Use of Galinstan as a Contact Agent for Additively Manufactured Components in Cryogenic Engineering

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Abstract.
We introduce a new, demountable, brush-on thermal interface material for cryogenic applications. A process has been developed that allows to removably provide contact e.g. between an additively manufactured component and its interface. The use of Galinstan as an industrial material for cryogenic applications and in particular for those materials used in additive manufacture is reviewed and explained. Thermal contact conductance values are also presented for dissimilar materials, that have not been investigated before.

1. Introduction
Whenever one has to design cryostats or cryogenic components with interfacing surfaces (e.g. cryocooler/cold plates) one needs to carefully consider multiple design constraints, e.g. minimum contact resistances, high bonding strength etc. Additional design and assembly complexities arise when we intend to separate those components from each other and in particular when those components tend to be of delicate structure, e.g. a heat switch. Interface separation usually requires removal of the component by de-soldering interfaces at high temperatures, de-brazing or de-bonding or generally breaking the contact with heat guns or other more invasive methods, etc. Furthermore, while that would be possible if the component can be removed easily, the latter is more the exception from the rule. Normally we deeply embed contacts within the cryostat so that we neither have access to the component nor do we have means to warm up the complete cryostat the component is in contact with, to above room temperature. In the following we show the quest for contact means for one particular cryogenic requirement that can be broken by warming up interfaces well below room temperatures and what is most important without applying any mechanical force on the interface. Given the high number of parameters for very low thermal contact resistances that are critical to quality (CTQs) for this system component electrically isolating interface fillers can be ruled out immediately. This refers to making “dry contacts” as well as “bonded” contacts of fillers providing electrical isolation. Emphasis was therefore placed to find fillers for dry contacts and those that create good metallic bonds.

An extensive literature search narrowed down this screening process further. The research papers by van Sciver [1], Salerno and Kittel [2], [3] and more recently by Gmelin [4] were most helpful as a guidance. Dissimilar materials were also researched by Fukuoka [5].
Most materials we use are either hazardous, involving Cd, Pb or other or in the case of Indium wire require a very high compressive force on the foil/wire for perfect contact. However, the author recalled one early publication of 1976 by Reynolds and Anderson of Urbana-Champaign that so far received only little attention in cryogenics in which they state the thermal resistance of Gallium between 2 copper contacts at 1 K was too small to measure and in the range of $6 \times 10^{-04}$ W/cm$^2$K [6]. Gallium is solid at room temperature but can be melted by body temperature. It is also one of the very few materials that expand upon freezing and thus assures tightly filling voids in joints. Unfortunately, pure Gallium is not readily suitable for use in an industrial environment and can cause health hazards. As an alternative, recent measurements by Gmelin [4] with GaIn have shown great promise using it between stainless steel surfaces. Unfortunately, this alloy can cause health hazards as well.

Recently the Minamata Convention on Mercury entered into force in 16 August 2017 with the effort of reducing mercury poisoning for mankind. As part of this effort mercury previously used in fever thermometers was replaced by Galinstan, a Rohs compliant liquid metal composed of Gallium, Indium and Tin (stannium).

Interestingly Galinstan has some features that lends itself to applications in cryogenics. One of them should be its use as a thermal interposer. But Galinstan has even more to offer at room temperature as recent publications show [7]. The low viscosity liquid seems to be suitable for many electronic applications. The Indium corporation of US gives the following composition for Galinstan (51E Alloy): Ga: 66.71 %, In: 20.38 %, Sn:12.91 %. This eutectic material is liquid at room temperature and solidifies at 16 °C. The liquid is usually stored in a refrigerator and in an air tight PE bottle just like EGaIn (eutectic Gallium Indium).

With the arrival of additive manufacturing in cryogenics new design challenges need to be addressed. In the past, cryogenic engineers for structural reasons always were very interested in special steels, e.g. Inconel or Titanium alloys, although those were cost prohibitive for some applications or difficult to obtain. Now, known or previously little used additive materials and alloys and even those with low interstitials, like TiAl6V4 ELI are becoming affordable. Unfortunately, the thermal contact for dissimilar materials has not be sufficiently been characterized for those materials.

In the following we describe the efforts of determining the thermal contact resistance when placing an additively manufactured component (thermal switch for superfluid helium) [8] sandwiched between two contact surfaces composed of similar or dissimilar materials. The key question that needed to be answered was whether it would be possible to find a filler material, also called thermal interface material, that would provide a near perfect temperature match between the 2 surfaces, resulting in zero temperature difference at very low heat loads at cryogenic temperatures.

After completion of all tests only Galinstan could meet the specific design targets.

### 2. Summary of Constraints

- Keeping additive manufacturing in mind, make interface between 2 parts of dissimilar materials, with different coefficient of thermal expansion (CTEs)
- Choose a filler with high thermal conductivity
- Ideally, the material should be suitable for “industrial use” applications
- The $\Delta T$ between the two mating surfaces should be below or equal to 0.1 K
- Thermal equilibrium across the interface should take not more than 1 to 2 hours max.
- The thermal contact conductance should not change during thermal cycling as this would otherwise affect the thermal balance of the cryogenic component and the operational parameters of the system
- No, or very little contact pressure should be applied to the interface and the mating parts
- Thermal contact between parts should be maintained during cooldown down to 4 K and lower and remain intact after multiple warmup/cooldown cycles
• The thermal contact surfaces should be able to recover from “hot” service temperature shocks without degradation, whereas the shocks can occur over a period of time of up to 30 minutes, however without reaching RT
• Occasionally, it should be possible to completely break the surface contacts without exceeding room temperature (300 K) at the contacts after a cryostat insert warmup
• It should be possible to break the contact safely at room temperature without any surface damage on both mating parts, which also includes maintaining the integrity of contact interfaces to repeatedly achieve the same contact conductance
• Chosen interposer/filler should not be affected by usual, technical and commercial surface roughness or non-perfect parallel surfaces
• The interposing filler material requires ease of handling when applying onto the surface
• The chosen material should be inexpensive
• Free of health hazards when in use, and should ideally be RoHS compliant (there are some interposers/solders that contain hazardous Pb, Bi or Cd, e.g. Wood’s metal (60 °C) or Field’s metal (63 °C))

3. Bond strength estimate of solid Galinstan interfaces

For a first bonding test we used a copper dumbbell with a diameter of one inch, following the procedure as shown in Figure 1. Remove any visible oxide layer on both surfaces with fine grit non-woven abrasive pad and brush apply Galinstan at both surfaces. Then, apply light, soft pressure to surfaces to expel air, remove flare using a syringe. Place assembly into a Styrofoam container and pour liquid nitrogen in a separate Styrofoam container. Pour over sample thus cold shocking the complete assembly. Continue fill until sample is immersed fully in nitrogen bath and wait until no bubbles are seen indicating the assembly has assume liquid nitrogen temperature. Take out of container, apply force on copper rod. Both surfaces could not be manually separated.

Figure 1. Cold bonding of copper samples (1) to (6).
We then replaced the copper plate with a second dumbbell and pulled the parts apart from each other. The force on the mechanical testing machines at operating temperature 80 K was 8000 N, indicating a strong cold bond well suited to our requirements. Since we looked at bonding of dissimilar materials typically used in additive manufacturing, coupon de-bonding tests were required to understand whether CTE mismatch between Galinstan and dissimilar materials may cause bond failures as shown in Figure 2:

The coupon size tested was 25.4 x 25.4 mm with a thickness of 3.175 mm. (shear stress mainly in X and Y bond direction)

**Figure 2.** Coupon test sample.

### 4. Thermal interface tests with Galinstan and various other interposers

**Setup schematics for material interface screening**

Figure 3 shows the schematics of the 2 test setup arrangements. The first setup was used for material interface screening experiments (I) measuring T0 to T3 (for experiments 1 to 12 in Table 1) and refers to results obtained by mounting the sample directly onto the copper cold plate. Experiments (II) measuring T0 to T5 (stack up for experiments 13 to 15 in Table 1) refer to results when using Interposer 1 (aluminum foil) between cold plate and sample top.

**Figure 3.** Sample test arrangement – schematics with temperature boundaries T1 to T5.

The cold plate (also called heat bus) is thermally linked to a standard SHI RDK408 cryocooler and vacuum sleeved. The bottom end of the sleeve is open to allow for direct contact between cooler and cold plate following GE standard procedures.
Lakeshore Cryogenics’ Cernox CX sensors were calibrated from room temperature to 1 K. For the cold plate to sample tests the Cernox resistors were calibrated from 100 K to 3.6 K. The sensors were held down by springs. The plates themselves were held together with a spring load of 330 N.

**Contact details:**

**Bus/cold plate**
- Contact area: 70 mm width, total contact bus length of 150 mm
- Thickness: 25 mm

**Plates**
- Contact area: 100 x 100 mm
- Thickness: 3.175 mm
- Surface roughness R$_a$: 4.1 µm Copper plated Titanium grade 2
- 3.3 µm Copper plated Inconel 718

Figure 4. Sample test arrangement with samples clamped directly to cold plate and sample bottom with foil heaters.

As mentioned, all samples from 1 to 12 (see Appendix) were directly mounted onto the cold plate surface. Figure 4 shows the 111 mm x 108 mm plate directly mounted on the cold plate held down in place using 3 spring loaded G10 bars. The test plate is shown “bottom up” and is designated as the bottom plate. The following Figure 5 shows a typical cooldown curve of cold plate and sample (see Figure 4). Galinstan was directly painted onto the cold plate surface and the copper coated or uncoated titanium plate and held together to remove air. As figure 5 shows, the coated as well the uncoated titanium plate failed to exhibit a good bond when directly mounted to the cold plate, in agreement with the executed coupon tests.

Figure 5. Graph of copper plate sample cooldown with Galinstan as compared to dry contact surfaces.
The test results summarized in Table 1 (see Appendix) revealed that Galinstan was the only thermal material interface (TIM) that did not depart from the cold plate and with no temperature difference without applied heat load, indicating that an excellent strong bond was maintained [9]. In general, sample cooldown is fast, from 100 to 5 K in approx. 45 minutes thus exerting a high shear stress between the test samples. The temperature differences during cooldown are shown exemplary in in Figure 6.

![Figure 6](image-url)

**Figure 6.** Graph of sample cooldown with dissimilar materials and Galinstan.

The following Figure 7 shows copper plated Inconel plates (111 x 108 mm) bonded together by brush-applying Galinstan onto both surfaces as contact medium. The bottom plate was slightly smaller (95 mm wide x 108 mm long) than the top plate to accommodate the temperature sensor. The bottom plate Cernox temperature sensor was mounted in close proximity to the heater. The top plate in touch with the cold plate was also fitted with a Cernox sensor. The top plate had aluminum tape as contact means between cold plate and sample.

Figure 8 shows the behavior of Galinstan as an interposer between 2 similar materials.
Figure 7. Test sample plates in contact and mounted on cold plate – assembly.

Figure 8. Cooldown curve of copper coated Inconel 718 samples.

Figure 8 shows the cooldown of two Inconel plates with Galinstan as interposer. The final dT measured was 0.03 K at 7.8 K and well within the targeted design range. Based on the satisfying results, the heat transfer across the plates as shown in Figure 9 was measured. The heat load was applied to the bottom of the sample (sample bottom).
5. Estimate of the thermal contact resistance through the interface

In the test setup as shown in Figure 3 and Figure 4 with the bottom plate temperature sensor at the bottom and the second sensor directly at the interfacing plate, we can write the simplified thermal resistance chain as follows:

$$R_d = \frac{1}{(\alpha * A)} + \frac{\delta}{(\lambda * A)}$$  \hspace{1cm} (1)

where \(R_1\) and \(R_2\) = thermal resistances (K/W)

while the first part of the equation refers to the contact resistance and the second part to the thermal conduction through one plate. With a \(\Delta T\) across the interface = \(\sum R_i * Q\) we obtain the following tabulated thermal conductance results:

\[1/R_d = 26.4 \text{ W/m}^2\text{K}\] for copper-coated Inconel / Galinstan / copper-coated Inconel surfaces, based on the measurements in Figure 9 at 15 K and 80 W/m²K at 25 K. The latter value being in close agreement with the measurements of Gmelin (M17) [4] for SS/InGa/SS but less than half of the Gmelin values at 15 K. Since the surface area for the plates was 0.01 m² it is assumed that the complete surface participates in the heat transfer process which may not be the case throughout the plate surface. In this case the thermal conductance would be higher. Figure 10 shows the summary of the conductance results with Galinstan and different plate materials.

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1. The thermal conductivity of Galinstan still remains unknown. The individual constituents of Galinstan are superconducting in the targeted operating range and in test setup. However, the eutectic form will not exhibit superconductivity. In operation, the sample will be exposed to a field of 5 T which will keep the eutectic form in normal state. \(T_c\) : Ga:>1.09 K, In 3.4 K, Sn 3.7 K.
Figure 10. Thermal conductance measurements with Galinstan as interposer.

Figure 11. Thermal conductivity (left axis) vs thermal conductance (right axis) of Inconel.

The measured thermal conductance values for copper/indium/copper are given for comparison and are 80 W/m²K for 0.2 W, 91 W/m²K for 0.4 W, 98 W/m²K for 0.6 W, 133 W/m²K for 0.8 W and 154 W/m²K for 1 W for the 3 to 5 K temperature range and at 0.011 MPa. This is nearly the same values as reported by Salerno [3] at 5.5 MPa confirming that high contact pressure applied at 4 K does not really help to increase the thermal conductance due to the phonon/phonon coupling mismatch.
We could not measure the heat flux through the copper/Galinstan/copper interface. However, given the results with 0 temperature difference and the very high thermal conductivity of the individual solder constituents the results at 4 K should be similar or better than Indium. Gallium is the main contributor to the thermal conductivity at 4 K. For pure metals the thermal conductivity at this temperature is as follows: Pure Gallium: 2400 W/mK, pure Indium: 850 W/mK, pure Tin: 2500 W/mK. Conductance and thermal conductivity of the sample pair seems to correlate with the plate base material as shown in Figure 11, although this is not understood yet.

Summary

Galinstan is the obvious choice for matching materials with very low heat resistance. However, only materials with the same CTE achieve the good bonding strength and high conductance at 4 K. Dissimilar materials fail even when copper coated due to the CTE mismatch. So far, the thermal and mechanical properties of the material remain unknown. Given the ease in which a repeatable thermal and mechanical contact can be made and maintained and separated at 16 °C for many applications this is a suitable alternative to high purity indium, other solders and greases.

References


Acknowledgment

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## Appendix

Table 1  Test results for various thermal interface materials

<table>
<thead>
<tr>
<th>Interface choice</th>
<th>Interposer / bond</th>
<th>$dT$ (K) @ &lt; 4 K</th>
<th>Fail T (K)</th>
<th>Sample geometry mm (pcs)</th>
<th>Comment</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper / Copper</td>
<td>Bare / dry</td>
<td>1.5</td>
<td>12</td>
<td>111 x 108 x 3.175</td>
<td>Vacuum / – no grease</td>
<td>1</td>
</tr>
<tr>
<td>Copper / Copper</td>
<td>Galinstan</td>
<td>0</td>
<td>–</td>
<td>111 x 108 x 3.175</td>
<td>GalSn - wetted</td>
<td>2</td>
</tr>
<tr>
<td>Copper / Copper</td>
<td>Grease</td>
<td>0.1</td>
<td>7.3</td>
<td>111 x 108 x 3.175</td>
<td>Apiezon® N (both surfaces)</td>
<td>3</td>
</tr>
<tr>
<td>Copper / Copper</td>
<td>Indium + Grease</td>
<td>0.055</td>
<td>–</td>
<td>25 x 25 x 0.038 (6)</td>
<td>Apiezon® N (both surfaces) In 99.99 %, pure</td>
<td>4</td>
</tr>
<tr>
<td>Copper / Copper</td>
<td>$\text{Al}_2\text{O}_3$ / Grease</td>
<td>0.145</td>
<td>9.5</td>
<td>25 x 25 x 0.045 (5)</td>
<td>Commercially available tape (Apiezon® N, both surfaces)</td>
<td>5</td>
</tr>
<tr>
<td>Copper / Copper</td>
<td>Graphite + Grease</td>
<td>2.6</td>
<td>15</td>
<td>25 x 25 x 0.16 (5)</td>
<td>Farnell / Element 14</td>
<td>6</td>
</tr>
<tr>
<td>Copper / Copper</td>
<td>Aluminum + Grease</td>
<td>0</td>
<td>7</td>
<td>25 x 25 x 0.12 (5)</td>
<td>3M 425 Alu 99.6% foil + grease</td>
<td>7</td>
</tr>
<tr>
<td>Copper / bare Titanium</td>
<td>Indium / Grease</td>
<td>0.2</td>
<td>15</td>
<td>20 x 20 x 0.127 (6)</td>
<td>Grade 2 Titanium, In 99.99 %, oxidized</td>
<td>8</td>
</tr>
<tr>
<td>Copper / Titanium</td>
<td>Grease</td>
<td>–</td>
<td>35</td>
<td>108 x 95.3 x 3.175</td>
<td>Apiezon® N</td>
<td>9</td>
</tr>
<tr>
<td>Copper / Titanium</td>
<td>Galinstan</td>
<td>–</td>
<td>30/17</td>
<td>108 x 95.3 x 3.175</td>
<td>2 runs, no coating</td>
<td>10</td>
</tr>
<tr>
<td>Copper / Cu plated Inconel</td>
<td>Galinstan</td>
<td>1.0</td>
<td>16</td>
<td>108 x 95.3 x 3.175</td>
<td>Inconel 718</td>
<td>11</td>
</tr>
<tr>
<td>Copper / Cu plated Titanium</td>
<td>Galinstan</td>
<td>–</td>
<td>12</td>
<td>108 x 95.3 x 3.175</td>
<td>Sputtered Cu single side</td>
<td>12</td>
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<tr>
<td>Cu plated Inconel / Cu plated Inconel</td>
<td>Galinstan</td>
<td>0.03+</td>
<td>–</td>
<td>108 x 95.3 x 3.175</td>
<td>Each plate Cu sputtered (both)</td>
<td>13</td>
</tr>
<tr>
<td>Cu plated Titanium / Cu plated Titanium</td>
<td>Galinstan</td>
<td>0.40</td>
<td>–</td>
<td>108 x 95.3 x 3.175</td>
<td>Each plate Cu sputtered (both)</td>
<td>14</td>
</tr>
<tr>
<td>Cu plated Titanium / Cu plated Inconel</td>
<td>Galinstan</td>
<td>0.61</td>
<td>–</td>
<td>108 x 95.3 x 3.175</td>
<td>Each plate Cu sputtered (both)</td>
<td>15</td>
</tr>
</tbody>
</table>

*Designation in table*

– experiment stopped before final $dT$ was reached, $dT$ too big, timeout

* 330 N of spring load on sample area

+ 2nd cooldown after warmup to RT

* bottom plate Inconel