Diffusion barrier coatings for graphite, C/C and C/SiC racks in vacuum heat treatment or high temperature brazing processes


In order to overcome the disadvantage of local carburizing of steel components in contact with light-weight graphite or carbon fiber reinforced ceramic racks alumina based thermal spray coatings are produced as diffusion barriers with improved life time compared to rapidly degrading alumina or boron nitride pastes. The powder flame sprayed coatings are also capable to prevent damage by excess filler material in high temperature brazing processes effectively. Besides graphite also C/C racks are coated with pure alumina, Al₂O₃-TiO₂ and Al₂O₃-Cr₂O₃. Conventional powder flame spraying is applied in order to provide a low-cost solution for realization of diffusion barriers. Coatings are characterized by means of optical microscopy and SEM with regard to the interface to the substrates and their porosity. Coated racks are used in field tests for case hardening of steel components. The life time of thermal spray coatings is compared to alumina and boron nitride based pastes. Comparative liquid metal corrosion tests are carried out with NiCr7Si4.5B3.1Fe3 filler at 1,050 °C.

1 Introduction

Racks for heat treatment or high temperature brazing processes are subject to severe stress. Due to technological and economical disadvantages heat resistant steels are more and more replaced by graphite or carbon fiber reinforced carbon (C/C) and silicon carbide (C/SiC). Their extremely high creep resistance results in high dimensional stability with simultaneously increased life time. The improved shape stability results in possibility to automate handling easily. Embrittlement and decrease of strength due to reactions with carbon or nitrogen in carburizing or nitriding processes are avoided and the reduced weight of the racks permits increased amount of components per batch and energy savings. The higher price of carbon fiber reinforced material is in most cases outweighed by the advantages in terms of high temperature strength and resistance against dynamic load due to high fracture toughness [1-3]. However, carbon based light-weight racks show the disadvantage of local carburizing of steel component areas in contact with the rack. Also in high temperature brazing processes exposure to excess filler material can result in severe damage [4-5]. Therefore diffusion barrier coatings are needed. State-of-the-art alumina or boron nitride based pastes provide protection function, but degrade rapidly. Thermally sprayed alumina based coatings are considered to provide long-term protection function. This paper comprises results of a study on the capability of low-cost conventional powder flame sprayed diffusion barrier coatings including field tests.

Table 1. Spraying parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Grit blasting pressure</td>
<td>300 kPa</td>
</tr>
<tr>
<td>Gun module</td>
<td>30</td>
</tr>
<tr>
<td>Powder orifice</td>
<td>2</td>
</tr>
<tr>
<td>Air pressure p_air</td>
<td>400 kPa</td>
</tr>
<tr>
<td>Oxygen pressure p_ox</td>
<td>300 kPa, 400 kPa</td>
</tr>
<tr>
<td>Acetylene pressure p_acet</td>
<td>50 kPa, 70 kPa</td>
</tr>
<tr>
<td>Spraying distance</td>
<td>100 mm</td>
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</tbody>
</table>

2 Experimental

2.1 Powder feedstock

For production of diffusion barrier coatings three types of powders by Castolin Eutectic GmbH, Kriftel, are used. In addition to pure alumina (99.8%) with grain size 22 μm < d < 45 μm Al₂O₃ - 2 wt.-% Cr₂O₃ and Al₂O₃ - 3 wt.-% TiO₂ powders with grain size 5 μm < d < 25 μm and 15 μm < d < 45 μm respectively are applied.

2.2 Powder flame spraying

Powder flame spraying is carried out with a Castodyn DS 8000 by Castolin Eutectic GmbH, Kriftel. The applied gun components and process parameters are comprised in Table 1. Graphite substrates are coated both without pre-treatment and after soft grit blasting. C/C substrates are grit blasted softly prior to coating deposition. Coatings covering the complete surface are produced within a single pass.

2.3 Coating characterization

Coating characterization includes visual inspection and metallographical evaluation by optical microscopy and SEM. Additionally graphite and C/C racks are coated and life time in vacuum case hardening heat treatment processes is determined in industrial field tests. The boundary conditions in these field tests impart maximum temperature of 1,050 °C, held constant for 60 min - 600 min, and cooling down from 860 °C to 400 °C in less than 60 s by nitrogen at 2 MPa. Finally tests concerning the corrosive attack of nickel based high temperature brazing filler material (NiCr7Si4.5B3.1Fe3; standard DIN EN 1044) on coated and uncoated graphite and C/C specimens are carried out. Filler paste is placed manually on top of specimens prior to heating up in vacuum to 1,050 °C. Temperature is kept constant for 1 h followed by slow cooling down. Corrosive attack is evaluated by means of metallographical inspection of cross sections.
3 Results

3.1 Microstructural investigations

Within single passes coatings with thicknesses between 70 µm (Al₂O₃ - 2 wt.-% Cr₂O₃) and 150 µm (Al₂O₃) are deposited both on graphite and carbon fiber reinforced carbon substrates. All three coating types show perfect interface with graphite substrates both in smooth and grit blasted surface state, Fig. 1 and 2. However, even gentle grit blasting can cause strong local material removal, which can result in segmentation of coatings. This might be desirable, because residual stresses are released and so spallation of large areas is avoided securely. In case of coatings deposited on smooth graphite substrates increased tendency to spallation of large coating pieces after cutting for preparation of cross sections is observed.

Fig. 1. Crack free Al₂O₃ - 3 wt.-% TiO₂ coating (top) and Al₂O₃ - 2 wt.-% Cr₂O₃ coating with segmentation cracks (bottom) on smooth and grit blasted graphite substrates respectively.

Despite great difference in thermal expansion behavior between alumina based coatings and carbon fiber reinforced carbon substrates cross section images point at strong bonding between coating and substrates. Alumina spray particle melt effectively fills undercuts at both graphite and C/C surfaces, Fig. 2. Optical micrographs suggest presence of different phases, especially in Al₂O₃ -3 wt.-% TiO₂ coatings. SEM investigations prove existence of titania besides alumina. However, titania content is much lower than second phase content observed in optical micrographs. As in SEM images no element contrast is found, the two phase microstructure may be attributed to phase transition from α- to γ-alumina phase during spraying. Coatings containing chromia show higher porosity and micro crack density than titania containing and pure alumina coatings.

Fig 2. SEM images of the interface between Al₂O₃ coatings and graphite (top) or C/C substrates (bottom).

In some places adhesion of thermal spray coatings to individual fibers exceeds the adhesion between fibers via the carbon matrix material in a pile of the woven fabric, Fig. 3. However, low adhesion between fibers within a pile might be due to the grit blasting pre-treatment. In cross sections segmentation cracks are found nearly exclusively in areas with fiber orientation perpendicular to the cross section plane. That means that low thermal expansion in fiber orientation is beneficial for prevention of crack formation.
If cracks are opened too wide, penetration of excess liquid filler metal to carbon based substrates cannot be avoided in high temperature brazing processes. However, large gaps between fiber piles in the woven fabric expose significantly larger surface areas to potentially corrosive filler metal melt, Fig. 4. At locations, where crossing fiber piles strike, thermal expansion is particularly complex. Therefore in these places crack formation is observed preferentially. Among the sprayed coatings \( \text{Al}_2\text{O}_3 - 3 \text{ wt.-% TiO}_2 \) shows least density of cracks at such locations and also lowest spacing between crack edges.

### 3.2 Field tests in heat treatment processes

In first test series with alumina coatings on graphite racks (Fig. 5) life time of 3 months, i.e. at least 100 charges, is achieved. In comparison for alumina and boron nitride based pastes life time amounts to 3 charges in average.

![Figure 5. Alumina coated graphite rack for case hardening heat treatment.](image)

### 3.3 Corrosion tests with liquid filler metal

Comparative corrosion tests with liquid nickel based filler material result in wetting and strong reactions both with graphite and C/C specimens, Fig. 6. Cracks propagate both through carbon matrix and fibers.

![Figure 6. Strong reactions between NiCr7Si4.5B3.1Fe3 filler material and C/C resulting in crack formation.](image)
In case of graphite specimens strong residual stress evolves during cooling, which results in detachment of the filler material with loss of significant amounts of adhering graphite. In contrast all types of alumina based powder flame sprayed coatings both on graphite and C/C provide secure protection of substrates and even prevent wetting of surfaces, Fig. 7.

Fig. 7. Prevention of wetting due to protective Al₂O₃ coating on graphite substrate.

Corrosion tests prove disadvantages of smooth graphite surfaces with respect to coating adhesion. Especially thick pure Al₂O₃ coatings spall off during thermal treatment as a result of thermal expansion mismatch. In contrast spallation is securely avoided both for grit blasted graphite and C/C substrates.

4 Summary

Powder flame sprayed alumina based coatings are sprayed on graphite and C/C composites in order to provide diffusion barrier function. All alumina based coatings show perfect interface with graphite and C/C substrates. Smooth graphite substrates permit deposition of crack free coatings, but tendency to coating spallation during thermal cycling is high. Grit blasting of graphite substrates results in segmentation cracks, which improve thermal cycling resistance significantly. For coatings deposited on C/C composites crack formation in fiber direction is observed. Generally good coating adhesion is based on penetration of molten alumina particles in substrate undercuts. Cracks do not affect capability to provide protection function against liquid filler material. Obviously cracks are not opened wide enough to permit penetration of filler material to the substrates. In field tests excellent performance with significantly improved life time compared to alumina and boron nitride pastes is observed. In conclusion an economically attractive solution for production of coatings providing diffusion barrier function for vacuum case hardening processes and protection against liquid filler material in high temperature brazing processes for carbon based light weight racks is developed.

5 Perspectives

In order to optimize powder flame sprayed alumina diffusion barrier coatings for graphite, C/C and C/SiC racks concerning life time in case heat treatment processes systematic thermal cycling tests will be carried out. Besides influence of chemical composition and size fraction of powder feedstock also pretreatment of rack surfaces will be investigated in detail. Further molten metal corrosion tests with more reactive filler alloys including iron based alloys will be conducted.

6 Literature