RESEARCH ARTICLE

Influence of Addition of Silver and Sifbronze Flux in Wetting and Spreading of \( \text{Zn}_{50} \) Alloys on Mild Steel Substrate (SAE1018)

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ABSTRACT

This work investigated the influence of addition of silver and sifbronze flux in wetting and spreading of \( \text{Zn}_{50} \) alloys on mild steel substrate. Seven (7) \( \text{Zn}_{50} \) alloys obtained in a design of experiments by Scheffe mixture method were subjected to the investigations. The wettability of the investigated \( \text{Zn}_{50} \) alloys was examined in a spread test. An optimum flow temperature of 740°C was used as predicted by the calculation of phase diagrams of the alloying elements. The spread test was done using a carburizing flame of oxyacetylene gas in an open air and under protective atmosphere of sifbronze flux. The influence of silver on wetting and spreading properties of the alloys were determined by its spread area on mild steel substrate and the influence of sifbronze flux was determined by the measurement of the degree of active atmospheric gases entrapment. The spreading test showed a beneficial influence in addition of silver up to 4.00%wt in wetting properties of the zinc-based alloys on mild steel substrate. It was also observed that sifbronze flux offered required shielding against excess influx of active atmospheric gases which are known to inhibit wetting of zinc-based alloy on mild steel substrate. The spread area increased with increase in the chemical flux up to 1g.


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INTRODUCTION

The science of adhesives is simply to develop a very intimate contact between mating surfaces. If an intimate surface is developed between a viscous liquid and a solid surface, a mechanical bond can be formed. The strength of the bond depends largely upon the degree to which the viscous liquid displaces air and fills up the gap on the solid surface. The more the gaps fluid can fill, the stronger the bond. In mechanical bonding, secondary atomic forces called Van der Waals bonds are what give joints its strength. These bonds are due to the electrostatic attraction between the nuclei of one molecule and the electrons of another. The Van der Waals bond varies according to the distance between molecules.

Another type of bonding is known as Ri-rai bonding. In this case, much stronger primary atomic forces are formed. These bonds enable joints to be of very high strength. Brazing, soldering and welding are joining operations which form primary bonds (Ri-rai bonds) of a type called metallic bonds.

Metallic bonds, as the name implies, are characteristics of metals. These are the bond which holds metals together and give them their unique properties. These include high electrical and thermal conductivity, ductility, shiny appearance when polished e.t.c. These bonds exist when atoms with easily detachable electrons come close together such that their electron can circulate freely between the atoms. Thus, the negatively charged sea of electrons in a metal crystal holds the positively charged metal ions securely in place. During brazing for instance, metallic bonds are formed due to extremely intimate contact between the brazing alloys and the base metals.

In addition, there is always some degree of alloying between constituents of the base metals with the brazing alloys. This action also forms metallic bonds while it is these bonds that allow the brazing alloys to adhere strongly to the base metals; the strength of the joint depends upon several other factors as well.

There are several theories of adhesion, but chemical adhesion is the one most likely to explain how liquid metals bond to solid metals. A critical factor to whether or not an adhesive sticks a particular material is its ability to wet the material to which it is applied (called adhered).
Wetting is the ability of a substance to spread and consequently become intimate with a surface. Wetting ability depends on the relative magnitude of two variables a) The adhesion between the liquid and the solid surface. b) The cohesion of the liquid.

In other words, wetting depends on whether a liquid sticks more tightly to itself or to something else. A measure of how well, a liquid wets a solid is the contact angle $\theta$ or spread area.

Since the ban of use in consumer goods in 2001 by the World Health Organization, a worldwide search for Lead-free brazing alloys has been a major issue. Based on a great number of publications on phase diagrams, structures and physical properties of alloys, a number of promising eutectic alloys including Sn-Ag, Sn-Ag-Cu, Sn-Zn and Zn-Al were selected (Pstrus et al., 2012). Sn-Ag, Sn-Ag-Cu and some other multi-component alloys of known constituents were broadly studied too (Xu et al., 2009; Moser et al., 2006). These are already in a commercial use. In general, wetting of base metals by liquid brazing alloys leads to formation of solid solution or intermetallic phases. Metals which do not dissolve one another and do not form intermetallic do not wet one another (Radomski and Ciszewski Lutowanie, 1971). Additionally, wettability depends largely not only on the purity of the parts to be joined, but, also on the degree of surface oxidation level of the brazed parts and the brazing alloys. Bartell F.E and Osterhof H.J., 1927, depended on changes of surface energy and proposed the three classes of wetting conditions; spilled, immersed and dissolved. These alloys of the above studies were used too (Jacobson et al., 2000; Massalski, 1986; Massalski et al., 2005). It was also proved that with high chemical composition of zinc ($\geq$46wt), the brazing alloys became very volatile. This condition limited the amount of zinc that could be added and temperature reduction attainable (Jacobson et al., 2002; Sisamouth et al., 2010). Sisamouth et al. (2010). In order to tackle the volatility of zinc, the gap filling ability of Ag-Cu-In brazing alloy on copper at temperature range of 677 to 770°C was investigated. The silver content in that test was fixed at 60%wt and indium was varied from 5 to 25wt%. It was discovered that increase in indium led to decrease in the brazing temperature, but, showed no significant effect in the capillary rise height (that is non-improvement in wettability).

Zinc alloys had been reported to have good mechanical properties and can be used in brazing of steel structures provided proper flux is used (Purwanto, et al., 2012). Despite good mechanical properties of zinc alloy, wetting properties of Sn-Zn are known to be inferior when compared to those of Sn-3Pb alloy. Moreover, based on literature survey, there are two reasons for poor wettability of Sn-Zn eutectic alloys. The first is the increase in surface tension due to the presence of zinc (Vaynman et al., 2004; Pstrus et al., 2006). The second reason for poor wettability of zinc based alloy is the presence of zinc oxide on the boundary of solder/base metal (Manko, 2001).

Furthermore, studies by Chatterjee et al. 1991 revealed the potential of some Cu-Mn-Sn alloys for successful joining of mild steel to mild steel at about 850°C and copper to mild steel at around 750°C. They also noted that a small amount of nickel has been found to be beneficial for improving the joints strength. Cerium addition seems to increase fluidity but, reduces joints strength. Chatterjee group further concluded that all copper-manganese based alloys examined, wetted mild steel satisfactorily at about 800°C.

Based on the above literatures, the brazing temperature ranges of the examined alloys are still high (850 to1000°C) compared to the annealing temperature of mild steel (900°C) and also lack test results on influence of recommended fluxes for joining mild steel. Hence, this project examined the Influence of addition of silver and sifbronze flux in wetting and spreading of Zn$_{50}$ alloys on mild steel substrate at 740°C.

**MATERIALS AND METHODS**

**Candidates and base metal selection**

Candidates selected for the wettability test were alloys of zinc, manganese and silver. These metals were reported to form solid solution and excellent mechanical mixture with each other when placed on ferrous metal surfaces.

The base metal selected for the test was Bright Drawn Commercial Quality mild steel of Society for American Engineers specification (SAE 1018). That was chosen due to its wide applications in artistic decoration, machinery parts and automobile body building among others.

**Development of design matrix**

The design matrix was developed by Design Expert 8.0.7.1, utilizing Scheffe quadratic mixture method. The Scheffe mixture method formed accounts for the natural constraints found in mixture models as the sum of all the components must equal to a constant. It did not have an intercept term as found in the slack form of mixture models and response surface methodology. The upper and lower limits of each component were coded. After several trial runs, the upper and lower limit coded values were determined as shown in Table 1.
Table 1: Iterated chemical composition limits of alloys components.

<table>
<thead>
<tr>
<th>Components</th>
<th>Limits (%wt)</th>
<th>Equivalent values</th>
<th>Mean</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
<td>Maximum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>46.00</td>
<td>50.00</td>
<td>0.00</td>
<td>46.00, 0.40=50.00</td>
</tr>
<tr>
<td>Manganese</td>
<td>33.00</td>
<td>35.00</td>
<td>0.00</td>
<td>33.00, 0.20=35.00</td>
</tr>
<tr>
<td>Silver</td>
<td>0.00</td>
<td>4.00</td>
<td>0.00</td>
<td>0.00, 0.40=4.00</td>
</tr>
<tr>
<td>Modifying element</td>
<td>11.00</td>
<td>15.00</td>
<td>0.00</td>
<td>11.00, 0.40=15.00</td>
</tr>
</tbody>
</table>

(Source: M.Eng project, 2013); There were twenty experiment runs consisting of ten main, five replicated and five estimates of errors.

Table 2: Design of experiments showing chemical compositions of alloys

<table>
<thead>
<tr>
<th>Experiment runs order</th>
<th>Zinc (%wt)</th>
<th>Manganese (%wt)</th>
<th>Silver (%wt)</th>
<th>Modifying element (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50.00</td>
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<td>0.00</td>
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<td>2.75</td>
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<td>4</td>
<td>48.67</td>
<td>35.00</td>
<td>2.67</td>
<td>13.67</td>
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<td>50.00</td>
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<td>3.33</td>
<td>13.67</td>
</tr>
<tr>
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<td>48.00</td>
<td>35.00</td>
<td>2.00</td>
<td>15.00</td>
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<tr>
<td>7</td>
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<td>2.00</td>
<td>15.00</td>
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<tr>
<td>8</td>
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<td>3.33</td>
<td>13.67</td>
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<td>9</td>
<td>50.00</td>
<td>33.67</td>
<td>1.33</td>
<td>15.00</td>
</tr>
<tr>
<td>10</td>
<td>48.67</td>
<td>35.00</td>
<td>4.00</td>
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</tr>
<tr>
<td>11</td>
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<td>12</td>
<td>48.50</td>
<td>34.00</td>
<td>4.00</td>
<td>13.50</td>
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<tr>
<td>13</td>
<td>48.33</td>
<td>35.00</td>
<td>4.00</td>
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<td>48.50</td>
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<td>4.00</td>
<td>13.50</td>
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<td>19</td>
<td>49.50</td>
<td>34.00</td>
<td>2.75</td>
<td>13.75</td>
</tr>
<tr>
<td>20</td>
<td>50.00</td>
<td>35.00</td>
<td>4.00</td>
<td>11.00</td>
</tr>
</tbody>
</table>

Source: M. Eng project, 2013.

The limit values of zinc, manganese, silver and modifying element were keyed and the possible alloys were generated by the program or read from the file as shown in Table 2.

Conducting experiment as per design matrix

Experiments were conducted with guide as information obtained from the design matrix. The procedures are presented in subsequent subheadings;

Alloy production

Zn-based alloys were produced from design matrix values using electrolytic zinc, manganese, silver and a modifier powder. For each mixture, the required amount of each element was calculated using the equation;

\[ A_i = 0.01E_dXW \]  \[ (1) \]

Where:

- \( A_i \) = amount of a component (g).
- \( E_d \) = experiments run value of a component (%wt).
- \( W \) = needed quantity of the alloy (g).

The calculated values obtained in equation (1) for each component (Zn, Mn, Ag and the modifier) were measured using a digital scale. The measured quantities were mechanically mixed by gravity and centrifugal method (Electric motor 3000rpm turning for 1 hour). A calculated quantity of flux was also measured and added/mixed with alloy by the same method. The required quantity of flux was calculated using the following relationship;

\[ F = 0.8W \]  \[ (2) \]

Where;

- \( F \) = quantity of flux (g)

Wetting test

Seven (7) Zn-based alloys prepared from electrolytic zinc, manganese and silver powder were collected and stored properly in glass reagent bottles. Their chemical compositions are as indicated in Table 3. Sifbronze flux was also collected and stored in the same manner. Furthermore, the base metal prepared was mild steel sheet of 40mmX40mmX1.7mm dimensions.

A simple technique to measure the brazing alloys spread area on base metal was used to characterize its melting and spreading behaviour at 740°C. Three tests were carried out on each alloy samples and average result taken. Investigations were carried out on 1g of Zn50 alloys (SC Nwigbo and SO Mbam, 2014) with silver concentration of 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0%wt. The added sifbronze flux was also varied by 0.2, 0.5, 0.8, and 1.0g. The tests were carried out in open air at the same temperature of 740°C using decarburizing flame (endodermic generated atmosphere of 70-71%N\(_2\), 56%CO\(_2\), 9-10%CO, 14-15%H\(_2\)) and 1g Zn50 alloys in each case (as in Table 3).

The substrate was preheated slightly for about 10seconds using oxyacetylene torch in an open air. The alloy mixed with flux was then gently placed at the middle of the substrate. Finally, it was heated using same acetylene torch to 740°C and allowed to cool in still air. These procedures were repeated for the seven (7) Zn50 alloys of different chemical composition. The diameters of the solidified couplees on the substrate were measured and the spread areas were determined. The spread area was assumed to be perfect sphere; hence, spread area was calculated as follows;

\[ S_a = \pi d^2 \]  \[ (3) \]

Where;

- \( S_a \) = spread area of the solidified alloys, \( d \) = the diameter of the solidified alloys deposit and \( \pi \) = constant.
The solidified Zn50 couples on the mild steel substrate was analyzed by Fourier transform infrared spectroscopy (FT-IR, Buck 530).

RESULTS AND DISCUSSION

The results of measurement of the spread area of the solidified alloys on the substrate with added flux of 1g are presented in Table 4. It could be seen that the spread area increased with increase of silver. The added silver in Zn50 alloys is believed to have eliminated or reduced to the barest minimum the high surface tension of zinc which was reported to exist on wetting of zinc alloys on mild steel substrate (Vaynman et al., 2004; Pstrus et al., 2006). This effect increased as the added silver increased up to 4.0%wt as shown in Table 4. Also, addition of silver was reported to increase the mechanical properties of zinc alloy (Purwanto et al., 2012).

Spreading test results of the Zn50 alloys on the substrate presented in Figure 2 indicate a strong influence of the added flux in its wetting properties. That could be explained by the flux varied degree of shield offered against the test environment active elements during the wetting test. It could be seen that addition of sifbronze flux strongly improved wetting of Zn50 alloys on mild steel substrate. The flux among other things was believed to have minimized the formation of zinc oxides, which was also reported in earlier research to inhibit wetting of zinc alloys on mild steel substrate (Janusz et al., 2012).

Sequel to the chemical compositions and brazing environment suitable for the filler alloys, within liquidus ranges, the brazed joints area is expected to be chemically active. In open air brazing, the joints area could absorb mainly hydrogen and oxygen-based functional groups such as -COOH, -CHO, -OH, -CO and –CH from the atmosphere, if the utilized flux was not effective. These elements are reported to inhibit wetting of the base metal (American Welding society Handbook, 2002).

The FT-IR bands are considerably narrow in shape and combination of reasonably strong, medium and weak bands as shown in Figure 2. Such results obtained will help discuss functional chemical groups present in the joint environment.

The above characteristic bands is as a result of presence of larger crystal sizes of the metallic particles in the Zn50 alloys compared to the size of IR active organic elements. These are known to have broader shape spectra. There is evidently the weakest band signal of 3695.6 cm⁻¹ as shown in Figure 2. That was attributed to very low hydrogen entrapment was the wetting process. The low hydrogen entrapment was attributed to vacuum brazing or flux shielding. Other bands noted within the hydroxyl functional groups region are evident at 3695.6, 3551.4, 3342.5 (with shoulder at 3500), 3174, 3035.3, 2882 and 2710.7 cm⁻¹ which were consistent with hydroxyl, linearly coordinated to different element specie and they indicated presence of different kind of metallic particles present in the tested alloys in this study.

![Image](317x491 to 533x615)

**Table 4:** Chemical composition of tested Zn50 alloys and spread area at 740°C with 1.0g of sifbronze flux

<table>
<thead>
<tr>
<th>S/N</th>
<th>Zinc (%wt)</th>
<th>Manganese (%wt)</th>
<th>Silver (%wt)</th>
<th>Additive (%wt)</th>
<th>Spread area (mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50.00</td>
<td>35.00</td>
<td>1.00</td>
<td>14.00</td>
<td>855.41</td>
</tr>
<tr>
<td>2</td>
<td>50.00</td>
<td>35.00</td>
<td>1.50</td>
<td>13.50</td>
<td>897.39</td>
</tr>
<tr>
<td>3</td>
<td>50.00</td>
<td>35.00</td>
<td>2.00</td>
<td>13.00</td>
<td>995.51</td>
</tr>
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<td>2.50</td>
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<td>1087.00</td>
</tr>
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<td>3.00</td>
<td>12.00</td>
<td>1146.23</td>
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<td>35.00</td>
<td>3.50</td>
<td>11.50</td>
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<td>7</td>
<td>50.00</td>
<td>35.00</td>
<td>4.00</td>
<td>11.00</td>
<td>1425.49</td>
</tr>
</tbody>
</table>

![Image](317x330 to 534x451)

**Fig. 1:** Effect of addition of silver and sifbronze flux on spread area of Zn50 alloys.

![Image](317x260 to 537x383)

**Fig. 2:** Typical spectrums of the Zn50 wetted capsules on the mild steel substrate.

The bands at frequencies 2114.5, 1968.2, 1865.7 and 1625.6 cm⁻¹ are related to species CO-Zn +2, CO-Mn +2, Ag +1-CO-Ag +1 which occurred due to lack of pre-reduction and also due to coalescence of other metal particles.

In fact, Lenarda et al. 2006 reported that frequencies of bands between 2112 and 2083 cm⁻¹ were consistent with carboxyl functional group, linearly coordinated to two different lead oxide species and they indicated the presence of two different kinds of metallic particles.

The bands at lower frequencies are evident at 1466.9, 1390.8, 1275.1, 1115.4 and 786.7 cm⁻¹ with shoulder at approximately 900cm⁻¹. Those bands were attributed to the stretching vibrations of P=O, P─O─C, C=C, C─C and C─N functional groups. That was as a result of release of some elemental phosphorus and carbon from the base metal and entrapment of some elemental oxygen and nitrogen from the atmosphere during wetting test.

Therefore, it could be observed that the spectra of the solidified alloys on the mild steel substrate indicated low presence of atmospheric associated functional group elements and very high presence of metallic associated...
functional group elements. These were attributed to good shielding against atmospheric gases by Sifbronze flux used in this study.

Conclusions

The wettability of Zn_{50} alloys on mild steel substrate at 740°C was investigated. The high surface tension that was known to exist in zinc-based alloy had been eliminated by addition of silver. Also, formation of heavy oxides that was known to inhibit wetting of zinc alloys on mild steel substrate was eliminated by use of appropriate chemical flux and decarburizing flame. The wettability of investigated Zn_{50} alloys was satisfactory at a temperature of 740°C but, depend more on the protective atmosphere.

Zn_{50} alloys with a modifying element can be used to join mild steel members in a protective atmosphere of sifbronze flux (mixture of boron and citric acid).

Recommendations

It is recommended that further research should be conducted in this area in order to substitute silver with another cheaper element that can further reduce the alloy’s liquidus temperature, surface tension, and volatility.

REFERENCES