Novel Hybrid Coatings

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Abstract
In order to address deficiencies in thermal spray coatings applied using air plasma spraying (APS) and high velocity oxygen fuel (HVOF), namely, adhesion, cohesion, porosity and line of sight limitations, novel hybrid coatings using post-thermal spray chemical vapor deposition via the pack cementation process were developed. Coatings based on tungsten carbide-cobalt chrome and chrome carbide-nickel chrome followed by boron or chrome diffusion were applied to multistage and single stage pump components for severe service applications in sand and alumina catalyst. Field testing established the effectiveness of using the dual coating approach.

Introduction
Thermal spray and pack diffusion coatings (“pack cementation”) are well established as efficient surface improvement technologies. Both techniques are generally used as stand alone methods to address problem in corrosion, erosion, galling, abrasion, oxidation or sulfidation. This paper examines use of both technologies in conjunction in order to extend improve service life of multi and single stage pumps operating in severe service.

Thermal Spraying
Thermal spray is well accepted as a premium method of applying hardfacings, corrosion resistant and high temperature coatings suitable for oxidation, hot corrosion and thermal barriers. Readers are directed to the following reference for detailed descriptions of the various different types of thermal spray [1]. Needless to say, as with any other surfacing technologies, each individual technique has its attributes and deficiencies. The major limitation of all thermal spray techniques is “line of sight” application. Use as barrier coatings in corrosive environments is also limited by interconnected porosity [2]. Furthermore, with the exception of spray and fuse and low pressure plasma spray all other techniques lead to mechanical bonding between the substrate and coating.

Pack Diffusion
Pack cementation, although commercially practiced since the 1960’s for providing oxidation resistant coatings on gas turbine components, is less known. This technique is a variation of chemical vapor deposition (CVD) [3]. The part to be coated is immersed in a powder pack consisting of the element to be diffused (e.g. Al, B, Si, Cr, and V) along with an activator; generally a salt (NaF, NaCl, NH₃Cl etc) and inert filler powder such as alumina. The pack is enclosed by a sealed retort and subjected to temperatures where the salt dissociates, forming halides of the coating element and is transported under a gaseous diffusion gradient to the substrate, where solid state diffusion occurs. Coating characteristics are a function of substrate chemistry, pack composition and consistency, time and temperature.

Advantages offered by this surfacing technique are:
1) The process is relatively inexpensive.
2) Simple equipment.
3) Complicated geometries can be coated including blind holes.
4) Hardness greater then that in thermal spray can be achieved.
5) A metallurgical bond is present.

The disadvantages are:
1) High processing temperatures can lead to distortion.
2) High temperatures may require re-heat treatment on some alloys.
3) Tight tolerances can not be maintained on complicated geometries.
4) Chemical stripping is required of most coatings.

Figure 1 shows the microstructure of a typical boride coating applied using pack cementation onto steel. One can notice that the treatment leads to two layers and considerable
diffusion into the grain boundaries. Table 1 lists common industrial pack diffusion coatings commercially available and their attributes.

Table 1: Commercially available diffusion processes.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Substrates</th>
<th>Application</th>
<th>Attribute</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boride</td>
<td>Fe, Ni, Co alloys and cermets</td>
<td>Pumps, valves, dies</td>
<td>DPH 1650, 12 – 125 µm thick</td>
</tr>
<tr>
<td>Aluminide</td>
<td>Fe, Ni, Co alloys</td>
<td>Gas turbine components, heat exchanger tubes in refineries</td>
<td>oxidation resistant, 12 – 75 µm typical,</td>
</tr>
<tr>
<td>Chrome</td>
<td>Fe, Ni, Co, Mo alloys</td>
<td>Gas turbines, boiler tubes</td>
<td>hot corrosion / oxidation resistance, 12 – 25 µm thick</td>
</tr>
<tr>
<td>Silicide</td>
<td>Fe, Co and Mo alloys</td>
<td>Pumps, valves, rocket components</td>
<td>Acid resistance and high temperature oxidation resistance for Mo alloys</td>
</tr>
<tr>
<td>Vanadium</td>
<td>High carbon bearing steels</td>
<td>Dies, punches</td>
<td>Forms vanadium carbide, DPH 2700-3000, 12 – 25 µm thick</td>
</tr>
</tbody>
</table>

This paper reports on coatings developed for specific pumping applications using thermal spray and diffusion coatings in conjunction in order to improve equipment life beyond what the individual technologies could achieve.

**Hybrid Coating Applications of Severe Service Pumps**

Severe service pumps refer to pumps operating in erosive or corrosive environments. The petroleum industry has many such applications, from catalyst pumps in refineries, to pumps involved in directly extracting sand laden oils from wells. Hybrid coatings applied via thermal spray followed by the pack cementation process are well suited to provide protective layers on severe service pumps.

**Multistage Submersible Pumps**

In this study multistage submersible pumps were coated using a dual HVOF-pack cementation system. These pumps are used where a small equipment footprint is required in direct extraction from wells and oil platforms. Sets of diffusers and impellers are stacked on top of each other to form a multistage pump. Figure 2 shows an eroded pump set. Wear was severe enough in this case that the impeller hub has worn off. The sidewalls of the diffuser also have significant material loss from sand laden oil swirling in this region. It was decided that a thick chromium carbide-nickel chrome (75Cr₃C₂-25NiCr) be applied via HVOF to the sidewalls of the diffuser and along the impeller hub and all other accessible areas, followed by boronizing of the whole assembly (Fig. 3). The sprayed coating composition was chosen since it was previously established that higher binder levels allowed for diffusion between substrate and coating and hardening of the matrix by formation of nickel and chrome borides. Boronizing also hardened the vane passages and other inaccessible areas subject to erosion. A further benefit of the carbide coating on the hub OD and diffuser bore allowed replacement of solid ceramic bearings and sleeves.
Complete coverage of all wetted areas was achieved using the hybrid coating process. A photomicrograph of the duplex coating is shown in Fig. 4.

No discernable difference in density was observed between boronized and as-sprayed HVOF Cr$_3$C$_2$-NiCr coatings. This was due to the high initial density of the as-sprayed coating. Knoop microhardness readings across the cross-section also had consistent values. However, the hardness between boronized and as-sprayed favored the boronized coatings (average 1100 HK boronized and 950 HK as-sprayed). The improvement is from particle–particle sintering at the boronizing temperature of 900°C. The boride layer was difficult to retain during diamond saw cutting and metallographic preparation. Therefore, microhardness tests were conducted on the polished top surface instead of the cross-section. The coating had a hardness of 1600 KH using a 100 g load, confirming the formation of borides. Thickness of the boride layer measured on remnants along the cross-section measured between 15 – 25 µm.

Boronizing HVOF carbide coatings does not lead to penetration of the boron vapor deep into the coating, but rather a thin continuous layer is formed on the surface as a reaction between the binder and boron occurs. It appears that boride growth is limited due to the slow diffusion rates across the initial layer that is formed. The primary purpose of the post-spray boronizing in this application is to provide hardening of areas not assessable by thermal spray.

Coated stages were assembled into pumps and operated in various locations known for having erosive conditions. Table 2 summarizes the performance of the coated stages against uncoated components.

Table 2: Performance of coated pumps.

<table>
<thead>
<tr>
<th>Location</th>
<th>Oil well condition</th>
<th>Life uncoated</th>
<th>Life coated</th>
</tr>
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<tbody>
<tr>
<td>California U.S.A. (Hillhouse and Henry, Platforms A,B &amp; C)</td>
<td>Erosion</td>
<td>Less then 170 days</td>
<td>392 days</td>
</tr>
<tr>
<td>Venezuela</td>
<td>Erosion</td>
<td>90 days</td>
<td>365-730 days</td>
</tr>
<tr>
<td></td>
<td>Corrosion</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The dramatic improvement in performance over a wide range of severe conditions justified the use of hybrid coating strategy. It must be pointed out that use of just HVOF type carbide coatings in this application is only partially successful since complete protection cannot be achieved using this process alone.

Centrifugal Pumps

Centrifugal type pumps used in catalyst service in refineries have also been subjected to dual HVOF/Diffusion treatment in order to combat alumina catalyst erosion. Larger pumps have fairly assessable areas and are amenable to successful HVOF application. Smaller pumps as shown in Figs. 5 and 6 have openings that cannot accommodate HVOF application in all areas. Pumps in this size range (impeller diameter of 450 mm (8") or less) are candidates for hybrid coating technology.

Traditionally, these types of pumps have had hardened wear rings in the pump case and impeller hubs. At the junction of the wear ring and pump component; case or impeller, an unhardened recess is normally present as a result of the manufacturing and ring installation process. Fine particle erosion will preferentially attack this area causing failure. As a preventive measure, refineries are increasingly requiring...
pump suppliers to use an integral wear ring design; in other words harden these areas directly without resorting to installing a ring.

As seen in Figs. 5 and 6 both the pump case and impeller have areas not assessable using the HVOF technique; therefore, these areas need to be hardened using a diffusion method such as boronizing. However, the wear ring areas have tolerances of ± 0.025 mm which cannot be maintained due to distortion at the high temperature used for boronizing. A series of trials established the amount of distortion for carbon steel and 13%Cr steel pumps of different sizes. In order to provide continuous protection in all areas including the ring area it was decided to use a thick HVOF tungsten carbide – cobalt chrome (86WC-10Co4Cr) coating on the ring areas as well as all other areas assessable to this line of sight technique. This coating was followed by boronizing of the entire assembly. Final diamond grinding re-established the critical tolerances on ring areas.

Centrifugal pumps coated using the technique described above have been installed in various locations over the past two years. Satisfactory performance has been reported to date.

**Conclusion**

The use of hybrid coatings applied via thermal spray followed by boronizing using the pack cementation process is well suited to providing protective layers on process pumps operating in severe service. The thermal sprayed carbide coatings allow thick hard coatings in areas assessable to line of sight application while pack cementation leads to thinner but harder surfaces in all other areas. Field performance of hybrid coated pumps show a considerable improvement over uncoated pumps.

**References**