Laser Fusion Coatings of Functional Parts

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ABSTRACT

Surface characteristics of functional parts made by Solid Freeform Fabrication techniques such as Selective Laser Sintering (SLS), Stereolitography Apparatus (SLA) or other fabrication techniques can be enhanced by the application of multi-element based laser fused coatings. Environmental protection and wear resistance, among other properties can be achieved by pre-depositing a slurry over the surface of the parts, followed by a high-speed scanning with a high power laser beam. Wetting of the part surface by the molten slurry is a main concern in this coating process. Wetting characteristics of molten slurry can be improved by the right combination of coating constituents, laser processing atmosphere, and laser processing parameters. Coating quality is also a critical issue to ensure good performance of the coatings especially for environmental protection. This paper presents results obtained for carbon-carbon composites coated with silicon-based slurries by laser fusion process. Criterion in selecting the coating constituents, laser process conditions, and oxidation test results are discussed.

Introduction

For more than two decades laser coatings have been successfully applied over metal substrates by several known techniques such as cladding, pre-deposited powders, foils or rods [1-3]. In all these laser processes, a bond is formed between the metal substrate and the coating as melting of the former facilitates the dilution of the coating elements into the substrate. On the other hand, when the substrate of the functional part is a ceramic material that decomposes rather than melts (e.g. carbon-carbon composite), coatings with good bonding characteristics and with overall wetting of the substrate are less likely to be obtained during laser fusion. Poor interfacial characteristics in laser fused samples can be attributed to lack of proper fusion temperature and inadequate dwell time as well as the presence of contaminants such as oxygen and moisture that alter the surface tension balance. Moreover, coating thickness, differences in coefficient of thermal expansion (CTE) between the coating and substrate have a major impact on the delamination or spalation behavior of the coatings [4]. Surface wetting by the chemical

slurry depends on the solubility, bonding compatibility, chemical reactivity of the substrate, and the coating constituents [5]. The degree of superheat of the molten slurry will also determine the viscosity of the coating as well as the reaction kinetics. The surface roughness of the samples may increase the interface area contributing to an increase in interfacial strength. However, a rough surface may have poor integrity because of poor wetting and sharp grooves [6]. Finally, the residence time of the molten slurry over the substrate will in turn control the thickness and evenness of the interface. Nonetheless, recent research on coating of ceramics using laser chemical decomposition and laser fusion has shown promising results [9].

Coating of Carbon-Carbon Composites

The surface of carbon-carbon (C/C) composite functional parts used in space vehicles (e.g. rocket nozzles and nose cones) requires environmental protection especially during atmosphere reentry maneuvers. Oxidation at high temperatures is deleterious to the performance of the C/C composites, which start oxidizing at 400 ºC in air. For more than 30 years, single and multi-layer coating techniques have been investigated to enhance the performance of C/C composite materials at high temperatures. Chemical vapor deposition (CVD) is widely used to deposit SiC layers over C/C composites; however, this is a slow and cumbersome process and requires operation under high vacuum conditions. Diffusion-based processes such as pack cementation or fused slurry techniques are also being used to form oxidation resistant coatings. However, these processes require that all of the part surface must be coated and they too need several hours for processing [7, 8]. The purpose of the current ongoing research program is to develop a laser fusion methodology to deposit protective coatings to improve oxidation resistance of C/C composites. The laser fusion coating methodology is based on the principles of laser-induced chemical reduction of a carefully selected mixture of metals/elements to form complex phase coatings [9]. Metal salts can be reduced to their native states by the application of laser irradiation. For example, a metal salt such as nickel formate can be reduced to form nickel by laser energy. The elements then get fused in the surface layers of the C/C substrate. Laser fusion coating process involves formation of a chemical slurry consisting of the coating constituents and the deposition of slurry on the sample surface, followed by laser processing. In this paper, the effects of coating composition and laser process parameters on the coating quality are discussed.

The work presented here is a continuation of the investigation on laser fusion coatings; however, now it incorporates a laser beam delivery system similar to that used in Selective Laser Sintering. Galvanometer driven mirrors are used to raster scan the focused laser beam back and forth at speeds up to 5 times faster than used previously. Overlapping between scanned tracks of almost 90% is used to provide enough residence time so that a high temperature can be sustained to allow for a complete reaction between the substrate and the molten elements. Because of the faster scanning rate and high percentage of overlapping, the heat diffusion time is longer than the time it takes for the laser beam to raster scan one line. Thus, the material is subjected to a rectangular heat source rather than a single moving spot. Infrared thermal mapping of the surface confirmed observation of this rectangular heat distribution, which favors uniform and

continuous coatings. The process is carried out inside a sealed chamber under rough vacuum back-filled with an inert-reducing atmosphere.


Experimental

Samples of 3D C/C composites were obtained from BF Goodrich, Santa Fe Springs, CA. Coupons were machined having dimensions of 28 mm in length, 12 mm in width and 3 mm in thickness. Samples were cleaned with acetone to remove contaminants from the surface before laser processing. Slurries were prepared by mixing finely ground powders (mesh –325) with isopropyl alcohol to form a viscous paste that was then deposited manually over the surface of the composite by means of a spatula. After the slurry had dried, the samples were placed inside the processing chamber, which was evacuated to 200-mTorr vacuum level, and then back filled with argon-4% hydrogen.

Figure 1 shows a schematic of the laser process. A high power CO_2 laser beam focused down to 0.35+/-0.05 mm was scanned at a speed (V_s) up to 10 m/min using a scan density of 1000 raster lines/inch. To prevent heat accumulation due to the finite dimension of the sample and keeping a constant temperature during laser processing the laser power was linearly ramped down from 700 to 350 Watts. The traverse velocity (V_t) used was of the order of 55-80 mm/min. Figure 2 shows a thermal image of the area scanned by the laser beam obtained by using an infrared camera. The longer axis of the rectangle corresponds to the width of the composite (i.e.,12 mm); therefore the minor axis measures between 2-3 mm. The temperature inside the rectangular zone is relatively constant during the entire process. The temperature generated in the sample must be high enough to melt the coating elements and still cause some degree of superheat to allow for spreading of the slurry over the surface. A chemical reaction between the molten elements and the surface of the composite is expected to take place; however, the extent of this reaction depends on the laser dwell time.
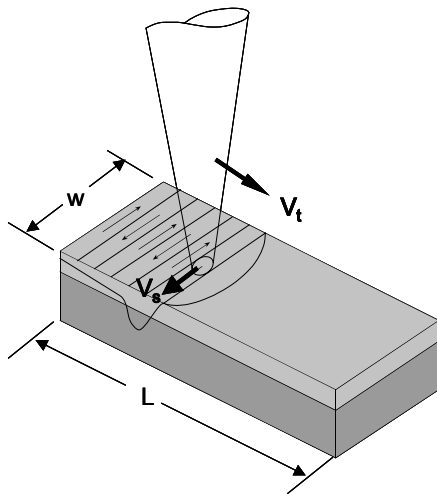
Figure 1. Schematic of the laser fusion coating process. The top layer is the coating on the composite surface.
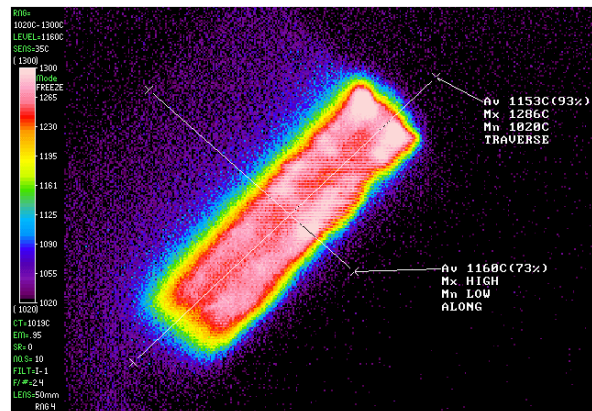
Figure 2. Infrared thermal image of raster scanned laser beam. The average temperature in the hot zone is 1160 ºC.

All the samples were examined using light optical and scanning electron microscopy (SEM). Light and electron optic techniques were used to characterize the microstructural features of the surface and interfacial regions. Microchemical analysis of the coating and coating/substrate interface region was conducted by using the electron microprobe and energy dispersive x-ray analysis (EDAX). Oxidation behavior of the coated and uncoated samples was evaluated by heating the sample at 1000°C in a tube furnace in still air. The samples were removed from the furnace at intervals of 30 minutes, followed by weighing until the failure of the coated sample.

Results and Discussion

Microstructural Characterization

Figure 3 shows the microstructure of the as-received sample of a C/C composite. It is observed that the surface is inherently rough, providing a larger interface area for mechanical interlocking. However, surface roughness hinders wetting and formation of a continuous chemical bond due to the presence of sharp grooves. Figure 4 shows the microstructure of a C/C composite surface coated with a pure silicon layer by means of laser fusion. Complete wetting of the surface with pure silicon was not achieved, most probably due to the presence of oxygen resulting in the formation of silica (SiO_2) layer. Presence of silica layer on the surface also alters the surface tension balance and favors solidification with higher wetting angles. A SiC interfacial layer at the substrate is most likely to form as soon as the molten silicon wets the surface. The thickness and extent of this interfacial layer will be a function of the laser dwell time during which time the silicon remains at or above its melting temperature. Longer dwell times involve slower scanning speed and larger beam overlap. However, longer dwell times will lead to longer exposure times of the slurry to contaminants that hinder the wetting of the composite surface. This suggests that an optimum dwell time exist that minimizes the wetting angle caused by exposure to impurities and maximizes the reaction layer thickness which is controlled by atomic diffusion.

In order to improve wetting of the C/C composite surface by silicon the composition of the chemical slurry was changed by adding 10 wt.% of HfC. HfC is a refractory compound that melts at about 3900°C. The high heat capacity of this carbide thermally stabilizes the melting front and helps in even spreading of the molten slurry possibly by a dragging mechanism, as the melt region is stirred by Marangoni´s type flow [1,2]. However, as seen in Figure 5, several long cracks can be seen on the surface most probably due to its high CTE relative to pure silicon and carbon. The formation of a eutectic-like pattern can be observed at higher magnification in Figure 6, the white microconstituents corresponding to HfC. This morphology may lower the melting point of the mixture and therefore increase the level of superheating, which in turn reduces the viscosity of the molten slurry allowing it to flow with less difficulty.
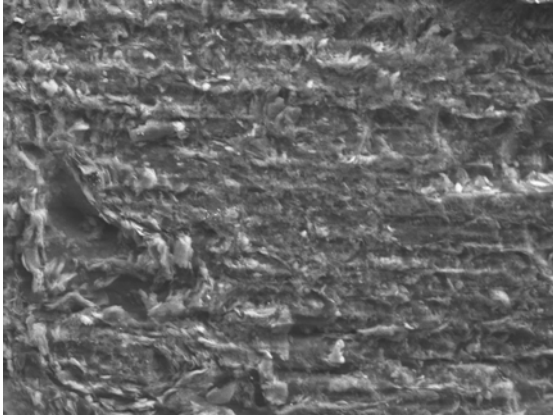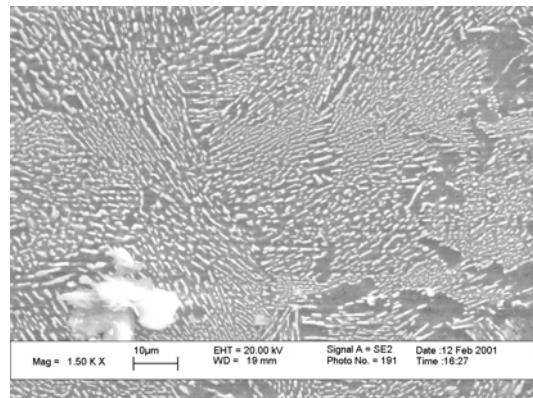
Figure 3. 3D C/C "shoe-brake" composite rough surface, 1000x.
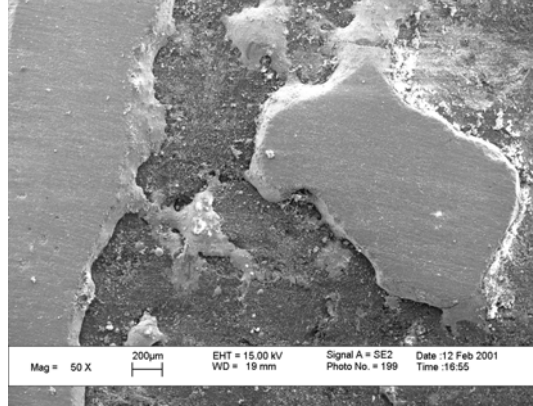
Figure 4. SEM image of Si coating indicating signs of incomplete wetting of the surface, 50x.
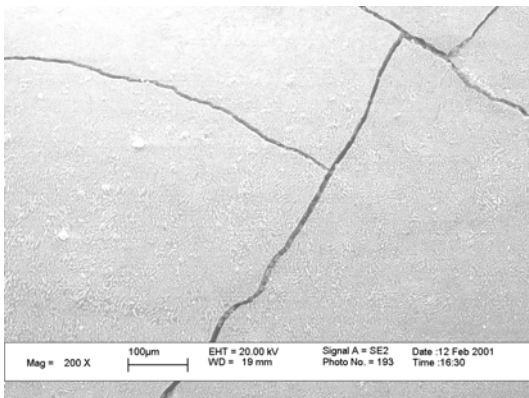
Figure 5. SEM image 200x of Si-10wt.%HfC coating showing signs of multiple cracks.

Figure 6. SEM image 1500x of Si-10wt.%HfC coating indicating a eutectic like morphology.

Figure 7 shows the microstructure of the primary laser fused CTE matching coating layer having the chemical composition of Si-20SiC-5Ti-5Al (all wt %.) EDAX analysis of the coating indicated the presence of aluminum and titanium silicates. Some cracks are observed on the surface caused by the CTE mismatch between the substrate and the coating. However, the sample showed improved wetting characteristics probably due to the addition of:

(a) Ti: which acts as an oxygen getter, helps to reduce the contamination by oxygen and thus enhance wetting
(b) Al: which lowers the melting point of the slurry thereby allowing for larger superheat that in turn lowers the viscosity of the melted slurry and enhanced wetting
(c) SiC: operates much in the same way as HfC by stabilizing the melt front due to its refractory properties, increasing drag on the melt and providing a dispersion of embedded particles that can help in arresting cracks.

Figure 8 shows the surface of the oxygen diffusion barrier coating - consisting of Si-15 HfC-10Ir-5Ti (wt.%). Iridium and HfC have been added to provide protection at temperatures where silicon can no longer provide sufficient oxidation protection.

632

Titanium was added to reduce oxygen contamination. However, severe cracking took place due to mismatch of the CTE between the diffusion barrier coating, the primary CTE matching layer and the substrate. It is possible that HfC and iridium can undergo a Lewis Acid-Base type exothermic reaction that creates a much more intermetallic compound which could lead to a further increase in the CTE mismatch [10]. The relative thickness of coatings can also lead to the formation of cracks. To mitigate the deleterious effect of the numerous cracks seen in Figure 8, a third coating was applied on the sample. This final coating step consisted of dipping the sample in a silica-based sealant agent (SILBOND^{TM}) for 10 minutes followed by drying in air for 24 hours. The sealant agent penetrated the cracks easily due to its extremely low viscosity and formed a glassy layer on the sample surface.

Figure 9 shows a cross-section of a coated C/C sample having a three-layer coating, namely: CTE matching layer of composition Si-20SiC-5Ti-5Al (wt %.), oxygen diffusion barrier layer of composition Si-15HfC-10Ir-5Ti (wt.%) and a SILBOND^{TM} layer. The coating thickness is clearly uneven, ranging from 5 to 20 μm. Good mechanical interlocking is observed. However, the thickness of the interfacial layer was not measured.
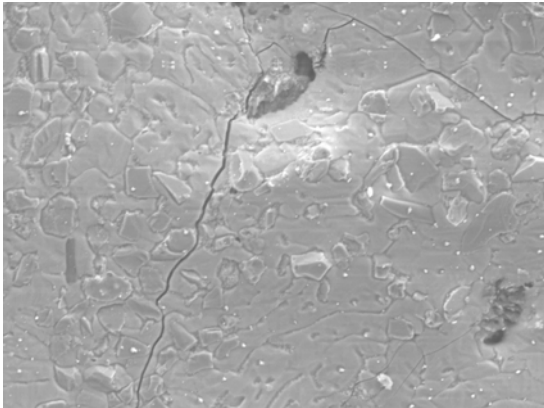
Figure 7. SEM image of Si-20SiC-5Ti-5Al (wt.%) CTE matching coating laser fused at 700 W and 55 mm/min over C/C composite surface, 500x.
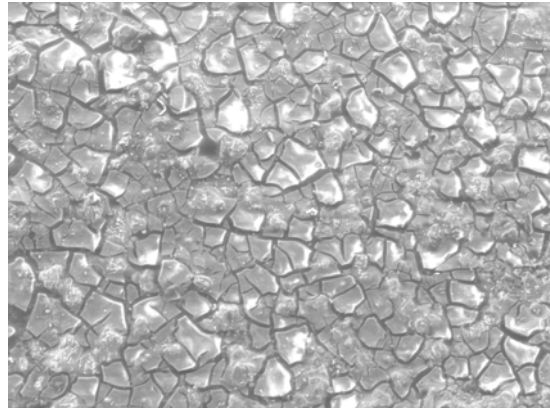

Figure 8. SEM image of Si-15HfC-10Ir-5Ti (wt.%) oxygen diffusion barrier coating laser fused at 560 W and 80 mm/min over previously deposited CTE matching coating, 200x.
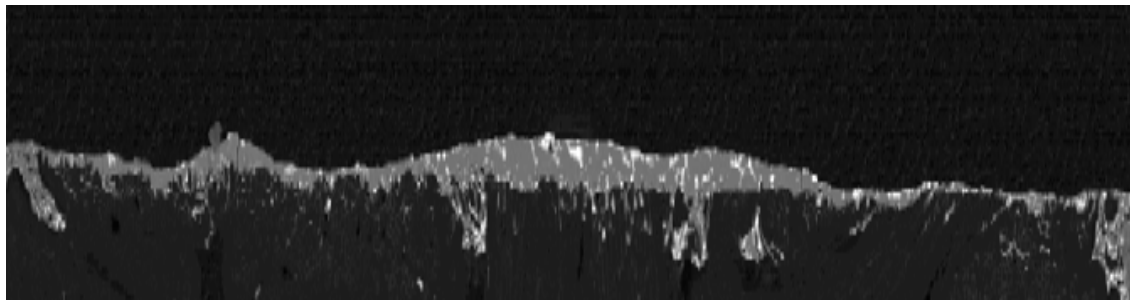

Figure 9. Scanning electron micrograph showing the cross-sectional view of the three-layer coating laser processed sample. Infiltration of the coating material into the voids or inter-fiber space is shown thereby providing mechanical interlocking of the coating to the substrate.

Oxidation Testing

Figure 10 shows a plot of the weight loss data for the coated and uncoated samples as functions of time at 1000ºC in still air. Coated sample consisted of: Si-20SiC-5Ti-5Al (wt.%) CTE matching layer, Si-15HfC-10Ir-5Ti (wt.%) oxidation diffusion barrier layer and SILBOND[TM] layer. After 1.6 hours of exposure the coated samples lost 57% of its original weight, whereas the uncoated sample was completely oxidized. Figure 11 shows a plot of the weight loss rate per unit area of sample surface for the coated and uncoated samples. These data points were obtained by computing discrete changes in weight loss with respect to time, normalized by the surface area of each sample. The coated sample maintained a weight loss rate of –0.012 gr/cm^2 for almost one hour, whereas for the uncoated samples it corresponded to –0.022 gr/cm^2, indicating a two-fold increase in oxidation.
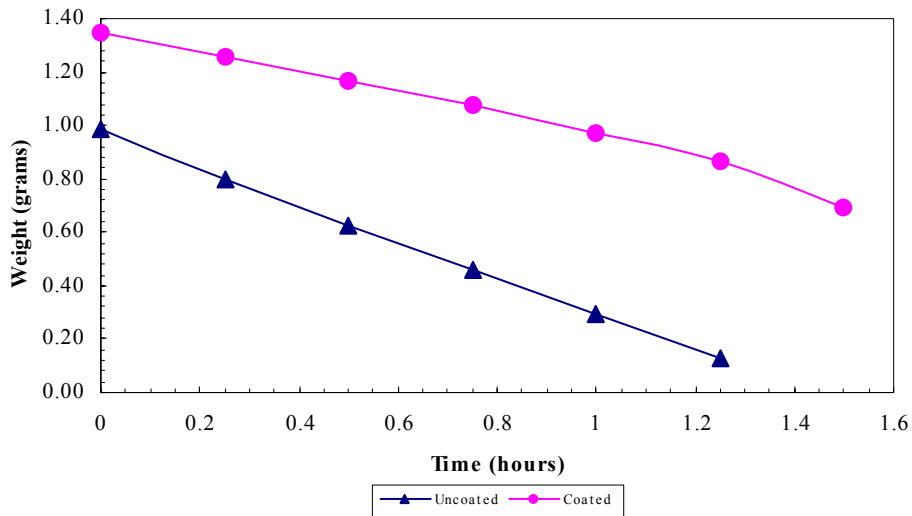
Figure 10. Weight loss data for coated and uncoated samples at 1000ºC. Coated sample consisted of CTE matching layer (Si-20SiC-5Ti-5Al wt.%), oxidation diffusion barrier layer (Si-15HfC-10Ir-5Ti wt.%) and SILBOND[TM] layer.
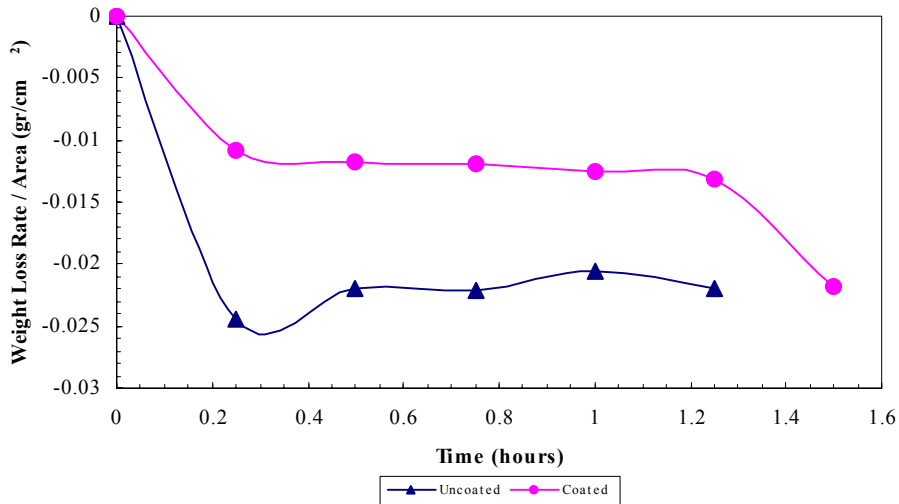
Figure 11. Weight loss rate versus time for coated and uncoated samples at 1000 ºC in still air.

Conclusions

Laser fusion coating of functional parts can be achieved by means of high-speed raster scanning of a pre-deposited slurry with a high power CO_2 laser beam. Unlike in other conventional laser processes, the experimental procedure used in the laser fusion process uses a rectangular energy source rather than a single beam. This allows for a uniform fusion temperature during the process thereby resulting in a more uniform coating.

High scanning speed used in the process helps in overcoming the effect of surface tension dragging of coating regions ahead of the melt front and lowers the exposure time to contamination. Use of high scanning speeds however, reduces the dwell time necessary to grow a complete interface layer.

Under rough vacuum conditions an addition of 5 wt.% titanium powder to the coating helped reduce oxygen contamination. The study also indicated that addition of 5 wt.% aluminum to the coating lowers the melting point resulting in larger superheating that in turns lowers the viscosity of the melted slurry thereby enhancing wetting. Addition of Si and SiC to the coating composition provides oxidation protection to the C/C composite at temperatures below 1500ºC due to the formation of a glassy SiO_2 layer, but at higher temperatures this coating layer delaminates. HfC and iridium are inherently refractory materials that provide oxidation protection at temperatures above 1500ºC. Addition of SiC and HfC particles to the coating composition also seem to help in lowering the wetting angle by dragging the melt more uniformly over the surface of the composite. Applying a crack sealant coating could mitigate severe cracking due to the mismatch in CTE between coating layers and the substrate. The study indicates a two-fold increase in the oxidation resistance of the coated C/C composites at 1000ºC in still air. Nonetheless, a crack free coating remains as the goal left to achieve by this laser fusion technique.

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