal halide is decomposed by ultraviolet radiation while the surface is heated using an infrared laser could result in coatings which are effectively the same as high temperature CVR coatings while being made at lower overall substrate coating temperatures. In order to test this hypothesis, initial coating studies have been performed using the TaC/graphite system.

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EXPERIMENTAL

The basic experimental setup consisted of a gas handling system for the $TaCl_5$ vapor and a deposition cell (see Figure 1). The $TaCl_5$ vapor was produced by heating solid $TaCl_5$ in a reservoir. The vapor pressure in the reservoir was calculated using the following relationship between 363 and 490 K [7]

$$\text{Log}\{P(\text{Torr})\} = 12.323 - \frac{4729}{T} . \qquad (2)$$

The gas from the reservoir was throttled through a heated needle valve and ducted to the deposition cell where it was directed onto the graphite sample through a nozzle. The graphite sample was attached to a heated stage whose temperature could be varied between room temperature and 700 K. Light from a carbon dioxide laser was focused on the graphite sample through a KBr window. Light from an excimer laser was admitted through a quartz window at 90° to the CO_2 beam. The excimer laser used was a KrF laser operating at 248 nm. This line was chosen since it is coincident with the absorption maximum of the $TaCl_5$ [6]. The graphite was locally heated with a 3.5 W, cw-CO_2 laser focused to ~ 1 mm in diameter.

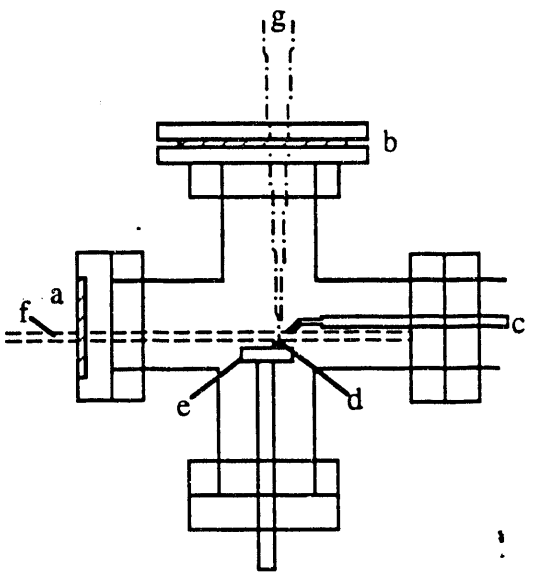

Figure 1. Schematic of deposition cell. a. Silica window; b. KBr window; c. $TaCl_5$ inlet nozzle; d. Graphite substrate; e. Heated sample pedestal; f. Excimer laser beam; g. CO_2 laser beam.

Experiments were performed by heating the deposition tube to a temperature some 10 to 20 K higher than the reservoir temperature. The sample in these tests consisted of a small piece of graphite (0.16 cm) embedded in a refractory disk and attached to the pedestal. The substrate pedestal was also heated at this time to the test temperature. Gas flow was then initiated by opening the reservoir needle valve and irradiation (infrared alone or infrared plus UV) was begun. Throughout the course of the experiment, system pressure, reservoir and substrate temperatures and excimer laser power were monitored. Upon completion of the test the gas flow was stopped and the apparatus was cooled to room temperature. The graphite sample was then examined using scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX).

An initial experiment was also performed with a graphite disk in place of the heated platform. In this test, only infrared radiation was used. Since the graphite remained at room temperature, $TaCl_5$ condensation on the disk in areas not heated by the laser was expected. In other respects, the experimental procedure was identical to that described above.

RESULTS AND DISCUSSION

Infrared Irradiation

The initial experiment on the graphite disk resulted in a limited thermal decomposition of the pentachloride in the region heated by the laser. During the course of CO_2 irradiation (about 5 minutes), the temperature of the area heated by the laser appeared to decrease dramatically. This was evidenced by a change in color of the graphite at the laser focus from bright white to dull orange to dark during the test. These changes indicate that the temperature went from a point where decomposition and carbide formation is thermochemically favorable to a temperature where only condensation of the chloride is expected. EDX examination revealed that the region irradiated by the CO_2 laser was in fact Ta rich and Cl deficient with respect to other areas on the disk. The presence of TaC could not be confirmed in this test.

Irradiation of graphite on the heated platform proved much more successful. With the platform at 573 K only minimal chloride was deposited. This was presumably due to thermal decomposition of the pentachloride at the surface resulting in traces of a lower vapor pressure chloride condensing during the course of the experiment. Direct heating of the pentachloride molecule itself by the 10.6 μm radiation can be eliminated from a consideration of the vibrational spectroscopy of the molecule [8]. EDX analysis was used to subtract the contribution of this chloride and the graphite background and, when this was done, only an x-ray spectrum of Ta remained (Figure 2). Thus, with CO_2 radiation alone, we observed complete thermal decomposition of the pentachloride can be accomplished leaving only Ta on the surface. The substrate surface temperature in this case was insufficient to cause a reaction of the Ta with the graphite substrate.

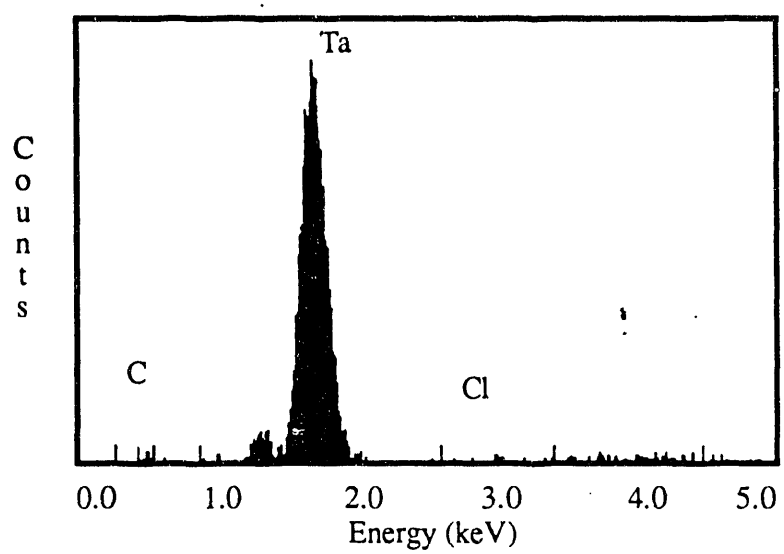

Figure 2. EDX spectrum of deposit on graphite disk after irradiation with infrared photons alone. The background contributions to this spectrum have been subtracted using the spectrum of an unirradiated graphite specimen under identical conditions. The deposition time in this experiment was 30 s.

Infrared plus Excimer Irradiation

Under experimental conditions identical to that of the infrared irradiation of a heated graphite substrate described above, the coincident irradiation of the gas phase pentachloride stream with excimer light at 248 nm resulted in the production of a coating which contained both Ta and C. Figure 3 shows an EDX spectrum of this coating after background subtraction. In this experiment, the UV flux density was on the order of 2 W/cm^2 as a result of irradiation with an unfocused excimer light. The pulse energy was ~ 145 mJ pulse and the pulse duration was on the order of 20 ns. The results of this experiment when compared with those of infrared

irradiation alone indicate that UV absorption by the $TaCl_5$ vapor is instrumental in allowing the carbide formation to proceed. The TaC film formed by this process is quite fine grained (on the order of a few micrometers). Figure 4 shows an SEM photograph of the film after 10 minutes of deposition. Although film coverage appeared to be uniform across the graphite surface, holes in the coating are evident at high magnification. Detailed characterization and testing of this coating has not been performed at this time. It should be noted that the grain size of these initial coatings is much smaller than that seen in the TaC films produced by the process described in Reference 2.

The photon flux density in these experiments was approximately three orders of magnitude higher than that used in the photo-CVD production of TaO [6]. Indeed, the laser power used is more consistent with multiphoton dissociation processes [9]. In those experiments, photodissociation of a variety of metal halides and carbonyls as well as other organometallic compounds was found to proceed in a step-wise fashion, ultimately producing electronically excited metal atoms. For photons at 248 nm, it can be readily calculated from thermochemical data [3] that a minimum of 2 photons would be necessary to completely dissociate $TaCl_5$. Such a process is expected to result in photon emission from the Ta(I). We are currently in the process of investigating the photophysics of this system.

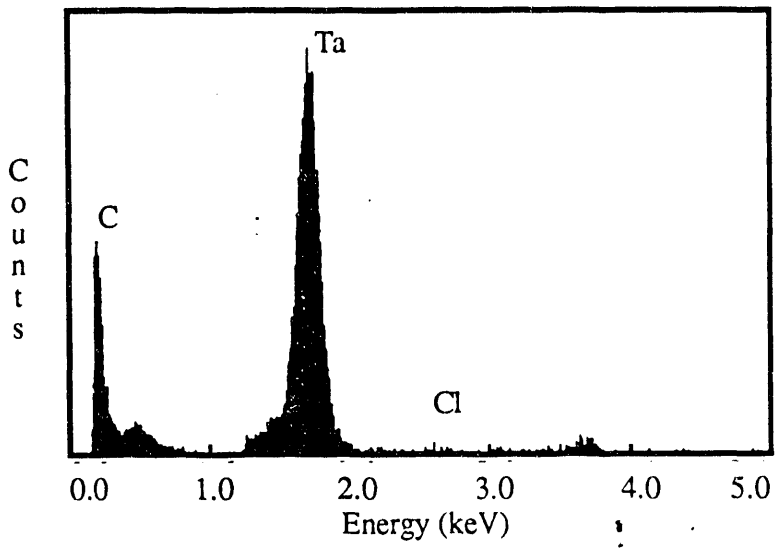

Figure 3. EDX spectrum of deposit on graphite disk after irradiation with both infrared and UV photons. The background contributions to this spectrum have been subtracted using the spectrum of an unirradiated graphite specimen under identical conditions. The deposition time in this experiment was 30 s.

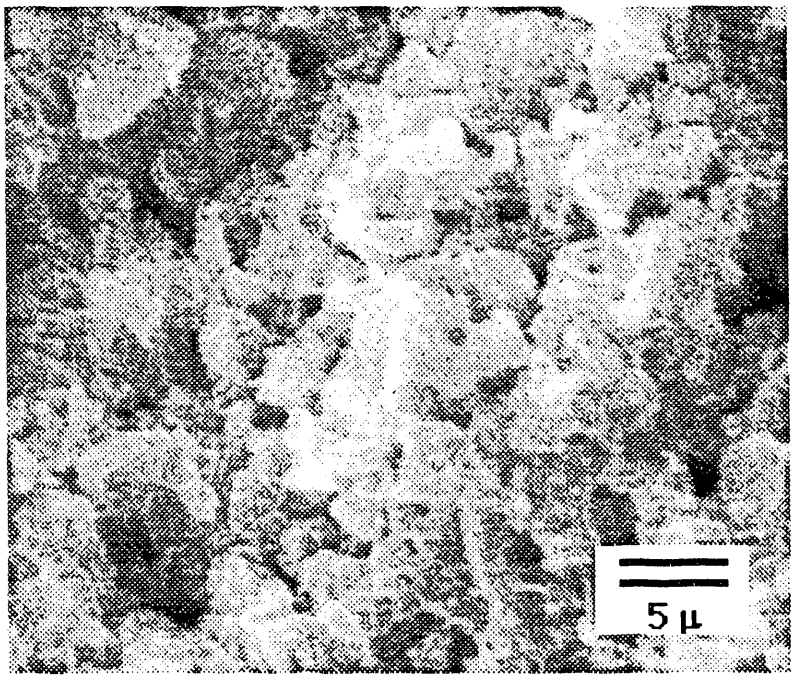

Figure 4. SEM photograph of TaC coating on graphite after 10 minute deposition (2000 X).

CONCLUSIONS

The results of these initial experiments indicate that it is possible to produce refractory metal carbides at very low substrate temperatures (< 700 K) using a two laser process. The photochemical process produces carbides via a CVR-like reaction in which the carbon source is the substrate itself. This carbide formation reaction has only been observed thermally at temperatures almost 2000 K higher. The UV photons in this carbide reaction give rise to dissociation of the halide reactant while infrared photons cause heating of the immediate substrate surface. We are currently in the process of investigating the details of the process (photochemistry, photophysics, deposition rate, coating characteristics and hydrogen permeability, etc.) and expect to extend our investigations of this multiple laser coating process to other coating systems.

ACKNOWLEDGEMENTS

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