

Polycarbosilazane passivation on graphite foil used as gasket seal

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Abstract. Gasket seals are often used in industry and laboratories where a leak-proof installation is needed in order to avoid loss of products or dangerous materials. Many of products transported inside tubes are at relatively high temperatures excluding polymeric gaskets. In the same line, many of transported materials contain solvents which can attack polymer sealings, therefore limiting their use. An alternative is to use graphite joints as sealings. These joints are a sandwich of graphite foil and stainless steel mesh as forming core. The problem that raises using graphite in contact with steel is that at temperatures of about 500 °C an interdiffusion of carbon on the steel structure occurs which produces adhesion of the graphite gasket on the metallic flange. Therefore this adhesion increases the time to change each gasket, since rests of previously adhered graphite has to be removed from the flange. In order to avoid the adhesion of the graphite on the flange, polycarbosilazane precursor was used as protective finishing on the graphite foil surface. After thermal transformation of the polymer into the corresponding PDC finishing, it acts in two manners: It avoids the direct contact between the carbon and the steel and it allows the sealing of liquids and gases. Adhesion tests were done and showed that the foils passivated with PDCs did not adhere to the steel flange. Moreover, the production methods and products are compatible to industrial environment and processes. The results found here show that the time to change the gasket in industry can be clearly reduced by using the PDC finishing on graphite gasket.

1. Introduction

Many industries and equipment which work with transport of fluids (i.e. liquids or gases) need pipelines and junctions to keep them together and avoid leakage of the fluid. Among many methods to promote sealing of pipes and junctions, a very common is the use of gaskets that can be made of several materials i.e. aluminium and other ductile metals, PTFE, asbestos fibres, graphite and others [1-4]. The work principle of gasket is that it promotes mechanical sealing which fills the space between two or more mating surfaces with or without roughening treatments. When a gasket is intended to be applied in harsh environment or at high temperatures, expanded graphite is often used [4-9]. The reason is that this material is resistant to most extreme conditions. It can endure pH from 0 to 14 and temperatures from -240 °C to 650 °C in oxidizing atmosphere (up to 3000 °C in inert atmosphere).

The problem that rises by using graphite as gasket on stainless steel flanges is the adhesion between graphite and steel alloys [2,7]. In order to avoid catastrophic failure, the graphite gasket applied to the flange in pipelines must be periodically removed and changed. Because of the adhesion of the graphite on the flange an additional step must be introduced in the maintenance procedure – cleaning of the



flange – which leads to extra costs due to longer cleaning times. Besides these costs, the cleaning process can be very problematic due to the location of the flange. Figure 1 shows examples of problematic adhesion of graphite on steel flanges.



Figure 1. Example of adhesion of the graphite gasket on the stainless steel flange.

In order to avoid the adhesion of the graphite gaskets on the steel flanges preceramic polymers were used to produce – after pyrolysis – a ceramic passivation on the graphite. The passivation is achieved through a sprayed layer that is formed on the graphite foil. In comparison to conventional finishing processes such as physical vapour deposition, chemical vapour deposition and thermal spraying [10], passivation with polymer derived ceramic (PDC) offers many advantages such as easy application on substrates of any shape, low temperature processing and relatively low costs [11]. PDC finishing are generally based on silicon containing precursors like polysiloxanes [12-13], polysilanes [14] and polysilazanes [11,15,17,18], and possess superior properties, such as thermal stability or oxidation and corrosion resistance [15-17]. In the case of the gasket, the PDC forms a barrier layer on the graphite, avoiding interdiffusion of carbon atoms from the graphite to the steel. Simultaneously, the PDC finishing acts as a protective layer on the graphite improving its ability to resist high temperatures and aggressive chemical environments.

In this work polysilazane and polycarbosilazane precursors are used to develop an improved PDC passivated graphite foil used to build gaskets that supplies the manufacturer technology and materials availability as well as the consumer needs for an affordable product with good performance.

2. Experimental procedures

Five preceramic polymers were selected to investigate their use as passivation finishing: PHPS (perhydropolysilazane), KiON ML33, KiON HTT1800, ML33S and HTT1800S. PHPS is available through AZ Electronic Materials (Germany) GmbH [19]. HTT1800 and ML33 were purchased from Clariant Advanced Materials GmbH (Germany) [20]. HTTS and ML33S are meltable solids, resulting from the partially cross-linking of HTT1800 and ML33, respectively. Although the precursors used in this work are partially sensitive to moisture and air, all handling and measurements were carried out under air atmosphere. The reason for this is that the final production and products has to be done in air atmosphere avoiding complex equipment and special precautions.

The commercially available PHPS polysilazane is produced by ammonolysis of dichlorosilane SiH_2Cl_2 . A solution of maximum 20% by weight of PHPS in dibutylether was used. HTT1800 is synthesised by coammonolysis of dichloromethylvinylsilane and dichloromethylsilane. ML33 is synthesised by coammonolysis of dichlorodimethylsilane and dichloromethylsilane.

The precursors HTT1800, ML33 and their partially cross-linked forms were used in a solution of 20 wt% in dibutylether. Additionally 3 wt% of dicumyl peroxide (DCP) and 0.015 wt% of platinum were used as a cross-linker materials in HTT1800 to promote a faster cross-linking at lower temperatures. No further cross-linking agents or catalysts were used for PHPS.

Graphite foils were supplied from Frenzelit Werke GmbH (Bad Berneck, Germany). The original size of the foils is $1 \times 1 \text{ m}^2$ and they were cut for laboratory procedures. The foil used has a thickness of about 1 mm and a graphite density of approximately 0.7 g/cm^3 .

The foils were initially treated by dipping into the respective precursor solution due to the better reproducibility of the application method. The pull-out speed was 0.3 m/min and immersion time was 10 seconds. After evaluating the necessary parameters the passivation was applied by spraying because this process is size independent, can be continuously applied and is easy to scale-up.

After the passivation of the samples, they were thermally treated at temperatures from 500 to 700 °C with a heating rate of 5 K/min. The dwell time was varied from couple of minutes up to two hours. Thermal treatment was also done in an industrial production line where the foils were annealed by continuous infrared furnace.

Thermal gravimetric analyses (TGA) were performed under air atmosphere with a heating rate of 5 K/min. Adhesion test were realized by pressing the gasket between two flanges that were closed with screws applying a torque of ~80 Nm. The set (gasket between two flanges) was thermally treated at 300 °C for holding times from 1 to 48 hours.

SEM analysis was used to observe the cross-section of the foils and precursor infiltration.

3. Results and discussion

Dip-coated foils were evaluated by TGA to observe the thermal behaviour of the samples. All samples subjected to the TGA analysis showed a similar trend during the test, as seen in figure 2. The graphite foil passivated with PHPS presented an increasing of mass, most likely due to the behaviour of pure PHPS under pyrolysis in air (Figure 3). Figure 3 also shows that the pyrolysis behaviour of the precursors behaves different due to differences in their chemical structures.

Figure 2 shows that the graphite foils passivated with precursors behave in similar way as the graphite foil without passivation but there is a reduction in the mass loss of the materials, which is a consequence of the oxidation protection effect of the precursors. The lowest mass loss of the graphite foil passivated with PHPS (Figure 2) is a consequence of its high ceramic yield, which gives a denser layer with lower shrinkage during pyrolysis.

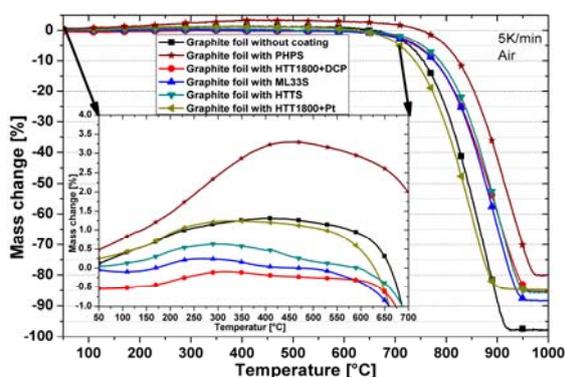


Figure 2. TGA of passivated graphite foils in air

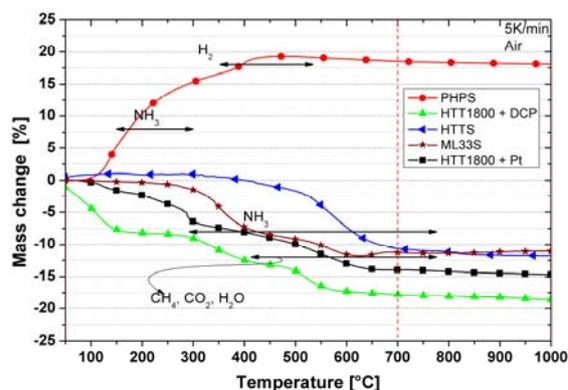


Figure 3. TGA of pure precursors in air

The use of platinum as catalyst for HTT1800 increases the ceramic yield of the precursor and improves the cross-linking at low temperatures.

Graphite foils were dip-coated using the parameters previously described. According to TGA of precursors (figure 3), the pyrolysis process is completed at 700 °C. Due to this, dip-coated foils were annealed at 700 °C and subsequent adhesion tests were done at 300 °C until adhesion was noted. Results are shown in figures 4 to 9.

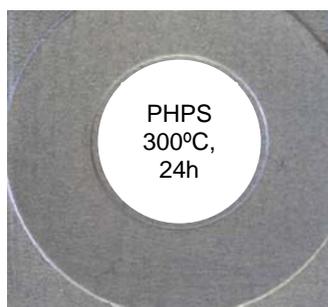


Figure 4. PHPS passivated foil after adhesion test.



Figure 5. HTT1800 + DCP passivated foil after adhesion test



Figure 6. ML33 passivated foil after adhesion test



Figure 7. HTTS passivated foil after adhesion test



Figure 8. ML33S passivated foil after adhesion test



Figure 9. HTT1800 + Pt passivated foil after adhesion test

The liquid polycarbosilazanes HTT1800+DCP and ML33 showed poor results in the adhesion tests even for short times (Figures 5 and 6). The cross-linked solid polycarbosilazanes showed better results in the adhesion tests also for longer times (Figures 7 and 8). The polysilazane PHPS (Figure 4) and the liquid polycarbosilazane HTT1800 with platinum as catalyst (Figure 9) also presented a good behaviour in the adhesion test.

HTT1800+Pt was selected for further analyses because its performance was similar to the solid precursors HTTS, ML33S and PHPS. The drawback that arises with the use of pre-cross-linked precursors (HTTS, ML33S) is the additional step to solidify the precursor. PHPS was not selected because it is relatively expensive and moreover it is very reactive and therefore requires special handling procedures, not very suitable for industrial use.

Since the graphite foils need to be passivated on only one side and preferably in a continuous method, spraying was used as finishing technique. Two different amounts of precursors were used on the graphite foils. The smaller amount has about 0.0038 mg/mm^2 and the larger amount has 0.0064 mg/mm^2 .

The annealing process was realized at temperatures from 500 to 700 °C in muffle furnace in air atmosphere. The dwell time was also varied to obtain non-adhesive foils after a short thermal treatment. The results of the annealing process are shown in table 1.

Table 1. Annealing process parameters.

| Annealing temperature | Minimal dwell time to obtain non-adhesive foils |
|------------------------------|---|
| 700 °C | 5 minutes |
| 600 °C | 30 min |
| 500 °C | 3 hours |

In figure 10, a SEM micrograph of the sample passivated with the smaller amount shows that the layer thickness is about 1.5 μm . In the case of graphite foil passivated with a larger amount the thickness of the layer is $\sim 3.5 \mu\text{m}$. Both passivated foils showed the same result regarding their anti-adhesion behaviour.

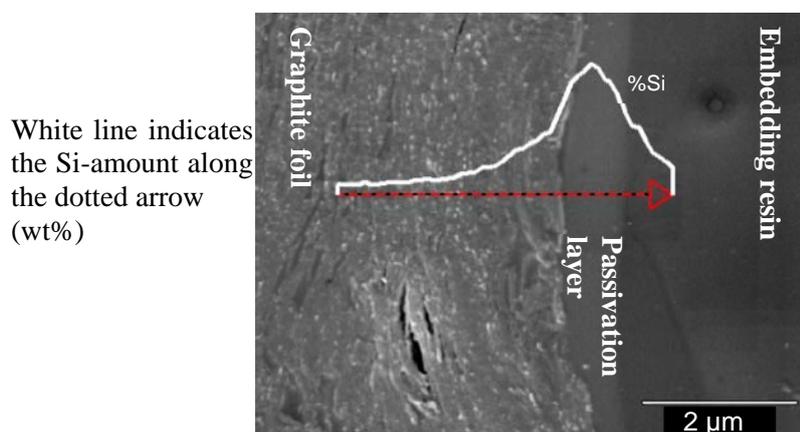


Figure 10. SEM-micrograph of 0.0038 mg/mm^2 passivated HTT1800(+Pt) graphite foil in cross section. (700 $^{\circ}\text{C}/5 \text{ min}$) with Si-EDX linescan.

The investigation of the infiltration behaviour was done by SEM-EDX analysis (Figure 10) and showed that small amounts of the precursor infiltrate the graphite foil. This infiltration seems to have a good influence on the thermal resistance of the graphite and also on its non-adhesive properties.

After a continuous annealing process under infrared field the passivated foils showed similar results as the foils thermally treated in muffle furnace.

The chemical resistance of the passivated foils was tested using a variety of organic solvents, strong acids and bases. The results showed that the passivated foil has at least the same, mostly better chemical resistance than the non-passivated graphite foil.

Spray-coated graphite foils that were annealed under infrared field were also tested regarding their adhesion on steel flanges. The graphite foil, which was pressed between the flanges at 300 $^{\circ}\text{C}$ for 48h, was removed intact with no sign of adhesion between the foil and the flange (Figure 11).

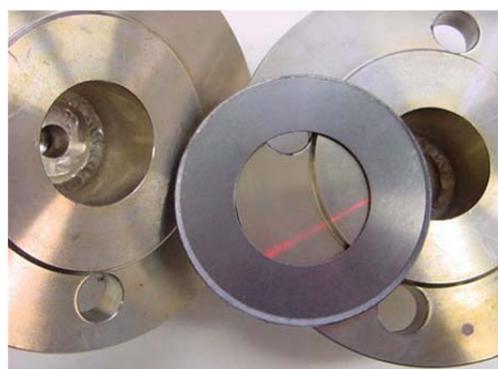


Figure 11. Final product (graphite foil passivated with HTT1800+Pt / IR-field annealed) showing no adhesion of the gasket on the flange (adhesion test parameter: 300 $^{\circ}\text{C}$ / 48h / $\sim 80 \text{ Nm}$).

4. Conclusion

Graphite foils were successfully passivated with polycarbosilazanes and showed improved properties compared to standard non-passivated graphite foils (non-adhesion behaviour, good chemical resistance and good oxidation resistance). Pyrolysis with infrared field and spray-coating are possible and feasible for industrial application.

Liquid precursors were preferably used because they avoid further steps in the production. Despite the good results of PHPS-based passivations they were not used due to the very high costs of PHPS.

Although the optimised foils have only a small amount of precursor passivation they showed no adhesion with the steel flange under pressure and temperature.

Due to the non-adhesion behaviour of the PDC passivated foils the maintenance of gaskets can be done more quickly and economically.

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