Transition Metal Coatings on Graphite
Via
Laser Processing

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Outline

- Objective & Motivation
- Introduction to Graphite
- Problems and Possible Solutions
- Laser Processing
- Results & Discussion
- Summary
- Future work
Objective:

- Thick metallic coatings on graphite, carbon fiber materials, carbon-carbon composites.

Motivation:

- Protection of carbon from oxidation/erosion
- Integration of carbon and metallic structures
Graphite: Introduction

- Low specific gravity
- High resistance to thermal shock
- High thermal conductivity
- Low modulus of elasticity
- High strength (doubles at 2500°C*)

“High temperature structural material”

Graphite: Problems & Solution

- Low resistance to oxidation at high temperatures
- Erosion by particle and gas streams

**Solution:** Well-adhered surface protective coatings !!

**Adherence:**

1. Metal/carbide and carbide/graphite interfaces are compatible since formed by chemical reaction.
2. Interfacial stresses can be created by the difference in thermal expansion.
Graphite: Surface Protection

Thermal Expansion

a) Mismatch in the thermal expansion develops interfacial stresses.

b) Large interfacial stresses lead to coating delamination/failure.
Graphite: Surface Protection

- The ideal coating material for a carbon material:
  - One that can form carbides, and
  - Whose coefficient of thermal expansion is close to that of the carbon substrate.

- The coefficient of thermal expansion of a carbon material depends on the its method of preparation.

- Transition metals are carbide formers.

- UTSI: Semiconductor grade graphite (7.9 x 10^{-6} m/m °C)
Graphite: Surface Protection

- Non-transition metal coatings like silicon carbide, silicon oxy-carbide, boron nitride, lanthanum hexaboride, glazing coatings, and alumina have also been deposited.

- Methods used: chemical vapor deposition, physical vapor deposition, photochemical vapor deposition, thermal spraying, PIRAC, and metal infiltration.
Graphite: Laser Processing

- CLA (UTSI): the first to demonstrate laser deposition on graphite.
- Early attempts were to make bulk coatings to avoid dilution in the coating due to melting of the substrate. Graphite does not melt, but sublimates at room pressure.
- CLA process: LISI™ !!
- LISI™ is a registered trademark of the University of Tennessee Research Corporation.

LISI: Laser Induced Surface Improvement
**LISI™ on Graphite**

- Prepare a precursor mixture by mixing metal particles and a binder.
- Spray the precursor mixture with an air spray gun on polished graphite substrates (6 mm thick).
- Dry for a couple of hours under a heat lamp before laser processing.
- Carbide forming ability among transition metals: Fe< Mn< Cr< Mo< W< V< Nb< Ta< Ti< Zr< Hf
- Titanium (<44 \(\mu\)m), zirconium (2-5 \(\mu\)m), niobium (<10 \(\mu\)m), titanium-40 wt% aluminum (-325 mesh), tantalum, W-TiC, chromium, vanadium, silicon, iron, etc.
- Precursor thickness: Ti (75 \(\mu\)m), Zr (150 \(\mu\)m), Nb (125 \(\mu\)m). Contains binder and moisture in pores.
LI$\text{SI}^\text{TM}$ on Graphite
Two-step Processing Chamber

1,2,12,13 – Overhead laser assembly; 4 – Argon; 16,17 – mechanical & turbo pumps
7 – sample, 8 – alumina rods, 9 – induction heating element, 18 – RF supply.
LISI™ on Graphite

Process variables: laser power ($W$), scanning speed (mm/s), focal spot size (mm), laser pass overlap (%),

$T = 800 \, ^\circ C$

Copper induction heating element

Graphite
**LISI™ on Graphite**

**Focal spot size (Intensity):**

Laser beam: near-Gaussian, $1075 \pm 5$ nm

Focal plane (Max intensity)  
$I = P / \text{spot area}$

Percentage of peak intensity:

- > 90 %
- > 75 %
- > 61 %
- > 50 %
- > 37 %
- > 25 %
- > 13.5 %
- > 5 %

# LISI™ on Graphite

## Precursor details

<table>
<thead>
<tr>
<th>Metal</th>
<th>Particle size (µm)</th>
<th>Binder (weight %)</th>
<th>Precursor thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium</td>
<td>&lt; 44</td>
<td>60</td>
<td>75</td>
</tr>
<tr>
<td>Zirconium</td>
<td>2 – 5</td>
<td>10</td>
<td>125 – 150</td>
</tr>
<tr>
<td>Niobium</td>
<td>&lt; 10</td>
<td>33</td>
<td>125</td>
</tr>
</tbody>
</table>

## Optimized laser processing conditions

<table>
<thead>
<tr>
<th>Coating</th>
<th>Laser power (W)</th>
<th>Spot size (mm)</th>
<th>Scanning speed (mm/s)</th>
<th>Overlap (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium</td>
<td>235</td>
<td>1.28</td>
<td>5</td>
<td>86</td>
</tr>
<tr>
<td>Zirconium</td>
<td>290</td>
<td>0.81</td>
<td>5</td>
<td>78</td>
</tr>
<tr>
<td>Niobium</td>
<td>348</td>
<td>0.93</td>
<td>5</td>
<td>81</td>
</tr>
</tbody>
</table>
LISI™ on Graphite: Results

- Scanning electron microscopy
- X-ray diffraction of the coating surface
- X-ray diffraction of the coating-graphite interface
- Microhardness of the coating
- Secondary ion mass spectrometry of the niobium coating

SEM was done at the VINSE, Vanderbilt University (field emission SEM)
X-ray diffraction was done on a Philips X’pert system with Cu Kα at 1.5406 Å
Microhardness was done on a LECO LM 300AT under a load of 25 gf for 15 seconds (HK)
SIMS was done on a Millbrook MiniSIMS: 6 keV Ga⁺ ions
Results: Titanium

SEM micrographs of the titanium coating.

XRD of the titanium coating surface (A) and its interface with the graphite substrate (B)

Oxygen: LISI™ binder or traces in the chamber

900-1100 HK

1 - Ti
2 - TiC
3 - Ti₃O₅
4 - Carbon
Results: Zirconium

SEM micrographs of the zirconium coating
Delamination and crack appear in some locations

XRD of the zirconium coating surface (A) and its interface with the graphite substrate (B)

\[ \text{Intensity (arbitrary scale)} \]

- 1 - ZrO_{0.35}
- 2 - Zr_{2}O_{1-x}
- 3 - ZrO_{2}
- 4 - Carbon
- 5 - ZrC_{0.7}

\[ \text{2-theta (degrees)} \]

\[ \sim 775 \text{ HK} \]
Results: Niobium

SEM micrographs of the niobium coating

XRD of the niobium coating surface (A) and its interface with the graphite substrate (B)

620-1220 HK
Proposed Mechanism

- Self-propagating high temperature synthesis (SHS) aided by laser heating. It is also called as combustion synthesis.

- Once triggered by the laser heating, the highly exothermic reaction advances as a reaction front that propagates through the powder mixture.

- This mechanism strongly depends on the starting particle size. In the present study, the average particle size is <25 μm.
Coating delamination

The coefficient of thermal expansion of titanium carbide is close to that of the graphite substrate than those of zirconium carbide and niobium carbide. Hence, titanium coating did not delaminate.

<table>
<thead>
<tr>
<th>Coefficient of thermal expansion (µm/m°C)</th>
<th>Metal *</th>
<th>Metal Carbide</th>
<th>Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium</td>
<td>7.6</td>
<td>6.99</td>
<td></td>
</tr>
<tr>
<td>Zirconium</td>
<td>5.04</td>
<td>6.74</td>
<td>7.9</td>
</tr>
<tr>
<td>Niobium</td>
<td>7.3</td>
<td>6.65</td>
<td></td>
</tr>
</tbody>
</table>

SIMS of the Niobium Coating

Chemical Image of as received Nb coating
A: Potassium, B: Magnesium
C: Oxygen, D: Carbon

Mass Spectrum
A: as received       B: slightly ground
Summary

- Successfully deposited fully dense and crack-free transition metal coatings on graphite substrates.

- All the coating interfaces contain carbide phases.

- Laser assisted self-propagating high temperature synthesis (SHS) has been proposed to be the possible reason for the formation of all the coatings.

- SIMS analysis proved that LISI™ binder forms a thin slag layer at the top of the coating surface post laser processing.
Future Work

- Heat treatment
- Advanced characterization (oxidation analysis, adhesion test)
- Calculation of various thermodynamic quantities
- Try different materials!!
Acknowledgements

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Questions ??

(or may be suggestions)
Thanks !!!

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