High-Density Infrared Cladding of Ta on Steel

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The addition of tantalum to the inside diameter of a gun barrel would reduce erosion during firing of medium and large caliber guns. In this work, chemical vapor deposited (CVD) Ta was bonded to A723 Steel. High-density infrared (HDI) heating was employed to bond Ta to steel at 1440°C while maintaining bulk steel temperatures below the 357°C threshold for retaining beneficial compressive stresses (autofrettage).

Through-thickness temperature evolution modeling was performed. Metallographic evaluation of claddings is reported. Characterization of the interface showed that metallurgical bonding occurred while keeping bulk temperatures low.

Keywords High density infrared processing; Steel; Tantalum.

INTRODUCTION

The environment that is a result of firing a projectile from a large caliber gun barrel is extremely damaging to a steel barrel. High-temperature, corrosive gases are released when the firing charge is ignited. Repeated firing of the gun causes these gases to degrade the integrity of the barrel and can lead to a catastrophic failure. The cost-effective addition of a refractory metal to the inside diameter (ID) of a gun barrel would help to reduce the amount of corrosive wear that is a result of firing and would extend gun barrel life. Metals such as tantalum and niobium, and alloys such as Ta-10W and Stellite could provide a suitable barrier to improve the life of the gun. Cladding refractory metals to steel is not a trivial undertaking. The high melting points of refractory metals make it very difficult to metallurgically bond to a steel substrate. This means that to drive a solid-state reaction, temperatures must be well in excess of 1000°C. But, heating the refractory to these temperatures for a substantial period of time would adversely affect the beneficial compressive stresses (autofrettage) that are the result of firing and would extend gun barrel life. Metals such as tantalum and niobium, and alloys such as Ta-10W and Stellite could provide a suitable barrier to improve the life of the gun. Cladding refractory metals to steel is not a trivial undertaking. The high melting points of refractory metals make it very difficult to metallurgically bond to a steel substrate. This means that to drive a solid-state reaction, temperatures must be well in excess of 1000°C. But, heating the refractory to these temperatures for a substantial period of time would adversely affect the beneficial compressive stresses (autofrettage) that are the result of firing and would extend gun barrel life. Metals such as tantalum and niobium, and alloys such as Ta-10W and Stellite could provide a suitable barrier to improve the life of the gun. Cladding refractory metals to steel is not a trivial undertaking. The high melting points of refractory metals make it very difficult to metallurgically bond to a steel substrate. This means that to drive a solid-state reaction, temperatures must be well in excess of 1000°C. But, heating the refractory to these temperatures for a substantial period of time would adversely affect the beneficial compressive stresses (autofrettage) that are the result of firing and would extend gun barrel life.

Steel substrates do not allow for adequate bonding and are prone to spalling of coatings when conventional surface coatings are applied. To prevent this, Ultramet applied a very thin surface conversion coating of Ta as an interlayer between the steel and the thick chemical vapor deposition (CVD) Ta surface coating. This interlayer was applied using a proprietary process at temperatures less than typical CVD temperatures for refractory metals but not as low as the threshold, post-autofrettage thermal soak temperature (357°C). It is typically on the order of 2–4 microns thick with a diffusion gradient that enables the coating to be bonded. Due to its high mobility and diffusivity, carbon (C) can potentially migrate from the steel into the Ta. The application of this interlayer improved adherence of subsequent surface coatings applied via conventional CVD. In this project, 2–3-micron-thick Ta/TaC conversion coatings were applied to the steel to promote adhesion between the subsequently deposited Ta CVD surface coatings and the steel substrates.

Conventional CVD deposition of Ta is accomplished at >800°C for a period of hours, depending on thickness, through the following reactions:

Tantalum (m) + Chlorine (g) → Tantalum Chloride (g)

Tantalum Chloride (g) + Hydrogen (g)

→ Tantalum (m) + Hydrogen Chloride (g)
Tantalum metal chips were reacted with chlorine gas at elevated temperatures in a precursor pot that was upstream of the substrate to form gaseous TaCl₅. The precursor gas then traveled downstream to the heated substrate where it decomposed in the presence of hydrogen (H₂) gas to form a Ta-metal coating. By-products, such as HCl and other unused halides, were extracted through a vacuum system. The CVD process yielded high purity, fully dense coatings and the processing temperature promoted as-deposited diffusion at the coating/substrate interface, producing good bond strength. This program evaluated the potential and effects of inducing even greater coating/substrate diffusion through HDI processing.

**Procedure**

The preliminary samples of Ta-cladded steel were produced by Ultramet (Pacoima, CA). Cylindrical ASTM A723 steel substrates measuring 2.54 cm in diameter (1.0 in) and 0.635 cm thick (0.25 in) were clad with a layer of Ta metal by chemical vapor deposition (CVD). Samples with cladings of 0.025 cm, 0.064 cm, and 0.102 cm thickness (10, 25, and 40 mils, respectively) were produced. Each of these samples was fitted with a thermocouple on the back of the substrate to track the temperature evolution during HDI processing. In order to metallurgically bond the Ta cladding to the steel substrate, it was necessary that the interface be at the appropriate temperature and the temperature inside the sample was at the appropriate temperature and the temperature in the bulk of the substrate relatively low.

**Plasma Arc Lamp**

The HDI process utilized a unique technology to produce extremely high-power densities of up to 3500 W/cm² with a single lamp. Instead of using an electrically heated resistive element to produce radiant energy, controlled and contained plasma was utilized. The lamp consisted of a quartz tube 3.175 cm in diameter and 10.16 cm long and sealed at the ends where the cathode and anode were located. Deionized water mixed with argon gas enters at the cathode side through high-velocity jets impinging at a given angle. Due to the high velocities and pressure, the deionized water was impelled to the wall of the quartz tube and spiraled down the length of the tube in a uniform 2 to 3-mm-thick film. This water film served two purposes: to cool the quartz wall and to remove any tungsten particulate that may have been expelled from the electrodes. The gas moved in a spiral fashion through the center of the tube. A capacitative circuit initiated the plasma. The plasma, which had a temperature in excess of 10,000 K, was stable and produced a radiant spectrum 0.2 to 1.4 μm. The spectrum was primarily in the infrared (0.78 μm to 1.00 μm) and was absorbed with high efficiency by metal surfaces.

The lamp system used for processing was a 300,000 W line focus lamp. The lamp can operate anywhere within the range of 2–100% of peak power and can change power levels in as little as 2.0 ms. The electric to radiant power conversion was 55% efficient.

In this work, sample processing was performed in an environmentally controlled box, which has a quartz window cover to permit processing of materials in a controlled atmosphere. The infrared reflector had a focal length that extends through the quartz and onto the material being processed.

**Process Modeling**

In order to optimize the experimental work performed, a temperature/time/power input model was employed. This math model has been used to predict temperature fields and phase changes during HDI processing of powder metal precursors to dense sheet and Ni coatings on steel [5, 6]. The math model is based on TELLURIDE, a multiphase casting simulation software code developed at the Los Alamos National Laboratory [7]. It has been modified at ORNL to accurately reflect the processing conditions of HDI. The TELLURIDE code requires that a full set of thermophysical properties for the Ta cladding (solid and liquid states) and steel substrates (solid state) as well as a proper geometry and mesh be devised. The model is equipped to handle the temperature dependence of the thermophysical properties and any anisotropy that may exist within the sample. In this work, the Ta cladding remained well below the 2998 °C melting point during HDI processing, requiring that only the solid-state thermophysical properties were crucial. Table 1 [8] shows the temperature-dependent thermophysical properties that were input into the TELLURIDE code for the Ta cladding and steel substrate. The density is assumed to be constant. Also, Kirchoff’s Law is assumed to apply such that the emissivity and the absorptivity are equal. The emissivity is also assumed to be normal spectral.

With the thermophysical properties defined, an appropriate geometry and mesh were devised. For simplicity, the problem was assumed to be one-dimensional heat flow. A small section of the entire geometry near the center of the sample was modeled by assigning four planes of symmetry for which all heat transfer coefficients are set to zero. The top surface was assigned the boundary condition representing the radiant heating input from the plasma arc lamp. The bottom surface was assigned a simple convective heat loss condition due to the lack of conduction between that sample and the processing apparatus. Three geometries

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature [°C]</th>
<th>Specific heat [kJ/kg·K]</th>
<th>Thermal conductivity [W/m·K]</th>
<th>Emissivity [0–1]</th>
<th>Density [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>25.0</td>
<td>0.15</td>
<td>55.0</td>
<td>0.57</td>
<td>16.65</td>
</tr>
<tr>
<td></td>
<td>2500.0</td>
<td>0.21</td>
<td>70.0</td>
<td>0.40</td>
<td>16.65</td>
</tr>
<tr>
<td>Steel</td>
<td>25.0</td>
<td>0.45</td>
<td>28.0</td>
<td>N/A</td>
<td>7.83</td>
</tr>
</tbody>
</table>
and meshes were devised for each of the three thickness claddings. Figure 1 shows the geometry and mesh for the 0.025-cm-thick Ta cladding.

The 0.025-cm-thick cladding contained 72 eight-node brick elements. The 0.064-cm and 0.102-cm-thick cladding contained a proportionate number of elements to the thickness based on the ratio of the 0.025-cm-thick cladding. With a complete set of thermophysical data and geometries with applied meshes, lamp processing parameters can now be predicted.

**MODELING AND PROCESSING RESULTS**

The processing time necessary for a 1500 W/cm² (maximum power density given experimental setup) pulse to heat the interface temperatures to 1440°C for a few seconds was predicted. The calculated temperature evolution is plotted along with the experimental temperature evolution for the substrate in Figs. 2–4. Processing times required to achieve the necessary interface temperature were approximately 0.2 s longer for each thickness. Also, all of the substrate temperatures on the back faces remained well below the 357°C limit given by Benet Laboratory, in order to retain the compressive residual stresses from the autofrettage process.

**POST-HDI MICROSCOPIC INVESTIGATION**

Following application of the thin surface conversion coating to the steel substrates, a specimen was sectioned for metallographic examination. Figure 5 is an SEM micrograph of a steel substrate with a surface conversion coating in the as-deposited condition (prior to HDI processing). Semi-quantitative EDS element analysis of this coating indicated the presence of both carbon and Fe. C content in the Ta diffusion coating can alter the coating hardness, and
excessive C diffusion can leave Kirkendall voids at the coating/substrate interface. As shown in Fig. 5, the Ta diffusion coating is highly conformal to irregularities in the steel surface and no voids exist at the coating/substrate interface.

Conventional CVD was then used to apply dense Ta surface coatings on top of the tantalum diffusion coating. The benefits of this dual-layer approach are that the conventional CVD Ta surface coating is applied to a Ta diffusion coating that is already integrally bonded to the steel substrate, and the diffusion coating protects the steel surface from reaction (etching) with compounds present in the conventional CVD Ta coating environment. Following CVD runs, selected specimens were sectioned for metallographic analysis. Figure 6 shows the CVD Ta coating (prior to HDI processing) on steel substrates with the tantalum conversion coating interlayer. From these micrographs, it was noted that a dense coating of tantalum with minimal porosity evident around the interlayer region was deposited on the specimens. The coatings also appeared to be well bonded to the substrates and showed no indications of delamination. The diffusion zone increased from the original 3 microns of the diffusion coating interlayer to approximately 25 microns during the application of the conventional CVD Ta surface coating. Microhardness measurements taken at various points on the substrate and coatings indicated that the diffusion zone contained sufficient carbon to promote a Ta-rich TaC layer. Ta–Fe intermetallics may also be promoting an increase in hardness. In spite of the increase in hardness, no cracks were evident in the diffusion zone even after being exposed to the thermal cycling of the deposition process. The layer retained good ductility. The average microhardness of the
Ta CVD coatings was 165 VHN, the interlayer conversion coating was 1580 VHN, and substrate steel was 315 VHN.

After HDI processing, all specimens were returned to Ultramet for metallographic analysis. The 0.025-cm-thick specimen was treated at a power density level of 1000 W/cm² for 0.5 sec. An SEM micrograph of the specimen after HDI processing is shown in Fig. 7. As seen in the micrographs, a clear diffusion zone near the interface of the coating and substrate is visible, and it is only marginally thicker than that achieved when the CVD Ta surface layer was applied over the Ta diffusion coating (i.e., minimal increase in thickness). Extensive EDS analysis of the diffusion zone was conducted and indicated higher levels of carbon than before exposure. Some Fe, nominally less than 3 atomic percent, was also noted in selected instances. The carbon level in the tantalum coatings gradually dropped off ahead of the diffusion zones, leading to pure tantalum (in the surface coating region). The formation of small void regions ahead of the diffusion front was also noted. Figure 7 also shows nominal microhardness values through the thickness of the specimens. The microhardness values of the coating and the steel did not change significantly as a result of the HDI process, thus indicating that the steel was not excessively heated.

It should be noted that what might appear to be delamination of the coating at the diffusion zone/steel interface in Figs. 6 and 7 is actually just a relief effect created by the polishing process because of the high hardness of the diffusion zone relative to the steel.

The 0.064-cm-thick specimen was treated at a power density level of 1500 W/cm² for 0.7 s. Metallographic analysis revealed results that were nearly identical to those found in the 0.025-cm-thick specimen. Figure 8 shows an SEM micrograph of the diffusion zone into the tantalum coatings with average microhardness values. Randomly selected measurements of the diffusion zone revealed a range of thicknesses from 24 to 30 microns. There did not appear to be a significant difference in the appearance or thickness of these zones based on the minor variations in processing that were used. EDS analyses again indicated carbon diffusion into the tantalum. Some porosity was also noted in these specimens, especially in the diffusion zone. It is expected that the significant diffusion zone that occurred during the relatively short duration of the process could lead to the formation of Kirkendall-type voids. These voids are commonly found in cases where rapid diffusion in a bulk material leaves vacancies that subsequently coalesce to form large void zones ahead of the diffusion front. The formation of these voids as a result of diffusion during the HDI process is not desired, as it is expected to reduce the overall adhesion of the coatings to the substrate.

The 0.102-cm-thick specimen was treated at a power density level of 1500 W/cm² for 1.0 s. Figure 9 shows representative cross-sectional SEM micrographs of the diffusion zone created in the coated specimen. Figures 10 and 11 show a more detailed view of the atomistic diffusion that occurred as a result of HDI processing. Zone thicknesses in this specimen ranged from 33 to 40 microns. The longer exposure time led to thicker diffusion zones.
The diffusion zone of the pulse-exposed, 0.102-cm-thick specimen was on the order of 10 microns thicker than the zones of the 0.025-cm-thick specimens. The thicker specimen would have a higher surface temperature because it would take longer for the thermal energy to diffuse through the coating and steel substrate to reach the backside and maintain a consistent maximum temperature of 350°C. Consequently, the interface region of the thicker specimen would have reached a higher temperature and would have had to maintain it for longer, thus allowing the C more time to diffuse from the steel into the tantalum coating. Significant void formation in the diffusion zone was also noted in this specimen. As seen in Fig. 9, a line of voids formed at the diffusion front, thus confirming that they are indeed Kirkendall voids. While this is definitive proof that the HDI process does indeed promote diffusion, the diffusion is dominated more by the interstitial diffusion of C than interdiffusion of the metallic elements. The formation of voids is obviously undesirable, as it has the potential to greatly reduce the adhesion of the coating to the substrate.

CONCLUSIONS

The cladding and metallurgical bonding of large caliber autofrettaged gun barrels with Ta metal can potentially extend barrel service life by allowing for more aggressive projectile firing charges. But, due to the autofrettage and the temperatures required to bond Ta to steel, conventional heating methods are not rapid enough to control the bonding of the two metals while keeping temperatures below 357°C and exposure times in the substrate as low as possible. Processing these coatings with plasma arc lamps was shown to achieve temperatures at the interface at which bonding could take place while the substrate temperature was held low enough to preserve autofrettage compressive stresses. Preliminary modeling showed that the maximum lamp power output would easily achieve bonding temperatures yet maintain low substrate temperatures. Substrate temperature evolution for experimental and calculated cases agreed extremely well. The goal of this project was to demonstrate a metallurgically bonded tantalum coating on steel using a combination of coating deposition technology and HDIR processing. Analysis of CVD Ta coated specimens after HDIR processing indicated significant diffusion of C and minimal diffusion of Fe into the tantalum coating. The diffusion zone thickness ranged from 20–40 microns, depending on the HDIR exposure time. This effect was demonstrated on coatings varying in thickness from 0.025 cm to 0.102 cm. While interdiffusion is typically beneficial to coating adherence, the formation of Kirkendall voids was witnessed behind the diffusion front for the 0.0102-cm-thick sample. The formation of these voids is undesirable, as they have the potential to severely degrade coating-substrate adherence. The as-deposited CVD Ta coating adhesion appeared to be quite good; however, rapid thermal cycling at the desired use temperature must be performed to determine actual in-service behavior. Future work should explore an interface thin film, e.g., chromium or nickel, which can prevent carbon diffusion into the Ta coating while potentially improving the metallurgical bond.

REFERENCES