Development of an Environmentally Friendly Substitute for Wood’s Metal

by Stephen A. Aubert and Eric C. Johnson

Approved for public release; distribution is unlimited.
NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer’s or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.
Development of an Environmentally Friendly Substitute for Wood’s Metal

Stephen A. Aubert
Weapons and Materials Research Directorate, ARL

Eric C. Johnson
Bowhead Science and Technology

Approved for public release; distribution is unlimited.
**1. REPORT DATE** (DD-MM-YYYY)  **2. REPORT TYPE**  **3. DATES COVERED (From - To)**
August 2012  Final  January 2011–July 2011

**4. TITLE AND SUBTITLE**
Development of an Environmentally Friendly Substitute for Wood’s Metal

**5a. CONTRACT NUMBER**  **5b. GRANT NUMBER**  **5c. PROGRAM ELEMENT NUMBER**

**6. AUTHOR(S)**
Stephen A. Aubert and Eric C. Johnson*

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**
U.S. Army Research Laboratory
ATTN: RDRL-WML-C
Aberdeen Proving Ground, MD  21005-5066

**8. PERFORMING ORGANIZATION REPORT NUMBER**
ARL-TN-0494

**9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)**

**10. SPONSOR/MONITOR’S ACRONYM(S)**

**11. SPONSOR/MONITOR’S REPORT NUMBER(S)**

**12. DISTRIBUTION/AVAILABILITY STATEMENT**
Approved for public release; distribution is unlimited.

**13. SUPPLEMENTARY NOTES**
*Bowhead Science and Technology, Belcamp, MD 21017.

**14. ABSTRACT**
A new low melting non-toxic eutectic metal composition consisting of bismuth, indium, tin, and silver has been formulated and tested. The new eutectic composition, designated as AJ’s metal, consist of 70% bismuth, 15% indium, 10% tin, and 5% silver. AJ’s melts at approximately 80 °C and has a density of 9.03 g/cm³, making it a suitable replacement for Wood’s metal. The new metal contains no lead or cadmium, as do most low melting castable compositions, thus providing suitable environmental acceptability. Thermal analysis using differential scanning calorimeter has been completed and is presented along with estimates of specific heat. The cost of the new composition is acceptable as bismuth is its major constituent and the more costly indium and silver content is minimized.

**15. SUBJECT**
Eutectic metal, wood’s metal substitute, low melting metal, thermal analysis, Henkin apparatus

**16. SECURITY CLASSIFICATION OF:**
Unclassified

**17. LIMITATION OF ABSTRACT**
UU

**18. NUMBER OF PAGES**
20

**19. NAME OF RESPONSIBLE PERSON**
Stephen A. Aubert

**19. TELEPHONE NUMBER (Include area code)**
410-278-0320

---

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18
Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Figures</td>
<td>iv</td>
</tr>
<tr>
<td>List of Tables</td>
<td>iv</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>v</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2. Important Factors in Selecting Substitutes for Lead and Cadmium</td>
<td>2</td>
</tr>
<tr>
<td>3. Formulation of a Suitable Metal Composition</td>
<td>3</td>
</tr>
<tr>
<td>4. Experimental Evaluation of Selected Eutectic Alloy Compositions</td>
<td>3</td>
</tr>
<tr>
<td>5. Conclusions</td>
<td>9</td>
</tr>
<tr>
<td>Distribution List</td>
<td>10</td>
</tr>
</tbody>
</table>
List of Figures

Figure 1. Diagram of Henkin apparatus.................................................................1
Figure 2. In/Sn thermograms .................................................................4
Figure 3. In, Sn, and Zn thermogram.................................................................5
Figure 4. Thermograms of In/Sn/Ag solder with and without Zn...............6
Figure 5. Thermograms of Bi, In, Sn, and Ag.........................................................7
Figure 6. Thermograms of AJ’s metal.................................................................8

List of Tables

Table 1. Salient properties of metals............................................................2
Table 2. Properties of some low melting alloys........................................3
Acknowledgments

Dr. Brian Roos provided support and critical review of this document. Eric Bukowski acted as the technical reviewer.
1. Introduction

The standard experiment for determining the critical temperature of an explosive was developed in the 1950s by Hyman Henkin. The test bearing his name (Henkin Test) is a time to explosion experiment, where a small quantity of explosive is heated isothermally at a controlled temperature until a violent reaction ensues and the time is noted. During the experiment, 40 mg of explosive confined in a no. 8 blasting cap is inserted into a molten metal bath held at elevated temperature and the time to event is recorded. The temperature is adjusted based on the result and repeated until the temperature at which no reaction ensues is determined to the nearest degree. The standard method uses Wood’s metal as the molten metal bath because of its low melting point 70 °C and its high density 9.5 g/cm³. The molten Wood’s metal bath is contained in a steel reservoir as is illustrated in figure 1.

![Diagram of Henkin apparatus.](image1)

Wood’s metal consists of bismuth (Bi, 50%), tin (Sn, 13.3%), lead (Pb, 26.7%), and cadmium (Cd, 10%) and although low in cost, its inclusion of lead and cadmium make it an undesirable choice for environmental reasons, which were not the concern in the 1950s to the degree they are today. Waste disposal is consequently costly as well. Field’s metal, which is a fusible eutectic alloy that melts at 62 °C and consists of Bi, Sn, and indium (In) in the ratio of 32.5, 16.5, and 51, is often used as an alternative to Wood’s metal due to its lower toxicity. However, it may not be the best substitute for the Henkin test due to a significantly lower density of 8.0 g/cm³, which is

---

attributable to its high In content. The cost of In is also considerable around $1000/kg. Another possible substitute is Rose’s metal, which melts at 100 °C and has a density similar to Wood’s metal but contains Pb, only eliminating the Cd component. Apparently however, a combination of Bi, Sn, and In could be a suitable replacement for Wood’s metal if it were possible to formulate it with a higher Bi and lower In content to maintain a suitable density. The objective of this effort was to achieve this end.

2. Important Factors in Selecting Substitutes for Lead and Cadmium

The factors influencing the choice of elements to constitute a suitable Wood’s metal substitute include melting point (mp), heat of fusion, and atomic weight, which affect the melt point of the composition of the metal. Of the 11 metals with properties of some suitability, thallium (Tl) and polonium (Po) were rejected due to toxicity; palladium (Pd) due to high cost, copper (Cu); nickel (Ni) molybdenum (Mo) due to excessively high melt points; and germanium (Ge); and antimony (Sb) due to low densities. This leaves In, zinc (Zn), and silver (Ag) as the possible elements that can be combined with the two remaining components of Wood’s metal, Bi and Sn. Zn has a low density but a reasonable melt point 419 °C, while Ag has a suitable density similar to Pb although a high melt point of 962 °C. In has both a low melt point and heat of fusion, but a low density as well. The properties of these metals are listed in table 1.2

Table 1. Salient properties of metals.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Density (g/cm³)</th>
<th>MP (°C)</th>
<th>C_p (J/g/K)</th>
<th>ΔH_fusion (kJ/mol)</th>
<th>Atomic Wt (AMU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>9.78</td>
<td>271.4</td>
<td>0.122</td>
<td>10.9</td>
<td>208.98</td>
</tr>
<tr>
<td>Sn</td>
<td>7.28</td>
<td>231.9</td>
<td>0.228</td>
<td>7.03</td>
<td>118.71</td>
</tr>
<tr>
<td>In</td>
<td>7.30</td>
<td>156.6</td>
<td>0.233</td>
<td>3.28</td>
<td>114.82</td>
</tr>
<tr>
<td>Pb</td>
<td>11.34</td>
<td>327.5</td>
<td>0.129</td>
<td>4.77</td>
<td>207.2</td>
</tr>
<tr>
<td>Cd</td>
<td>8.642</td>
<td>321.1</td>
<td>0.232</td>
<td>6.19</td>
<td>112.41</td>
</tr>
<tr>
<td>Tl</td>
<td>11.85</td>
<td>304.0</td>
<td>0.129</td>
<td>4.27</td>
<td>204.38</td>
</tr>
<tr>
<td>Po</td>
<td>9.196</td>
<td>254.0</td>
<td>0.126</td>
<td>13.0</td>
<td>208.98</td>
</tr>
<tr>
<td>Sb</td>
<td>6.684</td>
<td>630.6</td>
<td>0.207</td>
<td>19.87</td>
<td>121.76</td>
</tr>
<tr>
<td>Ge</td>
<td>5.35</td>
<td>938.2</td>
<td>0.320</td>
<td>34.70</td>
<td>72.61</td>
</tr>
<tr>
<td>Zn</td>
<td>7.14</td>
<td>419.5</td>
<td>0.388</td>
<td>7.32</td>
<td>65.39</td>
</tr>
<tr>
<td>Cu</td>
<td>8.94</td>
<td>1084.6</td>
<td>0.385</td>
<td>13.01</td>
<td>63.55</td>
</tr>
<tr>
<td>Ni</td>
<td>8.90</td>
<td>1455.0</td>
<td>0.444</td>
<td>17.57</td>
<td>58.69</td>
</tr>
<tr>
<td>Pd</td>
<td>12.02</td>
<td>1554.9</td>
<td>0.244</td>
<td>16.74</td>
<td>106.42</td>
</tr>
<tr>
<td>Ag</td>
<td>10.5</td>
<td>961.8</td>
<td>0.235</td>
<td>11.30</td>
<td>107.87</td>
</tr>
<tr>
<td>Mo</td>
<td>10.2</td>
<td>2623</td>
<td>0.251</td>
<td>27.61</td>
<td>95.94</td>
</tr>
</tbody>
</table>

3. **Formulation of a Suitable Metal Composition**

Observed melting points for compositions of In and Sn melt as low as 113–117 °C but have low densities (7.30 g/cm$^3$) compared to Wood’s metal. The In/Bi eutectic melts as low as 70 °C and the ternary mixture of In/Bi/Sn melts at 60 °C, but both have densities just under 8.0 at 7.97 and 7.95 g/cm$^3$, respectively. This is attributable to the low content of higher density component Bi. The issue then in finding a suitable Wood’s metal substitute would be to find a combination with a higher Bi content, as it has a density above 9 g/cm$^3$. However, its higher melt temperature and heat of fusion tend to limit its solubility in the lower melting In, which has a lower heat of fusion as well, making the issue more problematic. Data listed in table 2 suggest, however, that additions of Zn or Ag can alter compositions such that the Bi content can be increased above that of In without significant increases in melting point. Ag with a density of 10.5 g/cm$^3$ is the more beneficial component in maintaining a higher density. Ag, for example, has been used in small quantities in Sn/In-based solders. These data are shown in table 2.3

Table 2. Properties of some low melting alloys.

<table>
<thead>
<tr>
<th>Bi</th>
<th>In</th>
<th>Sn</th>
<th>Zn</th>
<th>Ag</th>
<th>MP (°C)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32.5</td>
<td>51</td>
<td>16.5</td>
<td>—</td>
<td>—</td>
<td>60.5</td>
<td>7.95</td>
</tr>
<tr>
<td>33</td>
<td>67</td>
<td>—</td>
<td>40</td>
<td>—</td>
<td>70</td>
<td>7.97</td>
</tr>
<tr>
<td>—</td>
<td>60</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>113</td>
<td>7.30</td>
</tr>
<tr>
<td>—</td>
<td>52</td>
<td>48</td>
<td>—</td>
<td>—</td>
<td>117</td>
<td>7.30</td>
</tr>
<tr>
<td>—</td>
<td>56</td>
<td>40</td>
<td>4</td>
<td>—</td>
<td>130</td>
<td>8.30</td>
</tr>
<tr>
<td>—</td>
<td>58</td>
<td>42</td>
<td>—</td>
<td>—</td>
<td>138.3</td>
<td>8.55</td>
</tr>
<tr>
<td>57</td>
<td>—</td>
<td>42</td>
<td>—</td>
<td>1</td>
<td>137</td>
<td>8.56</td>
</tr>
<tr>
<td>—</td>
<td>—</td>
<td>77.2</td>
<td>—</td>
<td>3.8</td>
<td>175</td>
<td>7.30</td>
</tr>
</tbody>
</table>

Composition is shown in weight percent.

4. **Experimental Evaluation of Selected Eutectic Alloy Compositions**

Differential scanning calorimetry (DSC) thermograms were obtained using TA instruments model Q10 and Q20 DSCs. Heating rates of 10 °C were employed. Aluminum Tzero pans with no lids were used. Samples were mechanically mixed and samples containing In were congealed with the aid of a solder pen. Examination of the thermograms in figures 2a and 2b shows the melting points of In and Sn compositions fall as low as 118 °C, which corresponds to that found in the literature.

---

Figure 2. In/Sn thermograms.
The addition of Zn in small quantities to the In/Sn composition further suppressed the melting temperature to ~109 °C, as is shown in figure 3. The onset of the melt endotherm for this composition was observed at 108 °C.

![DSC thermogram](image)

Figure 3. In, Sn, and Zn thermogram.

This was also observed in DSC scans of In/Sn solder containing Ag with and without Zn, which melted at 108.8 and 119 °C, respectively (figure 4).
Addition of Ag to In/Bi/Sn compositions melted at ~80 °C, but in addition allowed the use of much higher Bi contents to ~70% by weight, as is shown in figure 5. This combination of 70% Bi, 15% In, 10% In, and 5% Ag has a density in excess of 9 g/cm³ at 9.03 g/cm³, which is within 95% of that of Wood’s metal.

Figure 4. Thermograms of In/Sn/Ag solder with and without Zn.
A DSC scan of this composition 70/15/10/5 Bi/In/Sn/Ag (AJ’s metal) taken at a heating rate of 10 °C is shown in figure 6. A small endothermic peak is observed at ~60 °C, which corresponds to the In/Bi/Sn eutectic apparently of which there is a small quantity in the mixture. However, at ~84 °C, a major peak ~29x in area is observed corresponding to the remaining mixture. This suggests that the quantity of In/Bi/Sn eutectic is ~3.4% of the composition. There is also an additional small broad endothermic peak that appears at ~165 °C. This peak possibly corresponds to a very small excess of In/Sn/Ag component, which has a melt point in that range.
In accordance with the Law of Dulong and Pettit, the specific heat of a compound is proportional to the atomic mass of that compound\(^4\) (reference 4). From Dulong and Pettit, equation 1 is derived:

\[
\text{AtomicMass} = 26.4 \text{J/(Kmol)} / C_v
\]  

(1)

where \(C_v\) is the specific heat. It is also true that \(C_v\) and \(C_p\) are related in accordance with equation 2:

\[
\gamma = \frac{C_p}{C_v}
\]  

(2)

Consequently, it is reasonable that the specific heat of AJ’s metal can be estimated using a simple weighted average of the constituent components in accordance with equation 3:

\[
C_p = \sum C_{pi} W_i
\]  

(3)

where \(C_p\) is the specific heat capacity of the composition in J/g/°K, \(C_{pi}\) is the specific heat capacity of the individual component, and \(W_i\) is the weight fraction of the component. The average specific heat capacity for AJ’s metal was estimated to be 0.155 J/g/K and that of Wood’s

---

metal was 0.149 J/g/K. This is a reasonable expectation as both compositions contain ~70% by weight either Bi or Bi and Pb, elements of the 6th row of the periodic table with atomic number’s of 82 and 83, respectively, consequently having similar specific heats and that the other constituents, elements 47–50, also have very similar specific heats.

5. Conclusions

A substitute metal composition for Wood’s metal containing no Pb or Cd has been developed with a melting point of 80 °C, density 9.03 g/cm$^3$, and a specific heat of 0.155 that is within 4% of Wood’s metal. The new metal has been designated as AJ’s metal and consists of 70%, Bi, 15% In, 10% Sn, and 5% Ag. The melting point is in an acceptable range for providing suitable operability in the Henkin apparatus, and its density and specific heat provide for adequate heat exchange, similar to the former metal composition. The elimination of the Pb and Cd, substituting with the environmentally benign Bi and Ag, provides a composition that is non-toxic and green. One disadvantage of the new composition is the higher cost of the new constituents In and Ag, which cost ~$29 and $32 per ounce, respectively. However, since the Bi content was increased significantly, the content of In and Ag was minimized, which subsequently also minimized any cost increase.
<table>
<thead>
<tr>
<th>NO. OF COPIES</th>
<th>ORGANIZATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DEFENSE TECHNICAL INFORMATION CTR DTIC OCA 8725 JOHN J KINGMAN RD STE 0944 FORT BELVOIR VA 22060-6218</td>
</tr>
<tr>
<td>1</td>
<td>DIRECTOR US ARMY RESEARCH LAB IMAL HR 2800 POWDER MILL RD ADELPHI MD 20783-1197</td>
</tr>
<tr>
<td>1</td>
<td>DIRECTOR US ARMY RESEARCH LAB RDRL CIO LL 2800 POWDER MILL RD ADELPHI MD 20783-1197</td>
</tr>
<tr>
<td>1</td>
<td>DIRECTOR US ARMY RESEARCH LAB RDRL CIO LT 2800 POWDER MILL RD ADELPHI MD 20783-1197</td>
</tr>
</tbody>
</table>
NO. OF
COPIES
ORGANIZATION

1   MUNITIONS DIRCTRT AFRL
    RWME
    EGLIN AFB FL 32542

1   ARDEC
    SMCAR AEE
    BLDG 3022
    DOVER NJ 07801

1   DIRECTOR
    DEPT OF ENERGY
    LOS ALAMOS NATL LAB
    TECH LIB
    LOS ALAMOS NM 87545

1   DIRECTOR
    DEPT OF ENERGY
    LAWRENCE LIVERMORE NAT LAB
    TECH LIBRARY
    LIVERMORE CA 94550

1   DEPT OF ENERGY
    SANDIA NAT LAB
    TECH LIBRARY
    ALBUQUERQUE MN 87115

1   COMMANDER
    NAVAL SUFR WARF CTR
    TECH LIBRARY
    CODE 5246
    INDIAN HEAD MD 20640-0600

ABERDEEN PROVING GROUND

14  DIR USARL
    RDRL WML
    M ZOLTOSKI
    RDRL WML C
    S AUBERT (3 CPS)
    E BUKOWSKI
    E JOHNSON
    R MAULBETSCH
    N MEHTA
    T PIATT
    T PIEHLER
    L PRIDGEON
    B ROOS
    W SHERRILL
    K SPANGLER