The need for electronic applications to be able to withstand high temperatures has become more prevalent in recent years. With drilling in the oil and gas industry getting deeper, the operating temperatures are getting higher, with typical geothermal gradients of 25 °C/km.

Temperatures up to 250 °C are often seen by drilling operations, which is putting a greater strain on the electronics and associated packaging. Standard methods of cooling are not viable for these harsh environments, so new technology is required to negate the effects of the extreme temperatures. As well as the use of high temperature stable electronic components, High Temperature Getters are required to remove gaseous contaminants from electronic housings to negate the associated deleterious effect on performance.

The contaminating species to be removed are commonly H₂O, CO₂, and H₂, and sometimes short chain organic molecules. Conventional getter materials can remove damaging species at temperatures up to about 80 °C. New technology is however required to eliminate these species at temperatures up to 250 °C, where existing getter formulations would certainly fail.

Johnson Matthey has developed a range of getters that can remove multiple contaminants at both ambient and elevated temperatures. The first product in the series, HTA 1 can remove water and carbon dioxide. Addition of a metal oxide component in HTA 2 facilitates hydrogen removal at elevated temperatures, with capacities in excess of 70 cm³/g achieved. HTA 3 can adsorb unwanted organic contaminants in addition to removing water and carbon dioxide. HTA 4 is a combined getter capable of eliminating all of the aforementioned contaminant species.

These products, combined with the unique, precision engineered Hi-Rel encapsulation (Figure 1) allow getters to be supplied pre-activated, without the end user needing to apply a thermal treatment prior to use. The product can be fitted into any hermetic device to extend the lifetime, thus decreasing the number of failures within electronic assemblies, improving system reliability and preventing operations being shut down as frequently.

**Figure 1:** HTA materials encapsulated by Hi-Rel Lids Ltd for use within electronic devices.

**Introduction**

Electronic hermetic packaging is commonly fabricated from nickel plated Kovar™. These
devices are susceptible to damage from contaminants that can originate from the metal plating or leak into the package over time. Such contaminants include H$_2$O, CO$_2$ and H$_2$. These contaminants can be detrimental to the lifetime of the device resulting in the electronics requiring replacement to maintain functionality. For example, devices can be susceptible to failure mechanisms such as corrosion, electrical leakage and dendritic growth. The inclusion of a getter within these devices to remove these contaminants could be beneficial and cost-effective, by improving device hermeticity and therefore lifetime.

A particular field of study for the use getters is the drilling industry. The application of a high temperature getter may be required in drilling applications as electronics are often exposed, not only to the contaminants stated earlier, but also to extremely high temperatures (up to 250 °C). In addition to the accelerated release of H$_2$O, CO$_2$ and H$_2$, these harsh conditions result in the rapid degradation of any epoxide glues, used within hermetic packaging. Epoxide glues are unstable at such temperatures, and can degrade to small organic molecules.

Organic compounds will contribute to dendritic growth between circuitry and potentially cause the device to short-circuit. The down time, and indirect cost of replacing failed electronic components within such a harsh operating environment is substantial. This report will show a class of getter material with the ability to successfully remove contaminants; particularly moisture, hydrogen and organics, at temperatures of up to 250 °C.

Formulations

A range of materials in tablet form were prepared and assessed for high temperature scavenging capability. HTA 1 is a high temperature getter for moisture and CO$_2$ removal. HTA 2 is a scavenger for both moisture and hydrogen. HTA 3 is an adsorbent for eliminating organic molecules and water. HTA 4 is an all-in-one material for removal of water, hydrogen and organics to produce the most advanced high temperature getter available (Figure 2).

![Figure 2: HTA materials without encapsulation](image)

<table>
<thead>
<tr>
<th>Product</th>
<th>Moisture Capacity</th>
<th>H$_2$ Capacity</th>
<th>Organic Capacity</th>
<th>CO$_2$ Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTA 1</td>
<td>&gt;30 wt. %</td>
<td>-</td>
<td>-</td>
<td>&gt;10 wt. %</td>
</tr>
<tr>
<td>HTA 2</td>
<td>25 wt. %</td>
<td>70 cc/g</td>
<td>-</td>
<td>&gt;10 wt. %</td>
</tr>
<tr>
<td>HTA 3</td>
<td>25 wt. %</td>
<td>-</td>
<td>9 wt. %</td>
<td>&gt;10 wt. %</td>
</tr>
<tr>
<td>HTA 4</td>
<td>20 wt. %</td>
<td>60 cc/g</td>
<td>9 wt. %</td>
<td>&gt;10 wt. %</td>
</tr>
</tbody>
</table>

Quoted capacities for each of the materials described above are shown in Table 1. A range of analytical tests were subsequently performed on these materials to determine if measured capacities compared favourably to these idealised values.
Moisture removal

HTA 1 was analysed using thermo gravimetric analysis (TGA). The tablet sample was exposed to 1 % H₂O in flowing N₂ at temperatures of 50 °C, 150 °C and 250 °C, with mass increase monitored as a function of time. The results of these tests are shown in Figure 3. The y-axis values are normalised to the quoted capacity for water (Table 1) of the getter i.e. 100 % means full capacity achieved (30 wt. % for HTA 1). These results clearly show that HTA 1 is capable of efficient moisture absorption from 50 °C to 250 °C, with near theoretical maximum pick up achieved at all temperatures tested.

Figure 3: TGA showing weight increase due to water for HTA 1 material at a range of temperatures

HTA 1 was analysed again using TGA. The sample was exposed to 1 % CO₂ in flowing N₂ at a range of temperatures 50 °C, 150 °C and 250 °C with mass increase monitored as a function of time. As for the equivalent water experiments, the y-axis results are scaled such that 100 % refers to achieving the quoted CO₂ capacity of the materials shown in Table 1.

Figure 4 shows that the rate of absorption of CO₂ is slower than that of moisture at the range of temperatures analysed. The results also show that HTA 1 will not achieve the theoretical capacity expected for CO₂ after 1000 minutes. From the gradient of the curve, absorption is assumed to continue after this time. Given any leakage into an hermetic device would also be at a slow rate, it is not believed that this slower pick up rate compared to water affects performance in real operation. Evidence of this claim is provided by Residual Gas Analysis (RGA) measurements that were carried out on this product and are described below.

RGA was performed on packages to assess the performance of HTA 1 materials. These tests were performed by API Technologies. The encapsulated samples were secured in nickel plated Kovar™ devices with epoxy glues to artificially contaminate the packages, which were filled with N₂ at approximately 600 Torr and baked for 24 hours at 100 °C prior to aging at 190 °C (Table 2) and 210 °C (Table 3) for 7 days. Control tests on packages without HTA 1 material were also analysed for comparison. At the end of the 7 days at elevated temperature, the packages were analysed for gas composition.

It should be noted that the H₂O and CO₂ levels are substantial in the packages without getters. Further, as the temperature is increased, from 190 °C to 210 °C, the level of contamination
increases dramatically. For any devices that are sensitive to H₂O and CO₂, these results clearly demonstrate the need for a means of removal.

Table 2: RGA results at 190 °C, with and without HTA 1

<table>
<thead>
<tr>
<th>Analysis at 190 °C</th>
<th>Package (1) with HTA 1</th>
<th>Package (2) with HTA 1</th>
<th>Package (1) only</th>
<th>Package (2) only</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ (ppm)</td>
<td>&lt;100</td>
<td>&lt;100</td>
<td>3774</td>
<td>776</td>
</tr>
<tr>
<td>H₂O (ppm)</td>
<td>&lt;100</td>
<td>&lt;100</td>
<td>11100</td>
<td>5611</td>
</tr>
</tbody>
</table>

Table 3: RGA results at 210 °C, with and without HTA 1

<table>
<thead>
<tr>
<th>Analysis at 210 °C</th>
<th>Package (1) with HTA 1</th>
<th>Package (2) with HTA 1</th>
<th>Package (1) only</th>
<th>Package (2) only</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ (ppm)</td>
<td>&lt;100</td>
<td>&lt;100</td>
<td>5591</td>
<td>924</td>
</tr>
<tr>
<td>H₂O (ppm)</td>
<td>&lt;100</td>
<td>&lt;100</td>
<td>21800</td>
<td>6107</td>
</tr>
</tbody>
</table>

The results in Table 2 (190 °C) show there is a distinct benefit in using HTA 1 materials in the packages. H₂O and CO₂ contaminants are reduced to below 100 ppm in the presence of HTA 1. Similar results can be seen in Table 3 at 210 °C. These results very effectively demonstrate H₂O and CO₂ removal in duty.

Hydrogen removal

Within Johnson Matthey’s product range, palladium oxide has traditionally been used for removal of hydrogen at near ambient temperatures. To test for suitability in the current application, its ability to remove H₂ at a range of temperatures was assessed using a Chemisorption unit, (ASAP 2010C Micromeritics Model). Hydrogen uptake was measured on 10 wt. % PdO incorporated into HTA 1. Prior to measurement, samples were activated in air at 700 °C for 1 hr. More details on the technique are provided in a recent Johnson Matthey patent application, WO2015/01522. Results of these tests are shown in Figure 5.

The results show that at temperatures of up to 80 °C, there is substantial hydrogen capacity in the PdO/HTA 1 mixtures. However, as the uptake temperature is increased further to >80 °C, the capacity for hydrogen is reduced by a factor in excess of 6. This clearly makes this formulation inappropriate for the desired application.

Lange’s Handbook of Chemistry states, that palladium oxide decomposes at 879 °C to palladium metal and oxygen. However, a study by Ning shows this decomposition beginning as early as 720 °C, as measured by DSC (Differential scanning calorimetry). This puts decomposition of palladium oxide to palladium within the range of the 700 °C activation temperature used in these studies. The loss of palladium oxide prevents the following reaction from taking place:
PdO + H₂ → Pd + H₂O

This results in PdO being less effective as a hydrogen scavenger in this application. It was therefore necessary to assess other options for hydrogen removal at elevated temperature.

A transition metal oxide component was therefore considered as an active component for hydrogen removal in HTA 2, via the following mechanism: (Where M represents any reducible transition metal oxide)

MO + H₂ → M + H₂O

Other H₂ scavenging materials were analysed for stability at higher temperatures including some that had been developed in an earlier JM patent application, WO 2006/064289 A1. (4) Hydrogen capacity tests were repeated on a mixture of HTA 1, with 10 wt. % MO, before optimisation, with the results shown in Figure 6. Whereas the hydrogen removal capability of PdO reduces sharply above 80 °C, the opposite is true for HTA 2, with optimum performance at elevated temperatures. At ambient temperature negligible capacity was measured, but at temperatures of 80 °C and above, capacities are approaching being comparable with the performance of the PdO equivalent at ambient temperature.

The mechanism for hydrogen removal in HTA 4 is the same as for HTA 2. Hydrogen capacity measurements were subsequently ran on the finalised formulations at 180 °C using the method previously stated. The results in Table 4 show improved H₂ capacity.

<table>
<thead>
<tr>
<th>Product</th>
<th>H₂ Capacity cc/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTA 2</td>
<td>70</td>
</tr>
<tr>
<td>HTA 4</td>
<td>61.4</td>
</tr>
</tbody>
</table>

Table 4: H₂ capacity result on HTA products

Organic removal

A range of zeolites were trialled for suitability as high temperature organic scavengers. A range of zeolites with a silica to alumina molar ratio of at least 10 were shown to be appropriate for purpose.

HTA 3 and HTA 4 both incorporate a zeolite component optimised for organic adsorption between 180 and 250 °C. Performance was measured by exposing material to a range of organic solvents (cyclohexane and 1-butanol) at elevated temperature, followed by desorption analysis using a digital microbalance to assess how much organic material was retained by each sample. The results are shown in Figure 7.

The results show that the zeolite of choice for both HTA 3 and HTA 4 can adsorb organic solvents such as cyclohexane and 1-butanol with high capacity (15–25 wt. %).
A specific example of desorption analysis is shown for HTA 4 with 1-butanol saturated sample (25 wt. %). At low temperature the sample retained 25 wt. %, but as the desorption experiment proceeded this value reduced, stabilising at approximately 9 wt.% at 250 °C (Figure 8).

Conclusions

High temperature removal, of H₂O, CO₂, H₂ and a range of organic components has been demonstrated using Johnson Matthey products HTA 1, 2, 3 and 4, up to 250 °C.

A substantial reduction in water and CO₂ levels has been demonstrated in a customer’s package (API). At 210 °C, in the presence of HTA 1, water (21800 ppm in control) and CO₂ (5591 ppm in control) were both reduced to below 100 ppm.

HTA 2 for H₂ removal has a substantial capacity benefit over standard PdO based scavengers at high temperatures (70 cm³/g for HTA 2 compared to 5 cm³/g for PdO/HTA 1 mixture).

HTA 3 and 4 have both been shown to be able to pick up and retain a high level of organics (9 wt. %) following exposure to 250 °C.

References


Acknowledgements

Thank you to API Technologies for sharing their RGA analysis with us and Hi-Rel Lids Ltd for their joint development to ensure the activated HTA materials could be encapsulated to allow easy supply of activated materials for the end user.

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