Behaviors of Work Hardened SnPb-Solder Affected Copper on Corrosion Resistance in pH Varied Environments

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Abstract

Copper based materials are widely used in industrial and marine applications due to good mechanical properties and high corrosion resistant behavior. But the corrosion immunity varies for the variation of environmental factors. Moreover, alloying elements can have role on corrosion behavior, especially if it occurs through inclusion of Sn-Pb solder for repair works and environmental effects due to ageing. The present paper is an attempt to characterize the corrosion immunity level of copper after inclusion of tiny SnPb-solder material and work hardening in pH varied fresh water environments from pH1 to pH13 using gravimetric analysis, conductivity investigation and micrograph observation using optical as well as field emission scanning electronic microscope. The result reveals that solder material inclusion has increased the corrosion rate by about 14% in 30 days immersion in pH varied environments.

Keywords: Corrosion; Work hardening; SnPb-Solder inclusion; Copper; pH varied environment.

Introduction

Copper and copper alloys are widely used in industrial and marine applications as heat exchangers, pumps, valves, fasteners, bushes, bearings, pipelines and conductors in electrical systems due to many factors including high level of conductivity, mechanical strength, machinability and corrosion resistant behavior. With the rapid scientific and technological advancement as well as economic development, the requirement of copper is increasing continuously [1,2]. To meet the extensive demand of copper materials, it is an important issue to get copper from old products/items considering the depletion level of copper ores in the nature [3]. After a long span of operational life, there are two options with waste electrical and electronic equipment (WEEE), i.e., either recycling of copper through a rigorous extraction process or reusing the scrape materials at their leftover state for suitable engineering applications. Recycling is very difficult and costly affairs but preferred for regaining the properties as close to original state. On the other hand, reusing is very cheap but properties are yet to be predicted and suitable engineering applications are also to be explored [4-6].

If the second option is chosen, characterization of old copper in respect of different properties is a mandatory issue based on rehabilitation concept of waste copper items. In this regard, corrosion behavior of old copper remains a concern because of generally considered immunity of copper from corrosion due to its affiliation with novel metals in the periodic table. Its corrosion immunity is also based on a postulation on the existence of native copper in the earth’s crust [1]. In the atmosphere, a very thin layer of brownish-green or greenish-blue in color

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known as patina is formed [7,8]. Established patina becomes stable and remains as a permanent part of the copper object in the atmosphere. Examples of the corrosion resistance of copper materials are artifacts that have been found in nearly pristine condition after having been buried in the earth for thousands of years, and copper roofing in rural atmospheres has been found to corrode at rates of less than 0.4 mm in 200 years [1,9]. But, in contact of water, copper corrodes due to number of factors as considered differently by different researchers [10-18]. According to a group of researchers [10-16], the oxygen is consumed through hydrogen-oxygen reaction and the hydrogen is coming out from the reaction of copper with water. It is considered that the hydrogen-oxygen reaction is faster than the formation rate of the atomic hydrogen from the corrosion reaction itself on copper. Moreover, it is not possible to detect the hydrogen released from copper as long as the supply rate of oxygen to the surface exceeds the rate of hydrogen generation, which results in erroneous consideration that copper is fully corrosion resistant. On the other hand, few researchers [17,18] have expressed the disagreement on the corrosiveness of copper in pure water. However, the reaction rate varies with the variation of pH values, temperature and presence of other particles at the reaction region [19-22]. In addition, copper materials also show specific corrosion manifestations in the form of inter-crystalline corrosion and corrosion cracking [23].

Since, old copper wires and machine parts coming out from different sectors, such as, buildings, industries and ship breakings are many-a-times found to contain a little amount of solder materials comprised of lead, tin, silver, etc. Inclusion of such soldering materials in copper might be of very little amount, but its effect on the corrosion resistance may not be negligible. It is because the addition of alloying elements in copper has some role in corrosion behavior of the alloys being produced [24,25]. Moreover, old copper might have undergone work hardening over the long span of life due to operational and environmental conditions, which can have an influence on the corrosion behavior of metals and alloys [26]. Again, the corrosion of copper in a wide variety of media has remained a great concern to be examined, which have also been conferred by number of researchers through their works [9,16,18,27,28]. Considering the inclusion of SnPb-solder in copper over a long period of useful life as electric wires or machine parts, this paper is an effort to investigate the corrosion behavior of naturally developed work hardened high copper alloy (Cu-Sn-Pb alloy) to look for their suitable rehabilitations.

Materials and Methods

Sample Preparation

Copper wires and machine parts after extensive age of about five decades were taken as the material of focus to carry out the study. It was found that the collected old copper based material contains a little percentage of lead and tin. To ascertain the influence of these tin and lead individually on the corrosive properties of copper wires and machine parts, three more combinations of copper based materials were selected as to supporting the focused solder affected material. These additional sample materials were pure copper named as material-I, copper-tin alloy named as material-II and copper-lead alloy named as material-III. The SnPb-solder affected copper, i.e., material of focus under study, was named as material-IV. Material-I was collected as bulk copper ingots. Materials-II and material-III were developed through casting where tin and lead were taken as of similar amount found available in material-IV. Table 1 presents the chemical compositions of the four types of sample materials.

From the each type of materials, flat bars of size 300 x 15 x 12 mm were made through cutting and machining precisely keeping the effect on surface/edge grains minimal. The flat bars were at first homogenized for eight hours at a temperature of 500°C for the reduction of chemical segregation as well as grain size refinement and then solution treated for two hours at a temperature of 700°C to improve their workability.
Table 1. Chemical composition of sample materials (mass fraction %)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Material-I (Pure Cu)</th>
<th>Material-II (Cu-Sn Alloy)</th>
<th>Material-III (Cu-Pb Alloy)</th>
<th>Material-IV (Cu-Sn-Pb Alloy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>99.6298</td>
<td>98.4555</td>
<td>97.6570</td>
<td>97.1132</td>
</tr>
<tr>
<td>Sn</td>
<td>1.1335</td>
<td>-</td>
<td>1.2572</td>
<td>1.1949</td>
</tr>
<tr>
<td>Pb</td>
<td>0.1372</td>
<td>0.1415</td>
<td>0.1129</td>
<td>0.1726</td>
</tr>
<tr>
<td>P</td>
<td>0.2330</td>
<td>0.2695</td>
<td>0.2564</td>
<td>0.2621</td>
</tr>
</tbody>
</table>

Thereafter, work hardening was done using roller machine operated at room temperature by reducing the thickness of 75%. To carry out such reduction of thickness, roller was operated at the lowest possible speed and only about 0.1 mm feed was applied for each roll pass so that the normal temperature could be maintained for desired work hardening of all four sample materials.

**Experimental Investigation**

All the four groups of samples were sized up such that they are suitable to carry out the examinations of corrosion behavior along with the observation of conductivity and microstructure. To carry out corrosion tests, coupons of 56 mm x 15 mm x 3 mm size were made following the ASTM G4 guide line and mechanically ground with 160, 300, 600, 900 and 1200 grits of SiC emery paper successively. On completion of dry grinding, all the samples were wet polished using alumina paste and dried up through air blow at room temperature. Then the metallographic images were observed using optical electronic microscope (OEM) with the magnification factors of 100x, 180x and 300x.

The electrical conductivity values of the samples were measured using Type 979 Meter with an accuracy of ±0.1 % IACS (International Annealed Copper Standard). At this stage, the samples were weighed in a high precision digital weighing machine to get the initial weight before their immersion in the stagnant solution of wide ranging variation of pH values (pH 1 to pH 13) for corrosion test. Solutions of pH 1, pH 3 and pH 5 were prepared by adding 10N HCl of 20 mL, 0.2 mL and 0.002 mL respectively into 2000 mL of distilled water having pH level of 7. On the other hand, the solutions of pH 9, pH 11, and pH 13 were prepared by adding 1N NaOH of 0.02 mL, 2 mL and 200 mL respectively into 2000 mL of the same distilled water. The solution was used for the corrosion test at room temperature i.e 25°C. After the exposure for a designated period in the solution medium, the samples were taken off, cleaned with distilled water and dried up naturally keeping on absorbent papers. The first experimental reading was taken after one day (24 hours) exposure of samples in solutions. Here, weight loss and conductivity variation of the samples were determined, and OEM micrographs were observed to visualize the consequence of initial corrosion attack. Thereafter, weight losses and conductivity variations of the samples were determined at various time intervals up to 30 days exposure. Weight loss and corrosion rate were calculated according to the following equations respectively [29].

Weight loss of metal was calculated with equation 1:

$$ \Delta W = \frac{(W_o - W_f)}{A} \quad (1)$$

Corrosion rate was calculate with equation 2:

$$ R_{corrosion} = \frac{(K \times \Delta W)}{(\rho \times T)} \quad (2)$$

Where:

$$ \Delta W = \text{Weight loss per exposed surface area (gm/ cm}^2)$$
\[ W_i = \text{Initial weight (gm)}; \]
\[ W_f = \text{Weight after designated period (gm)}; \]
\[ A = \text{Exposed surface area (cm}^2}; \]
\[ R_{\text{corrosion}} = \text{Corrosion Rate (mm/year)}; \]
\[ K = \text{Unit conversion factor}; \]
\[ \rho = \text{Density of metal (gm/cm}^3); \]
\[ T = \text{Exposed time (hour)}; \]

On completion of 30 days immersion, microstructures were observed again for all samples using OEM. In addition, for the samples exposed to two extreme solutions (pH 1 and pH 13), field emission scanning electronic microscope (FE-SEM) images as well as SEM coupled energy dispersive X-ray (EDX) were observed to investigate the effect of corrosion on the surfaces of the samples at the corresponding medium.

**Results and Discussion**

**Gravimetric Analysis**

In chemical terms, copper is demarcated in the noble metal family and considered as highly resistant to corrosion and oxidation. Copper’s resistance to corrosion is attributed mainly to a thin oxide film called patina that forms on the surface of the copper when exposed to a medium. This patina firmly adheres to the outer surface of the copper material and protects the underlying copper layers from further corrosion [7]. However, the water chemistry and other factors cause the medium increasingly aggressive towards copper breaking up the patina to some extent. This phenomenon is comprehensive in the gravimetric analysis of the present experiment. Here, the weight loss per unit exposed surface area \((\Delta W)\) calculated using equation (1) for all four material samples as a function of pH after immersion for the first day and the first three days are revealed in Fig. 1(a) and 1(b). Both the figures depict that all four materials have shown the maximum weight loss in pH1 environment amongst the pH range of 1 to 13. The highest dissolutions of all three alloying elements (Cu, Sn and Pb) present in the four sample materials i.e., material-I, -II, -III and -IV, have occurred at pH1 with the values of 1.016 gm/cm², 1.282 gm/cm², 2.246 gm/cm² and 1.681 gm/cm², respectively, after one day and 1.985 gm/cm², 2.972 gm/cm², 4.687 gm/cm² and 3.713 gm/cm², respectively, after three days due to the surface attack by the aggressive chloride ions of the solution. If the whole pH range is observed for material-I (pure Cu), the weight losses are found to be of least values throughout the pH range compared to other three copper based materials for the immersion period of one day as well as three days. Material-II (Cu-Sn) has followed the pattern of weight loss curve of material-I with closely higher values over the whole pH range, and both the curves are looking like bath tab. From the maximum weight loss at pH1, steady state low weight loss of nearly zero values are observed from pH3 to pH11, and thereafter, the curves rise at pH13 for both material-I and material-II. With the maximum weight losses occurring at pH1 like material-I and material-II, the weight loss curves of material-III and material-IV have not been found steady; rather, there is a pick at pH5 due to higher corrosive tendency of Pb present in both the materials. The weight loss remains low and almost steady from pH7 to pH11, and thereafter, the curves have shown the rise at pH13 making all four curves almost parallel in higher pH environments. However, the aggressiveness of NaOH on copper alloy is significantly less than that of HCl as observed in pH1 for the immersion period of one day and three days. As a whole, the lowest weight loss occurs for material-I (pure Cu), then little higher for material-II (Cu-Sn alloy), further higher for material-IV (Cu-Pb-Sn alloy) and the highest for material-III (Cu-Pb alloy). Therefore, corrosion attacks on the elements are of similar pattern at pH1 as well as pH13.

Once the immersion time is increased, the weight loss ascends steadily in the environment of pH1 for all four material samples. But the weight loss patterns in the environment of pH13 for all four material samples are quite different. Here, weight loss shows increased trend at the initial stage for all four material samples. For higher immersion period i.e., after few days, the weight
loss curves have shown a descending trend up to 18 days immersion and have come closer with steady state condition showing no further loss of weight at the end. Therefore, inclusion of Sn or Pb or solder in copper has not affected badly on the point of corrosion resistance of copper based material while they are immersed in pH13 environment for prolong period.

The relative corrosion rates have been calculated from weight-loss tests using equation (2) for the experimental four sample materials at various pH values after immersion for different time interval up to 30 days. It is found that the corrosion rates are increasing at the initial attack period for each value of pH ranging from 1 to 13 and reached to the highest pick after 24 hours of immersion. Since fig. 1 indicates that the weight loss rates of all four sample materials are observed as the highest for pH1 and then the second highest for pH13, the corrosion rates for these two corresponding pH environments are presented in fig. 2(a) and 2(b) respectively.

As shown in fig. 2(a), the highest corrosion rates of all four sample materials for pH1 environment are observed as 0.4144 mm/year, 0.525 mm/year, 0.9129 mm/year and 0.6868 mm/year respectively just after immersion of the samples for one day. On the contrary, fig. 2(b) shows that the highest corrosion rates for pH13 environment are observed for material-I, -III and -IV after one day’s immersion and for material-II after 3 days’ immersion with the values of 0.1201 mm/year, 0.2915 mm/year, 0.2192 mm/year and 0.0784 mm/year respectively. Therefore, the lowest peak value of corrosion rate is observed in pH1 environment for material-I (pure Cu) and in pH13 environment for material-II (Cu-Sn). On the contrary, the highest peak value of

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corrosion rate is observed in both environment of pH1 and pH13 for material-III which is just Cu dominated material with only addition 1.9% Pb in it. The material-IV i.e., solder affected copper has shown the peak of intermediate level below material-III, and ultimately, the rate of corrosion in acidic medium is higher due to inclusion of solder materials in copper, whereas the rate is lower in alkaline medium after such inclusion of solder materials in copper. This disproportionate dissolution rate in chloride medium can also be agreed with the researches carried out using electrochemical analysis [27,28].

After prolong immersion period, the corrosion rates are declining for all four sample materials irrespective of pH values in the solution. The gradual declining trends are culminating to almost zero in all environments after 30 days immersion with an exception to pH1 where the corrosion rates have been dropped gradually from its peak value, but remained steady for all four materials with the average value of 0.3936 mm/year, 0.4268 mm/year, 0.4466 mm/year and 0.4541 mm/year, respectively, with little fluctuations as shown in fig. 2(a).

Conductivity Investigation

The electrical conductivity on the metal surface is generally reduced as an effect of corrosion while the corroded layer remains adhered on the surface [30,31]. But, if the corroded materials are removed, this understanding harvests a question, and how far it is agreeable, has been examined through measuring the conductivity before and after the occurrence of corrosion in the pH varied environments. Before immersion in the aggressive environment, the original conductivity values of material-I, -II, -III and -IV have been found as 57.61 S/µm, 34.72 S/µm, 54.19 S/µm and 27.64 S/µm respectively. After the immersion in the solutions of varied pH environments, the conductivity values of the four sample materials have been found on average as 57.373 S/µm, 35.941 S/µm, 54.453 S/µm and 27.964 S/µm respectively for one day, and 58.006 S/µm, 35.697 S/µm, 55.719 S/µm and 28.463 S/µm respectively after three days, which are very close to their corresponding original values. Fig. 3 indicates that the conductivity values have not been harshly affected by the environments of wide pH range from 1 to 13 after the immersion of samples for one day and three days.

![Fig. 3. Conductivity variations of four sampling materials as a function of environmental pH after immersion for: (a) 01 day and (b) 03 days](image)

However, there are little variations in conductivity values with respect to pH values of the solutions for both the immersion period of the samples. The ranges of such fluctuations for one day immersion, i.e., minimum to maximum values for material-I, -II, -III and -IV are 56.911 to 57.561 S/µm, 35.097 to 36.969 S/µm, 54.096 to 55.261 S/µm and 27.418 to 28.974 S/µm respectively, resulting the corresponding standard deviations of 0.222 S/µm, 0.669 S/µm, 0.396 S/µm and 0.531 S/µm. The conductivity values have been found to be of little higher with the
increase of pH values. This phenomenon is considered to be the result of pit formation and diffusion of aggressive ions leading to porosity on the surface at irregular forms occurring in lower pH solution in contrast to thin films of copper oxide and hydroxide in the solution of higher pH solution. Moreover, anodic polarization of copper may result in anodic dissolution or film formation depending on pH value of the solution.

![Fig. 4. Conductivity variations of four sampling materials as a function of time in the environment of: (a) pH1 and (b) pH13](image)

The conductivity variations over immersion periods are not also significant. The fluctuations are somehow observed at the initial period of immersion. After immersion for 3 days and onwards, fluctuations are found very minimal and at the end level of 30 days observation the conductivity values are found to be quiet steady as shown in fig. 4 for the environment of pH1 and pH13.

**Microstructure Observation**

The OEM images of all four sample materials as cast condition and after submersion for 30 days are observed in different pH environment. Amongst them, micrographs of corroded samples in pH1 and pH13 environments along with uncorroded samples are presented by rows in fig. 5. The topmost row shows the micrographs of sample materials as cast condition, where fresh polishing marks are visible without any foreign particles in the grain boundaries. The microstructure of the as-cast alloy consists of α-phase, which is a face centric cubic copper, and little dark β-phase, which is martensitic and intermetallic particles. Thus the main visible feature is the granular structure of pure copper with equiaxial grains in random orientations. After 30 days immersion in pH varied environments, the martensitic areas have appeared as dark, which indicates that it has been attacked preferentially. The micrographs also indicate less attack on α-phase areas. The effect of pH value can be differentiated through the presence of dark β-phase. Hence, there has been a change of stacking sequence in the grains through the twinning mechanism. The micrographs for pH1 solution have been found to be the darkest amongst all environments and for pH13 the second darkest, which confirm the highest and the second highest corrosion rates respectively as observed through gravimetric analysis.

The microstructures of corroded samples after 30 days immersion in different pH environments have also been observed using SEM and Few of such SEM images along with EDX spectra are presented in figures 6 and 7 for the environments of pH1 and pH13, respectively. These figures indicate some pits in all four sample materials with randomly nucleated orientation; demonstrating that the samples have suffered from pitting corrosion attack. It is considered that the pits are formed either by intermetallic dropping out from the surface due to the dissolution of the surrounding matrix or selective dissolutions of the intermetallics or particles during immersion period. Moreover, the pits are found to be more prominent for pH13 environment than those of pH1.
environment. It may be perplexing with the gravimetric analysis results, where corrosion rates have been found more for pH1 environment than those of pH13.

![Microstructure of alloys](image)

Fig. 5. Microstructure of alloys with the magnification factor of 300x: (a) Material-I before corrosion, (b) Material-II before corrosion, (c) Material-III before corrosion, (d) Material-IV before corrosion, (e) Material-I after 30 days in pH1, (f) Material-II after 30 days in pH1, (g) Material-III after 30 days in pH1, (h) Material-IV after 30 days in pH1, (i) Material-I after 30 days in pH13, (j) Material-II after 30 days in pH13, (k) Material-III after 30 days in pH13, (l) Material-IV after 30 days in pH13

However, if EDX spectra are noticed, significant insertion of chlorine is observed in the samples by 30 days immersion in pH1 environment in addition to the inclusion of carbon and oxygen. On the other hand in pH13 environment, inclusion of only carbon and oxygen has been observed in the samples after the immersion period of 30 days. Basically, the insertion of chlorine i.e. chloride formation has played pivoting role for higher corrosion rate in the environment of pH1 than that of pH13. Moreover, EDX spectra indicate more oxygen for pH13 solution due to higher amount of oxide formation than that of pH1. As such pouring marks on SEM images are also more for pH1 solution than that of pH13 solution, and thus pits are not prominently observed on samples immersed in pH1 solution as compared to pH13 solution.
**Fig. 6.** SEM images and EDX spectra after exposure in pH1 solution for 30 days: (a) SEM of Material-I, (b) EDX of Material-I, (c) SEM of Material-II, (d) EDX of Material-II, (e) SEM of Material-III, (f) EDX of Material-III, (g) SEM of Material-IV and (h) EDX of Material-IV
Fig. 7. SEM images and EDX spectra after exposure in pH13 solution for 30 days: (a) SEM of Material-I, (b) EDX of Material-I, (c) SEM of Material-II, (d) EDX of Material-II, (e) SEM of Material-III, (f) EDX of Material-III, (g) SEM of Material-IV and (h) EDX of Material-IV

In overall consideration, high uniform global corrosion rate values are obtained for pH1 than that of pH13 in contrast to the formation of pits. Here, the variations of oxide and chloride...
contents for four sample materials are not such significant, but surface images indicate the corrosion rates are quite different for all four sample materials.

Conclusions

The notable findings of the present experimental investigations can be summarized as follows:

The corrosion immunity levels of work hardened copper materials are affected marginally in pH varied environments. However, pH1 solution has been found to be the highest corrosive environment and the next is the pH13 solution for all four copper based sample materials.

Overall leaching losses have been found to be increased for addition of Sn and/or Pb in Cu for each pH value. The highest loss is found to be of Cu-Pb alloy amongst four sample materials. Cu-Pb alloy is followed by SnPb-solder affected copper, then Cu-Sn alloy and the lowest loss is of pure copper. It indicates that alloying of copper with tin or lead has reduced its corrosion resistance especially in acidic environment.

Corrosion rates of all four sample materials have been found to be the highest by the first immersion period, and then their rates have come down to the steady values for all pH varied environments. After 30 days of immersion, the corrosion rates for all four sample materials have been found to be close to zero with the exception of pH1 environment.

The conductivity values of sample materials have not been significantly affected over the immersion period. However, there have been little fluctuations in conductivity values due to corroded surface and pit formations.

The microstructures of the corroded surfaces observed through OEM and SEM images have confirmed the highest surface corrosion in pH1 solution amongst all environments.

References


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