Research Article

Corrosion Behavior of Work Hardened SnPb-Solder Affected Copper in the Bay of Bengal Water Environment

M. Muzibur Rahman (ID),[1,2] **S. Reaz Ahmed,**[1] **and M. Salim Kaiser**[3]

[1]*Department of Mechanical Engineering, Bangladesh University of Engineering and Technology, Dhaka 1000, Bangladesh*
[2]*Department of Naval Architecture & Marine Engineering, Military Institute of Science and Technology, Dhaka 1216, Bangladesh*
[3]*Directorate of Advisory, Extension and Research Services, Bangladesh University of Engineering and Technology,*
 Dhaka 1000, Bangladesh

Correspondence should be addressed to M. Muzibur Rahman; muzib1061@gmail.com

Copper and its alloys are extensively used in marine applications due to high corrosion resistant behavior. But the corrosion immunity of copper varies with the environmental factors especially the sea water ingredients. Many researchers investigated corrosion level of copper materials in different oceans/seas. Unfortunately, such study is missing in the Bay of Bengal water. Moreover, inclusion of alloying elements can have influence on the corrosion behavior of copper, especially the addition of SnPb-solder for repair works and environmental effects due to ageing. In fact, the urge of using old copper to manufacture new components for marine applications necessitates the characterization of various properties. In this context, present paper is an attempt to investigate the corrosion behavior of copper and solder affected copper to enhance the reuse potential of SnPb-solder affected old/waste copper in contact of the bay water along with comparison with commercial copper alloys. Here, the result shows that overall leaching is increased for the addition of Sn and/or Pb in Cu over the whole immersion period in the stagnant water of the Bay of Bengal. The highest loss is found to be of Cu-Pb alloy which is followed by SnPb-solder affected copper, then Cu-Sn alloy and the lowest loss is of pure copper. The cold-rolled work-hardening has reduced the corrosion rate for all copper alloys. It also reveals that the solder affected copper is more corrosion resistant than commercial copper alloys such as brass and bronze.

1. Introduction

Endeavors to explore the maritime domain is the civilization activity over a prolong period and has enlarged the impetus with increased sea-borne shipping, generation of ocean thermal/wave energy, exploitation of oil and minerals, etc. [1]. All the sea-borne activities are facing problems linked to the maintenance of marine vessels, offshore structures, systems, and machineries because of corrosiveness in sea water. As such, the most important quality of a material for recommendation in sea service is the corrosion behavior. Corrosion is basically the destruction of materials under actions of the surrounding environment and the reaction taking place at the interface due to the heterogeneity of the metal surface that creates local anodic and cathodic sites

resulting in corrosion. With the exception of noble metals all materials do corrode and transform into substances similar to their mineral ores from which they are extracted [2]. In this situation, copper and its alloys are very prevalent in the marine field and extensively used by shipbuilders for their corrosion resistance level along with suitable mechanical properties. At the same time, the rapid technological advancement has derived higher demand of copper [3] but copper ores are being depleted in the nature [4]. As a result, copper collection from old/scraped items can be a time demanding issue and there are two options with the waste copper items, i.e., recycling by extracting the pure copper or reusing the leftover copper. Here, reusing is significantly cheaper than recycling but important properties are desirable to be anticipated, and thus, while reusing choice is

preferred, it becomes necessary to characterize the associated properties to explore the suitable engineering applications of such scraped copper [5–8].

Generally, corrosion immunity of copper is considered attributable to its association with noble metals, which has the basis with the supposition on survival of copper as in-born in the Earth's crust [9]. A very thin brownish-green layer known as patina is formed while copper stays in the atmosphere [10, 11]. This patina grows over a period and becomes an enduring portion on the copper items. The corrosion resistance of copper is illustrated by artefacts that were obtained in unspoiled state after remaining submerged in the Earth for several hundred years, and copper roofs found in rural area with corrosion rates ≤0.4 mm in 200 years [12]. But, copper gets corroded inside water or in contact of water by numerous factors considered in different manners. Few researchers [13–16] consider that consumption of oxygen occurs due to the oxy-hydrogen reactions and hydrogen produced in copper-water reaction but not being detected so long as oxygen supply to the surface surpasses hydrogen generation rate, which results in erroneous consideration for corrosion resistance of copper. Conversely, another group of researchers [17, 18] have stated that copper does not corrode in clean water. However, all have agreed on that the reaction rate can vary with salinity, pH value, temperature, flow condition, and existence of certain atoms/molecules at the reaction zone [19, 20]. Besides, copper shows specific appearances as intercrystalline corrosion and corrosion cracking [21], and there is an effect of alloying elements [22]. As such, corrosion behavior of copper remains a concern especially in sea water environment due to aggressiveness of ingredients in the sea water.

It may be noted that scraped copper collected from diverse sources are found to have a tiny amount of soldering elements such as tin, lead, silver. Though the insertion of these elements in copper is very little, its effect may not be neglected on corrosion aspect [6, 22, 23]. Furthermore, old copper materials might have been work hardened in manufacturing process or in their product life span causing the microstructural dislocations, which eventually results in altering the properties including corrosion resistance [24]. Again, the corrosion of copper is to be of different nature as observed over the world for various environments including seas and gulfs [25–31].

In this connection, the Bay of Bengal (BoB) has the call for adequate attention since the sea-borne activities are growing up over this bay [1, 32, 33], and it is thus imperative to investigate the corrosion behavior of solder affected copper in BoB water. Therefore, the present study has made an effort to characterize the solder affected copper and compare with commercially used copper alloys such as brass and bronze on corrosion aspect to look for suitable rehabilitations of scraped copper in corrosive environments.

2. Sample Materials Preparation and Details of Experiments

2.1. Preparedness of Samples.
Very old (far-reaching age of more than five decades) wires and machine parts made of copper were engaged as focusing material to undertake the present investigation and 80 kg plus of them were assembled from various sites such as buildings, factories, and ship-breaking. After collection, they were melted in the furnace and the chemical compositions were measured employing X-ray fluorescence (XRF) analyzer of model Olympus DPO-2000-CC. It was observed that the old copper wires were containing little percentage of soldering elements, such as, lead and tin. The composition tests of such melted copper wires have revealed that there are considerable percentages of Sn and Pb with Cu. They are amounting Cu (97–98%), Sn (0.8–1.5%), Pb (0.8–1.4%), and few negligible elements. At this situation, the impact of tin and lead as individual elements on the corrosive properties of old solder-affected copper was considered important to estimate, and thus, two more copper alloys, such as Cu-Sn alloy and Cu-Pb alloy having trace amount of Sn and Pb, respectively, were selected as supporting materials. For the development of two alloys about 150 kg copper ingot were required and they were casted in furnace adding trace amount of tin and lead so that the developed alloys can be comparable with old/scrape copper. After collecting/developing four sample materials, i.e., pure copper (Material-I), Cu-Sn alloy (Material-II), Cu-Pb alloy (Material-III), and solder affected copper (Material-IV), their chemical compositions were scrutinized using XRF analyzer and the attained percentages are presented in Table 1.

From each sample material, several numbers of small bars of dimensions 300 mm × 15 mm × 12 mm were made, and in this work, effort was made so that the surface/edge grains of sample materials were affected at the minimum level. The prepared flat bars were homogenized at first at 500°C for eight hours to reduce chemical segregations and then solution treatment was performed at 700°C temperature for two hours to improve workability. The treated flat bars were then work hardened using a heavy duty roller machine very slowly to avoid the rise of specimen temperature and it was performed maintaining the lowest possible speed of the machine during the rolling operations. As such, the applied rolling machine feed was restricted to only 0.1 against the roll pass and a reasonable pause was given in between two passes. In this way, cold-rolled work hardening was performed by reducing the bar thickness gradually at various stages/levels. Flat bars of each material were divided into four categories for different levels of cold-roll work-hardening. Few of them were kept as cast/as original (as of zero work hardened), few were work-hardened of 25% cold-rolled, few were of 50% cold-rolled, and the remaining bars were work-hardened of 75% cold-rolled condition. As a result, sixteen categories of samples were obtained from four materials at four cold-rolled work-hardening conditions.

To carry out corrosion tests, coupons of size 60 mm × 15 mm × 3 mm were prepared as per the guide line of ASTM G4 and they were ground mechanically using 180, 300, 600, 900, 1200, and 1500 grits of SiC abrasive papers in successions. Then, all the coupons were polished using Al_2O_3 in presence of water and air blown at the atmospheric temperature to be made ready for the experiments.

TABLE 1: Chemical composition of sample materials used in the study (mass fraction %).

Materials/ Elements	Pure Cu	Cu-Sn alloy	Cu-Pb alloy	Cu-Sn-Pb alloy
Cu	99.9862	98.4555	97.6570	97.1132
Sn	—	1.1335	—	1.2572
Pb	—	—	1.9737	1.1949
Si	0.0026	0.1415	0.1129	0.1726
P	0.0112	0.2695	0.2564	0.2621

2.2. Experimental Procedures. To examine the corrosion resistance of four copper based materials, i.e., pure copper (Material-I), Cu-Sn alloy (Material-II), Cu-Pb alloy (Material-III), and solder affected copper (Material-IV) in the sea water environment, water (2000 liter) was collected from each of three locations of the Bay of Bengal. Locations, date, time, and sea conditions related to the collection of water are given in Table 2. The collected BoB water was tested in the laboratory to find out the ingredients/parameters relevant to corrosion, and the results for the sea water of three locations are found to be very similar in nature. However, test results indicate little higher salinity value in St. Martine's water. Considering the salinity point, the corrosion test was carried out using St. Martine's water. Table 3 presents the laboratory test results for pH value, dissolved solids, suspended solids, sulfate, chloride, etc. It may be mentioned that the salinity of sea water is measured using the following expression given by International Council for the Exploration of Sea [34, 35].

$$S^o/oo = 0.03 + 1.805 \times C^o/oo, \tag{1}$$

where S^o/oo is the Salinity of sea water and C^o/oo is the Chlorinity measured as gram of chloride ions in one kilogram of water

In the present study, corrosion investigation was conducted using gravimetric method. The weights of coupons prepared following the ASTM G4 guideline were measured using a high precision (0.00001 g) digital weighing machine (model: ASB-60-220-C2) to get their initial values before immersion in BoB water. At this time, the metallographic pictures were taken using computer interfaced optical electronic microscope (OEM) with magnification ranging from of 100x to 1200x. The electrical conductivity of prepared coupons was also traced out using electric conductivity tester (Model: TMD-101) with the accuracy level of ± 0.01 IACS (International Annealed Copper Standard). Then, coupons were kept immersed in sea water for a designated period and removed, washed in distilled water and dehydrated naturally leaving them on absorbent papers. The first reading for change in weight was taken after 24 hours exposure of sample materials in sea water. In addition to weight change, electrical conductivity variations of the coupons were monitored and their microstructures were witnessed to visualize the importance and aggressiveness of material degradation in the first incursion. Subsequently, mass degradation, and electrical conductivity of the coupons were measured in similar manner at the time interval of 3 days up to 36 days of submersion in BoB water. Mass degradations per exposed area and the corresponding

corrosion rates were calculated using two equations as shown below [36].

Mass degradation of material.

$$\Delta W = \frac{(W_o - W_f)}{A}. \tag{2}$$

The rate of corrosion.

$$R_{\text{corr}} = \frac{(K \times \Delta W)}{(\rho \times T)}, \tag{3}$$

where
$\Delta W =$
Mass degradation per exposed surface area (gm/cm^2),
W_o = Initial mass (gm),
W_f = Mass after designated submerged period (gm),
A = Surface area exposed in the media (cm^2),
R_{corr} = Rate of corrosion (mm/year),
K = Unit conversion factor =
87.6×10^3 for corrosion rate in mmpy,
ρ = Density of material (gm/cm^3), and
T = Exposed duration (hour).

Once 36 days of immersion is completed, final readings were taken and microstructures of the corroded surfaces were viewed for all samples using OEM to observe the corrosion type and mechanism. Besides, images of field emission scanning electronic microscope (FE-SEM) were observed and energy dispersive X-ray (EDX) readings were taken using a machine of model JEOL JSM-7600F to inspect severity of corrosion on the surfaces of copper and its alloys.

3. Results and Discussion

3.1. Gravimetric Analysis on Effect of Alloying and Work Hardening

3.1.1. Mass Loss for Corrosion. Sea water is without question a severe corrosion agent because of its complex electrolytic behavior for the presence of several minerals, biological elements, suspended silts, dissolved gases, etc. Similar contents with different magnitudes have been noticed in BoB water as presented in Table 3. As a result, copper being affiliated with noble metal family could not remain immune from the attacks of chemical/electro-chemical corrosion, and thus, all four copper-based sample materials have demonstrated the loss of weight in such aggressive sea water environment. From the readings, the mass degradation per surface area exposed in the media (ΔW) is computed using equation (2) for all four coupons of material I, II, III, and IV, and the gravimetric analysis of the present experiment is performed accordingly after the immersion of samples for different periods up to 36 days.

However, there are differences in the mass loss amount per surface area exposed in the media with respect to immersion period amongst the sampling materials under different cold rolled work hardening levels as seen in Figure 1. All the graphs in Figure 1 are showing the similar pattern of weight loss with the rise of immersion period, and

TABLE 2: Particulars of location of Bay of Bengal for sea water collection.

Location	Latitude and longitude	Date and time	Sea state	Depth from surface (mm)
Off St. Martin's Island	20°37.5′,92°20.88′	1830 hrs on 11 Nov 2018	Smooth	100
Off Kutubdia	22°08.18′,91°39.73′	0630 hrs on 12 Nov 2018	Moderate	100
Outer Anchorage of Chittagong	20°08.97′,91°41.15′	1030 hrs on 12 Nov 2018	Smooth	100

TABLE 3: Contents and properties of sea water used for investigation.

| Parameter	Unit	Concentration present	Standard for inland water	Analysis method
pH	—	7.14	6–9	pH meter
Total dissolved solids (TDS)	mg/L	28000	≤2100	Conductivity meter
Total suspended solids (TSS)	mg/L	48	≤150	UVS
Turbidity	NTU	76.9	—	Turbidity meter
Sulfate (SO_4^{2-})	mg/L	1320	—	UVS
Dissolved oxygen	mg/L	7.29	4.5–8	DO meter
Electric conductivity	μS/cm	45000	≤1200	Conductivity meter
Chloride	mg/L	20000	≤6001	Titrimetric
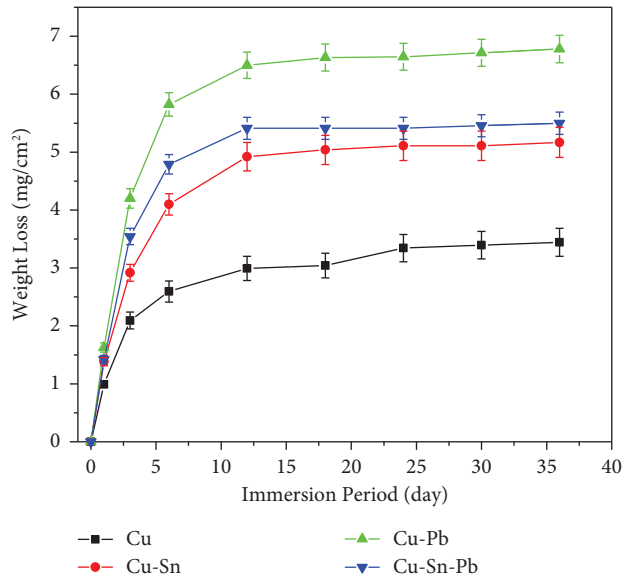
(a)
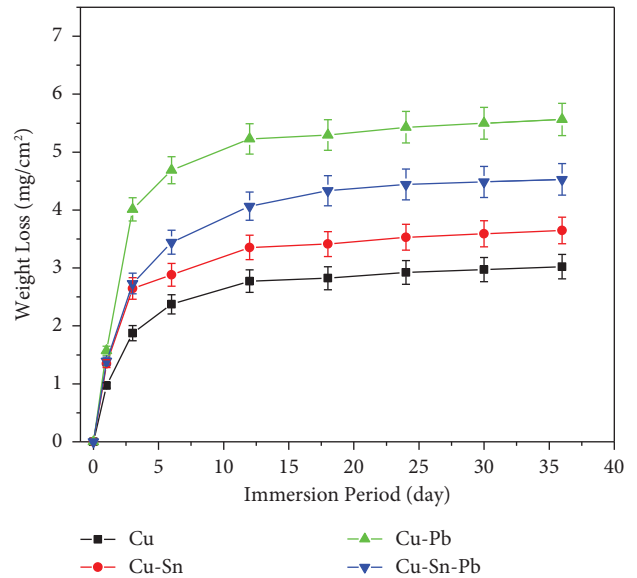
(b)

FIGURE 1: Continued.
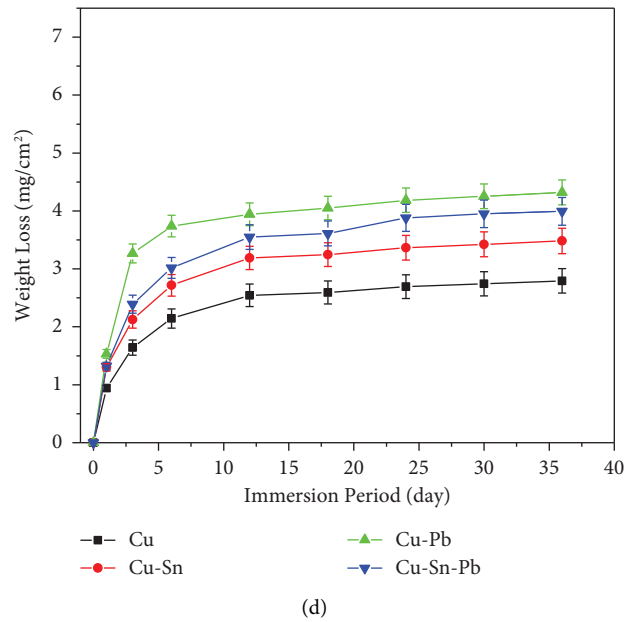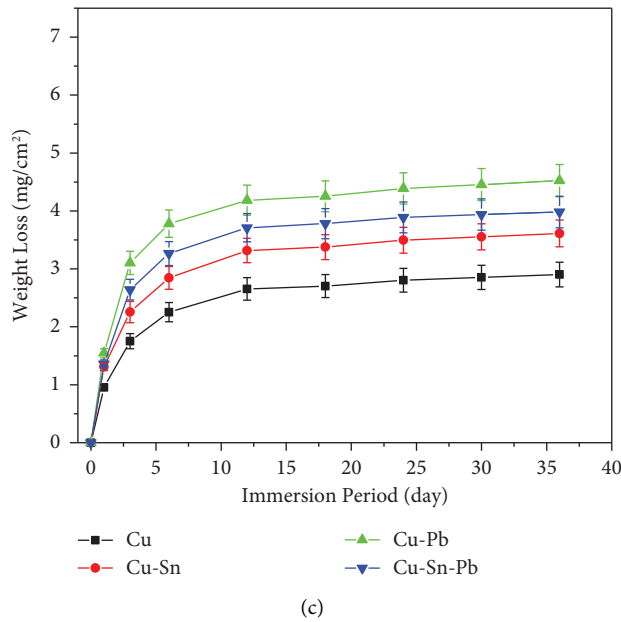
FIGURE 1: Corrosion mass loss of copper and its alloys against immersion period in sea water for the samples of: (a) 0%, (b) 25%, (c) 50%, and (d) 75% cold rolled hardening.

initially, they are seen sharper which indicate comparatively higher values of mass loss per surface area exposed to the media by the first strike of aggressive components present in sea water. Then, the mass loss tendencies of all four group coupons for all cold rolled hardening levels are observed to be reduced with the escalation of submerged period, and after a prolong immersion period, the curves have become almost horizontal with negligible slope values. The main reason for such weight loss pattern might be of necessary timing delay for the development of copper patina on the exposed surface area, and once the patina is formed, corrosion attack has become restricted. This finding agrees with previous works, i.e., the corrosion for commercial copper alloys in sea water [32] and solder affected copper in pH varied environments [6].

Figure 1(a) depicts the weight degradation of sample materials at their cast condition, i.e., without work hardening. Here, the loss of weight over the whole range of immersion period is found to be the highest for Cu-Pb alloy (Material III) which is followed by solder affected copper (Material IV), then Cu-Sn alloy (Material II) and the lowest values for pure copper (Material I). By 36 days immersion all four samples are showing flat pattern of weight loss curves with the maximum values of 3.44 mg/cm^2, 5.17 mg/cm^2, 6.78 mg/cm^2, and 5.50 mg/cm^2, respectively. It is thus observed that the cumulative degradation of weight in sea water has been increased by 50.1% for only 1.133% tin with copper in Material-II, by 96.9% for only 1.197% lead in Material III and 59.7% for the inclusion of approximately 1.257% Sn and 1.195% Pb in combination for Material IV than that of pure copper.

Figure 1(b) illustrates that weight loss of sample materials at their 25% cold rolled hardening condition. Here also, the mass loss over the whole range of immersion period is found to be the

highest for Cu-Pb alloy (Material III) which is followed by Material IV, then Material II, and the least corrosion values for Material I, and the trends are very similar to that of cast condition for the immersion period of 36 days. The cumulative mass losses of 25% cold worked materials during 36 days' immersion in sea water are found to be 3.02 mg/cm^2, 3.65 mg/cm^2, 5.57 mg/cm^2, and 4.53 mg/cm^2, respectively, which are correspondingly 12.19%, 29.41%, 17.93%, and 17.64% less than that of cast condition.

Figure 1(c) shows that weight loss of sample materials at their 50% cold rolled hardening condition. The loss of weight over the whole range of immersion period is found to be the highest for Cu-Pb alloy (Material III) which is followed by Material-IV. It is then followed by Material-II and the least corrosion values are seen for pure copper (Material I). The trends are very similar to that of cast and 25% cold rolled conditions. The cumulative weight losses during 36 days immersion in sea water for 50% cold worked copper materials are found to be 2.90 mg/cm^2, 3.61 mg/cm^2, 4.52 mg/cm^2, and 3.98 mg/cm^2, respectively, which are correspondingly 15.68%, 30.10%, 33.29%, and 27.59% less than that of cast condition.

Figure 1(d) displays that weight loss of sample materials at their 75% cold rolled hardening condition. The weight degradation over the whole range of immersion period is also found to be the highest for Cu-Pb alloy (Material III) which is followed by Material IV, and it is then followed by Material II. The least corrosion is seen for Material I and the trends are very similar to that of cast, 25% cold rolled and 50% cold rolled conditions. The cumulative weight losses during 36 days' immersion in sea water for Material I, II, III, and IV are found to be 2.79 mg/cm^2, 3.48 mg/cm^2, 4.32 mg/cm^2, and 3.99 mg/cm^2, respectively, which are correspondingly 18.87%, 32.61%, 36.28%, and 27.35% less than that of cast condition.

As a whole, cold work level from zero to 25% has reduced the weight loss for all four sample materials to remarkable level. Further 25% cold rolling, i.e., 50% cold-rolled work hardening has also reduced the weight loss tendency further, but the extent is little less than that of 25% cold rolled condition. For 75% cold rolled condition, weight losses are again reduced with very negligible extent. Therefore, the cold rolling reduces the loss of weight for copper-based materials in sea water corrosive environment.

3.1.2. Corrosion Rate in Sea Water. Equation (3) was employed to calculate the relative corrosion rates from weight-loss data obtained from the experimental readings of sample materials after submersion for different intervals up to 36 days. The results are presented for the cold work level of 0%, 25%, 50%, and 75% in Figures 2(a)–2(d), respectively. Figure 2(a) portrays that the corrosion rate of Material III is the highest at cast condition, which is tailed by Material IV, then Cu-Sn alloy (Material II) and the least corrosion rates for Material I over the whole range of immersion period of 36 days. The maximum corrosion rate values of pure copper (Material I), Cu-Sn alloy (Material II), Cu-Pb alloy (Material III), and solder affected copper (Material IV) are found to be 0.404 mmpy, 0.566 mmpy, 0.661 mmpy, and 0.580 mmpy, respectively, after the first day of immersion. It indicates that the rate of corrosion is increased by 50.72% for the inclusion of only 1.133% tin with copper in Material-II, 96.31% for the addition of 1.197% lead for Material III and 60.03% for adding approximately 1.257% tin and 1.195% lead together for solder affected copper (Material IV) than that of pure copper (Material I). These pick values have fallen down sharply with the formation of copper patina. Once the initial attack period is over, the corrosion rates are gradually reduced against the rise of immersion period and by 36 days of immersion in sea water, corrosion rates of all samples reach to the minimum values with the curves also becoming almost horizontal. Figures 2(b)–2(d) are very similar to Figure 2(a) with only variation of magnitudes of corrosion rate due to the effect of cold rolling.

Figure 3 illustrates that the pick corrosion rates after 24 hours' immersion and steady state corrosion rates after 36 days' immersion are reduced with higher cold rolled hardening for all four copper based materials. After the immersion of one day, the corrosion rate of pure Cu, Cu-Sn alloy, Cu-Pb alloy, and solder affected Cu are reduced by 5.05%, 5.98%, 5.83%, and 6.92%, respectively, for cold roll hardening level of 75% deformation as shown in Figure 3(a). Similarly, after the immersion 36 days, the corrosion rate of pure copper (Material I), Cu-Sn alloy (Material II), Cu-Pb alloy (Material III), and solder affected copper (Material IV) are reduced by 18.87%, 32.61%, 36.28%, and 27.35%, respectively, for cold roll hardening level of 75% deformation as shown in Figure 3(b). It indicates that the corrosion rates of all four copper based materials with 75% cold rolled hardening have partially nullified the adverse effect of soldering elements, i.e., Sn or/and Pb inclusion in Cu. This is undoubtedly a significant achievement on the improvement of corrosion resistance through cold rolled work hardening.

3.2. Conductivity for Corrosion in Sea Water. The work hardening levels have been found to be an influencing factor for the electrical conductivity values both before and after corrosion. Figure 4(a) illustrates the electrical conductivity of sample materials before corrosion at different cold rolled hardening levels. It is observed that conductivity values of pure copper (Material-I) is influenced very slightly with the variation of work hardening level (black line in Figure 4(a)). Basically, pure copper (Material I) has shown no sign of increasing conductivity at any level of work hardening, rather at higher work hardening level there is a little reduction in conductivity. As a result, the electrical conductivity of material I after 75% cold-rolled deformation is found to be 1.53% less than that of cast condition. However, the electrical conductivity of three copper alloys, i.e., materials II, III, and IV have been seen increasing slightly at lesser cold rolled hardening levels and fallen again for higher cold work levels as labeled by colored lines of red, green, and blue in Figure 4(a), respectively. But work hardening effects on conductivity are found to be diminishing after immersion in sea water environment due to corrosion as observed in Figures 4(b) and 4(c).

3.3. Comparison of Corrosion Behavior in Sea and Fresh Water. The corrosion rates of pure copper (Material I), Cu-Sn alloy (Material II), Cu-Pb alloy (Material III), and solder affected copper (Material IV) in sea water and plain water (distilled water) for the immersion period up to 36 days have been presented in Figures 5(a) and 5(b). In both the figures, reduction of corrosion rates is observed over the immersion period. Figure 5(a) illustrates that the corrosion rates of the samples in BoB water are the highest for the first day of immersion amounting 0.38 mmpy, 0.53 mmpy, 0.62 mmpy, and 0.54 mmpy, respectively. Figure 5(b) depicts that their corrosion rates in plain water are also the highest for the first day of immersion, but the magnitudes are very little, i.e., 0.006 mmpy, 0.021 mmpy, 0.078 mmpy, and 0.046 mmpy, respectively. It indicates that copper-based materials possess significant immunity level of corrosion in plain water environment, whereas certain degree corrosion in sea water. The giant differences in the average values of corrosion rates of four sample materials are shown in Figure 6.

3.4. Corrosion Behavior between Solder Affected Cu and Commercial Cu Alloys. The commercial copper alloys used in marine environment are mainly brass and bronze. So, the corrosion tests of these two alloys were carried out side by side to the cold rolled solder affected copper to assess the corrosion resistance performance of solder affected copper compared to that of brass and bronze. The corrosion rates of the three sample materials in the same sea water environment against the immersion period are presented in Figure 7. It indicates that solder affected copper is showing similar trends of brass and bronze with initial high attack and then gradual reduction of corrosion rate against the increase of immersion period. Amongst these three copper based materials, brass is found as the most corrosive over the whole immersion period with the maximum and average
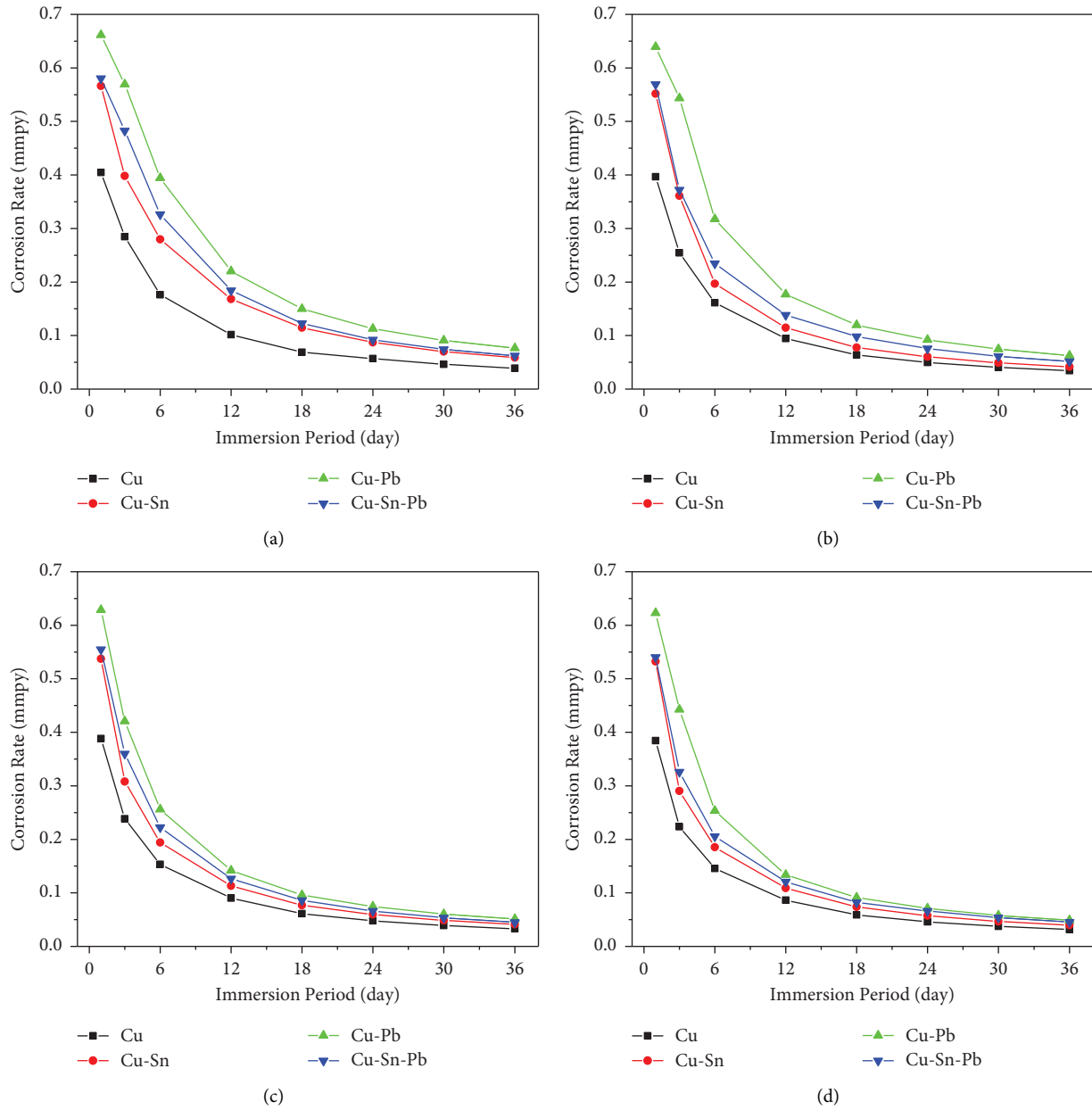
Figure 2: Corrosion rate of copper and its alloys against the immersion period in sea water for: (a) 0%, (b) 25%, (c) 50%, and (d) 75% cold rolled hardening.

corrosion rates of 0.676 mmpy and 0.243 mmpy, respectively. Another commercial copper alloy, i.e., bronze is found less corrosive than brass but more corrosive than SnPb-solder affected copper at the initial period of immersion. With the increase of immersion period, the corrosion rates of bronze have lower for certain immersion period, but again become higher than that of solder affected copper. At the final day, the corrosion rate sequence after prolong immersion becomes as similar to that observed at the initial attack. As a whole, commercial copper alloys can be considered more corrosive than solder affected copper proving its worthiness in corrosion resistant applications. Here question may come on the presence of tin both in bronze and solder affected copper, the why bronze corrodes

more than solder affected copper. The amount of tin present in solder affected copper is very little (~1.2%) which is completely consumed to form intermetallic compounds (Cu_xSn_y) resulting in less rate of corrosion. On the other hand, tin present in bronze is about 9.3% and of which a part is consumed to form such intermetallic compounds and the excess tin available in the alloy forms the solid solution resulting in increase of corrosion rate of bronze than that of SnPb-solder affected copper (Material IV).

The maximum and average values of corrosion rates of two commercial copper alloys and solder affected copper are shown in the bar chart in Figure 8. It also indicates that brass is the most corrosive copper alloy with its on average corrosion rate 21.8% more than that of bronze and 25.8%
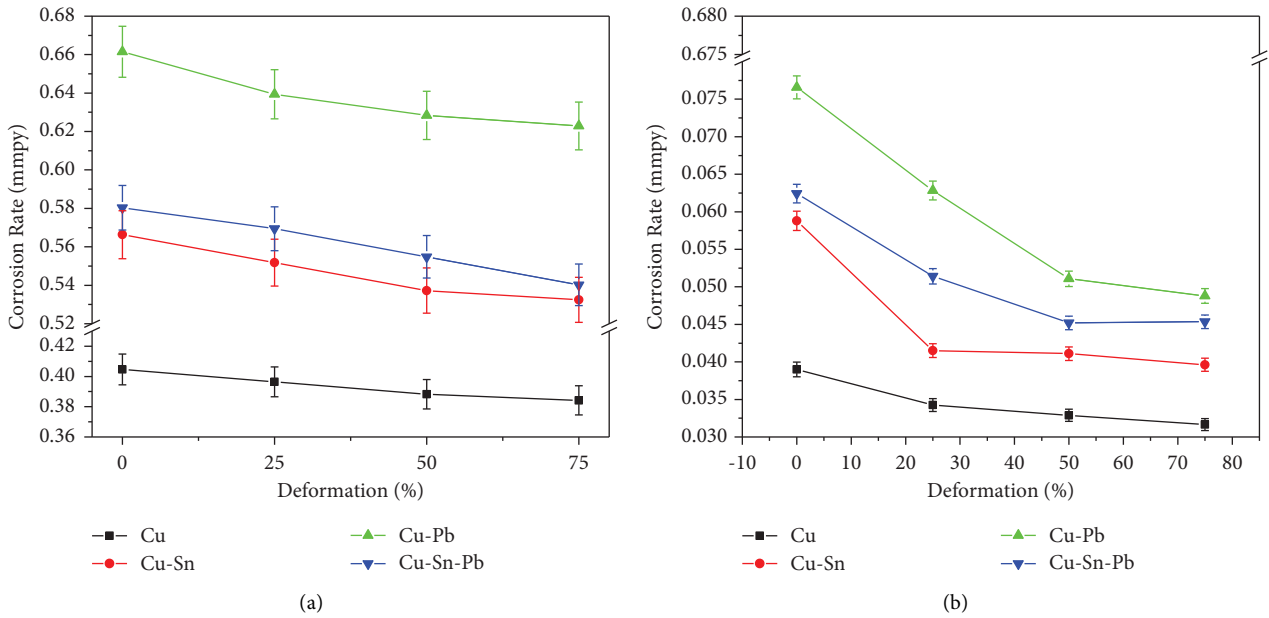
(a)

(b)

FIGURE 3: Corrosion rate (mmpy) as a function of work hardening of cold rolling percentage for immersion in sea water: (a) after one day and (b) after 36 days.
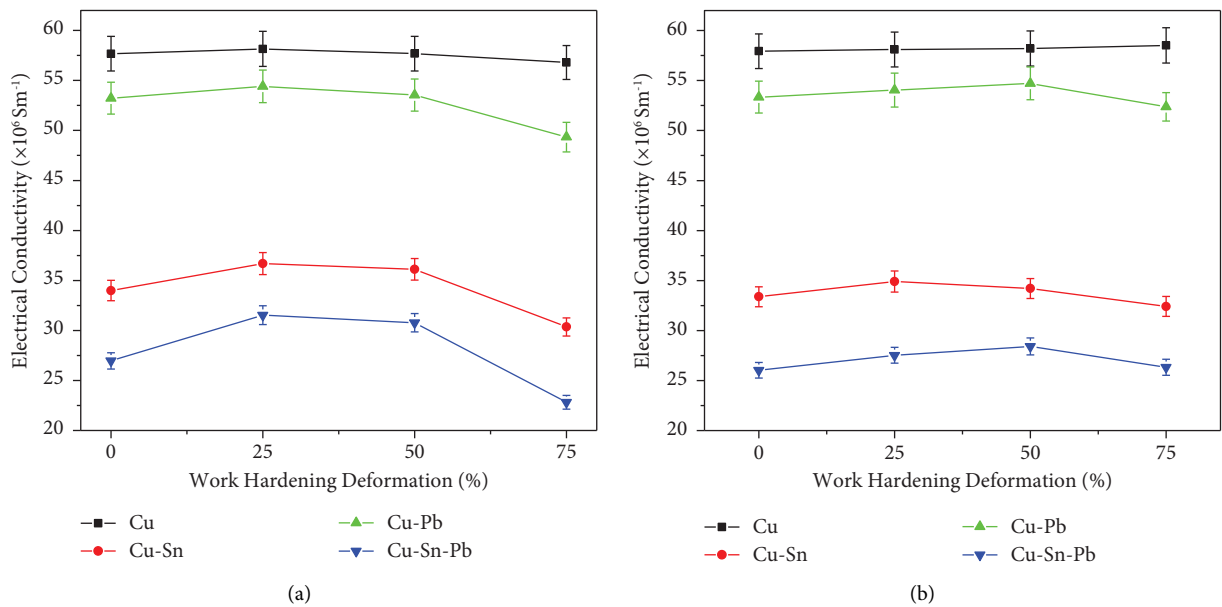
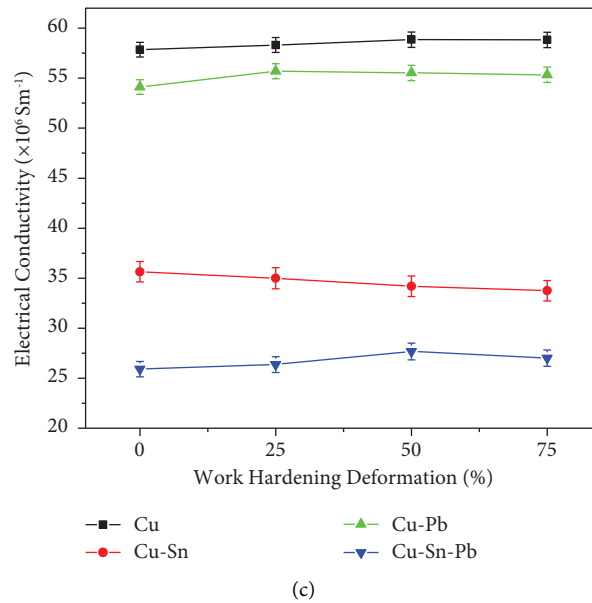

(a)

(b)

FIGURE 4: Continued.

(c)

FIGURE 4: Conductivity of copper and its alloys for corrosion in sea water against work hardening levels: (a) before corrosion, (b) after one day corrosion, and (c) after 36 days corrosion.
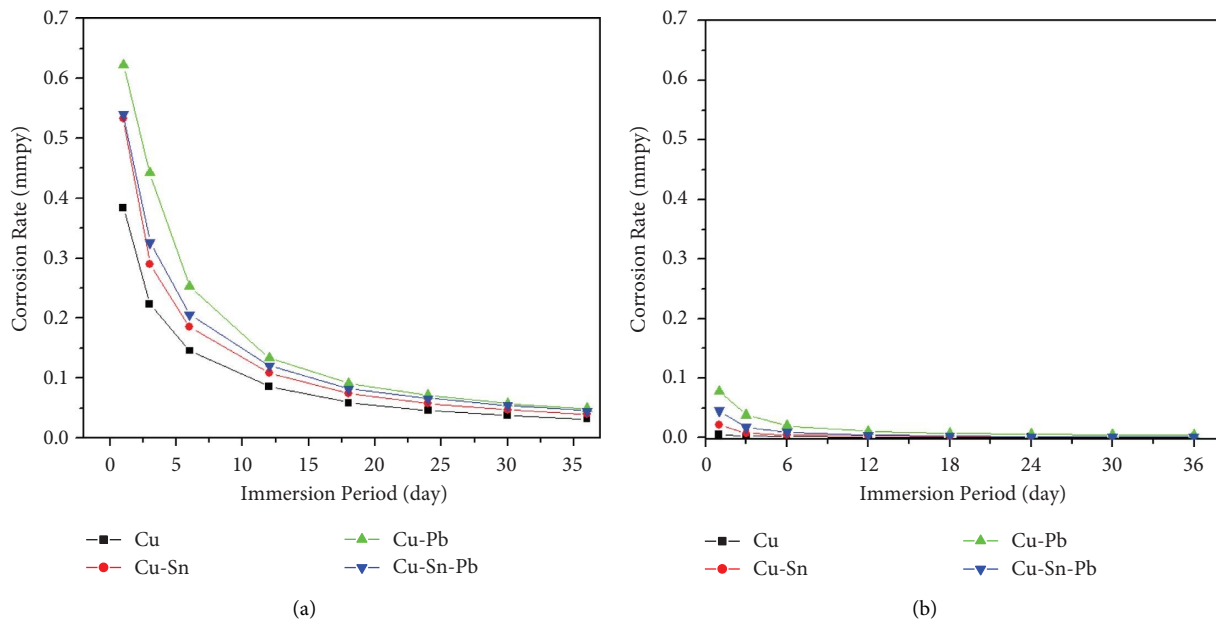

(a)

(b)

FIGURE 5: Corrosion rate of copper and its alloys against immersion period in (a) sea water and (b) fresh water environments.

more than that of solder affected copper. Therefore, solder affected copper can very well be considered as one of the most useful material for the applications in such sea water environment on corrosion resistance.

3.5. Microstructure of Corroded Surface in Sea Water. Figure 9 shows the microstructure images of cold rolled samples observed using OEM after 36 days' immersion in the sea water, which provides distinct signs of general corrosion on the surface of pure copper, but material II,

III, and IV are showing a combination of corrosions in different forms. The marks of rolling and polishing have been faded away from the surfaces because of corrosion occurred and it matches with weight degradation and corrosion rates observed during gravimetric analysis. In addition to general corrosion, a good number of pits and inter-granular corrosion marks are observed especially on the surfaces of Cu-alloys after 36 days' submersion in sea water. Alloys have been seen severely affected than pure copper.
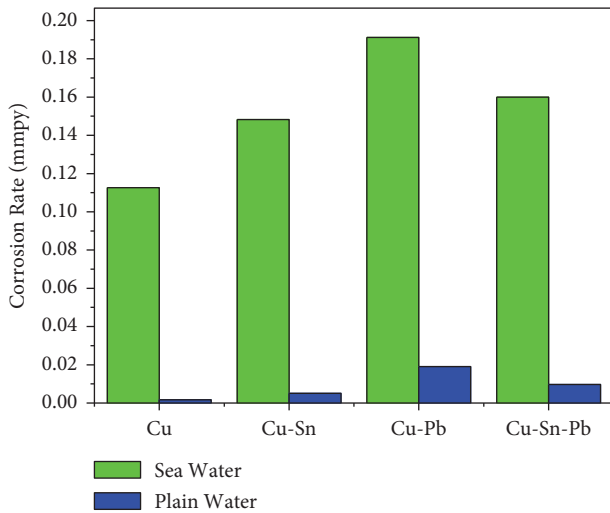
Figure 6: Average corrosion rates of copper and its alloys over immersion period of 36 days in sea water and plain water environments.
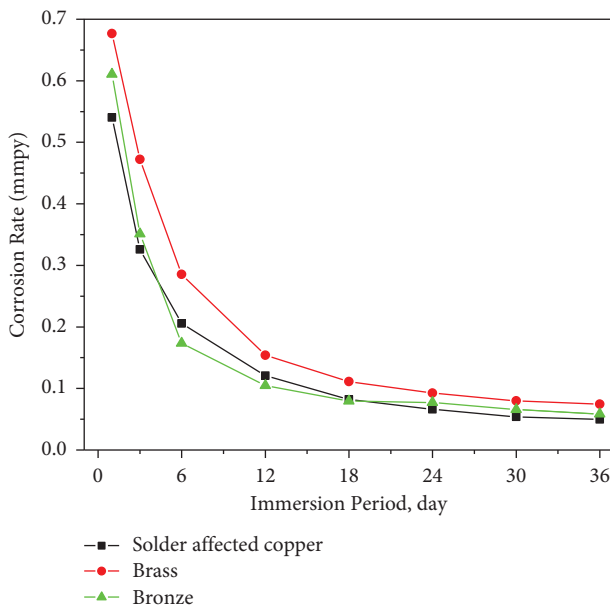

Figure 7: Corrosion rate of solder-affected copper and commercial copper alloys against immersion period in sea water environment.
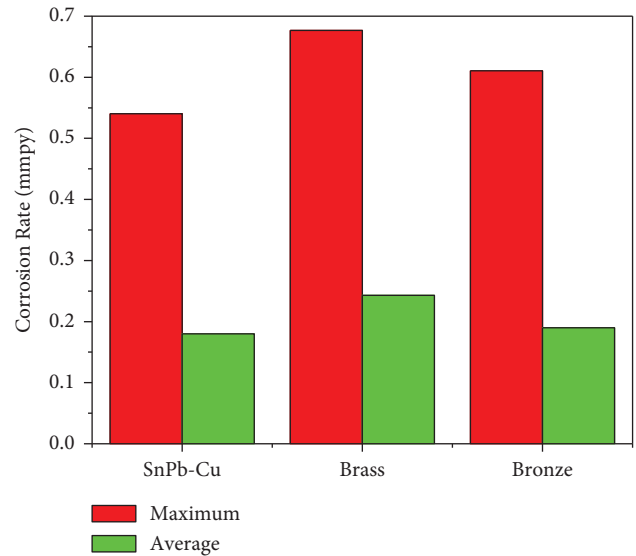

Figure 8: Maximum and average values of corrosion rates of solder-affected copper and commercial copper alloys.

also visible in Figures 10(c) and 10(d). The pits might have been formed either by dropping out intermetallic particulates from the surface due to the dissolution of the surrounding matrix or by dissolutions of the intermetallic particles during the period of immersion in sea water. Figure 10(c) signposts some massive corrosion marks that are severe than normal pits due to high dissolution tendency of lead than that of copper or tin. Figure 10(d) indicates combined configuration of Figures 10(b) and 10(c) with few pits such as material II as well as few severe surface removals such as material III.

Figure 11 indicates the corroded surface of two commercial copper alloys such as brass and bronze to compare the corrosion resistance performance level of SnPb-solder affected copper in sea water environment. It is observed that brass is corroded almost uniformly, which results in smooth surface of the sample. But bronze has shown rough and scratchy surface indicating irregular removal of surface crystals. Comparing these two SEM images of Figure 11 with the SEM image of SnPb-solder affected copper shown in Figure 10(d), it may be mentioned that SnPb-solder affected Cu is of more corrosion resistant than both brass and bronze.

The masses of elements in percentage obtained through the analysis of EDX profile for pure copper after 36 days corrosion in sea water are as 1.37% C, 9.85% O, 1.46% Cl, and 87.32% Cu. The masses of elements in percentage obtained through the analysis of EDX profile for solder affected Cu are as 1.14% C, 9.50% O, 2.75% Cl, 82.76% Cu, 2.17% Sn, and 1.68% Pb. Similarly, the mass percentages for brass are obtained as 38.09% O, 2.37% Na, 0.16% Al, 2.49% Cl, 35.59% Cu, 17.54% Zn, and 3.75% Pb. The masses of elements in percentage obtained through the analysis of EDX profile for bronze are as 23.72% O, 0.10% Al, 0.19% Cl, 62.43% Cu, 12.88% Sn, and 0.68% Pb. These percentages of elements indicate that the corrosion occurred in sea water has a notable outcome on the chemical composition of the surface

SEM images of 75% cold-rolled four sample materials after corrosion in sea water for 36 days are presented in Figure 10. Figure 10(a) indicates that pure copper (Material I) is affected less by corrosion attack than other three copper alloy materials, i.e., material II, material III, and material IV (solder affected copper) as presented their SEM images in Figures 10(b)–10(d), respectively. SEM image of material I also indicate smooth and uniformly distributed corrosion over the whole surface. But SEM images of other three sample materials indicate irregular corrosion on the surface due to presence of alloying elements in the samples. Figure 10(b) indicates several corroded zones and a number pits with random nucleated orientations. Similar pits are
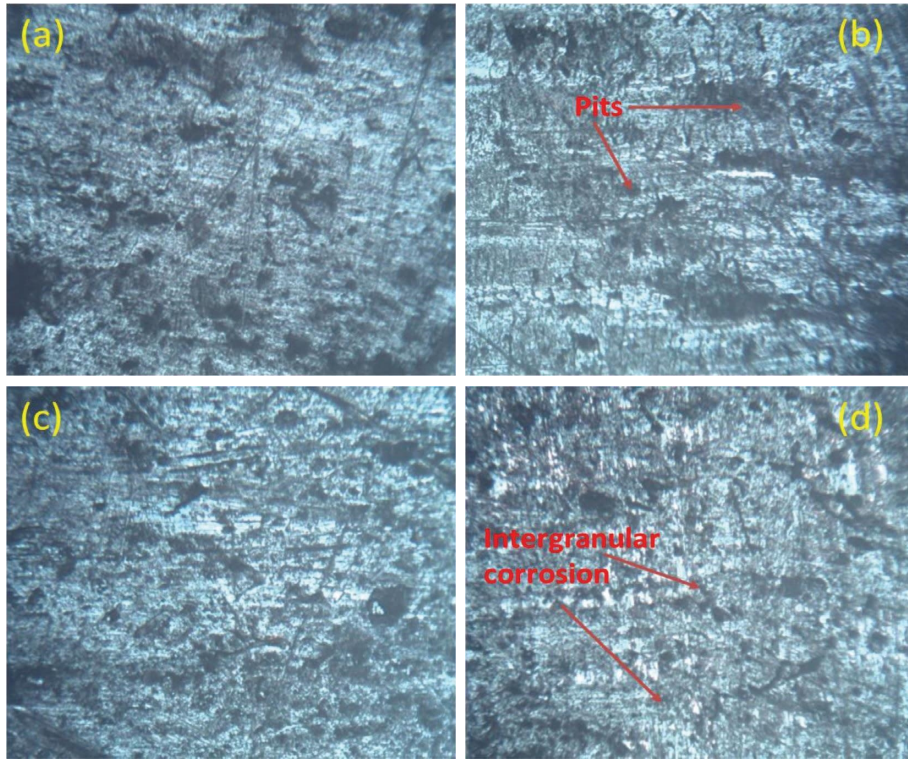
FIGURE 9: Microstructure at 300x after corrosion for 36 days in sea water (a) material I, (b) material II, (c) material III, and (d) material IV.
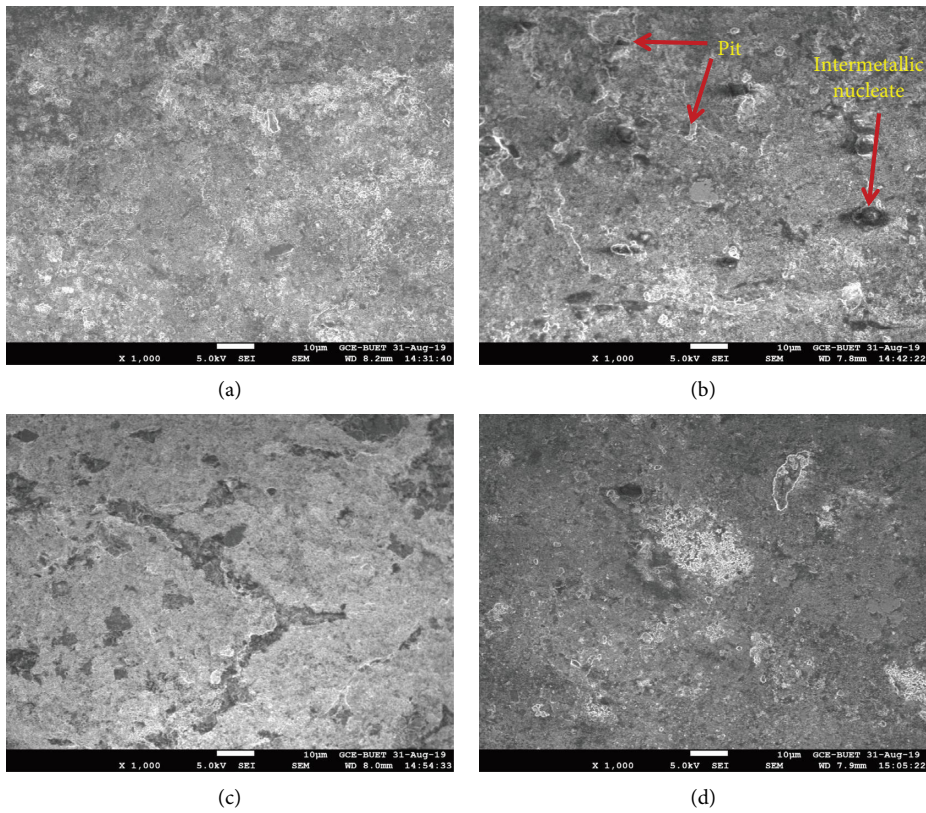

FIGURE 10: SEM images of copper and alloys having cold-rolled level of 75% with magnification factor of 1,000 after corrosion in sea water for 36 days: (a) material I, (b) material II, (c) material III, and (d) material IV.
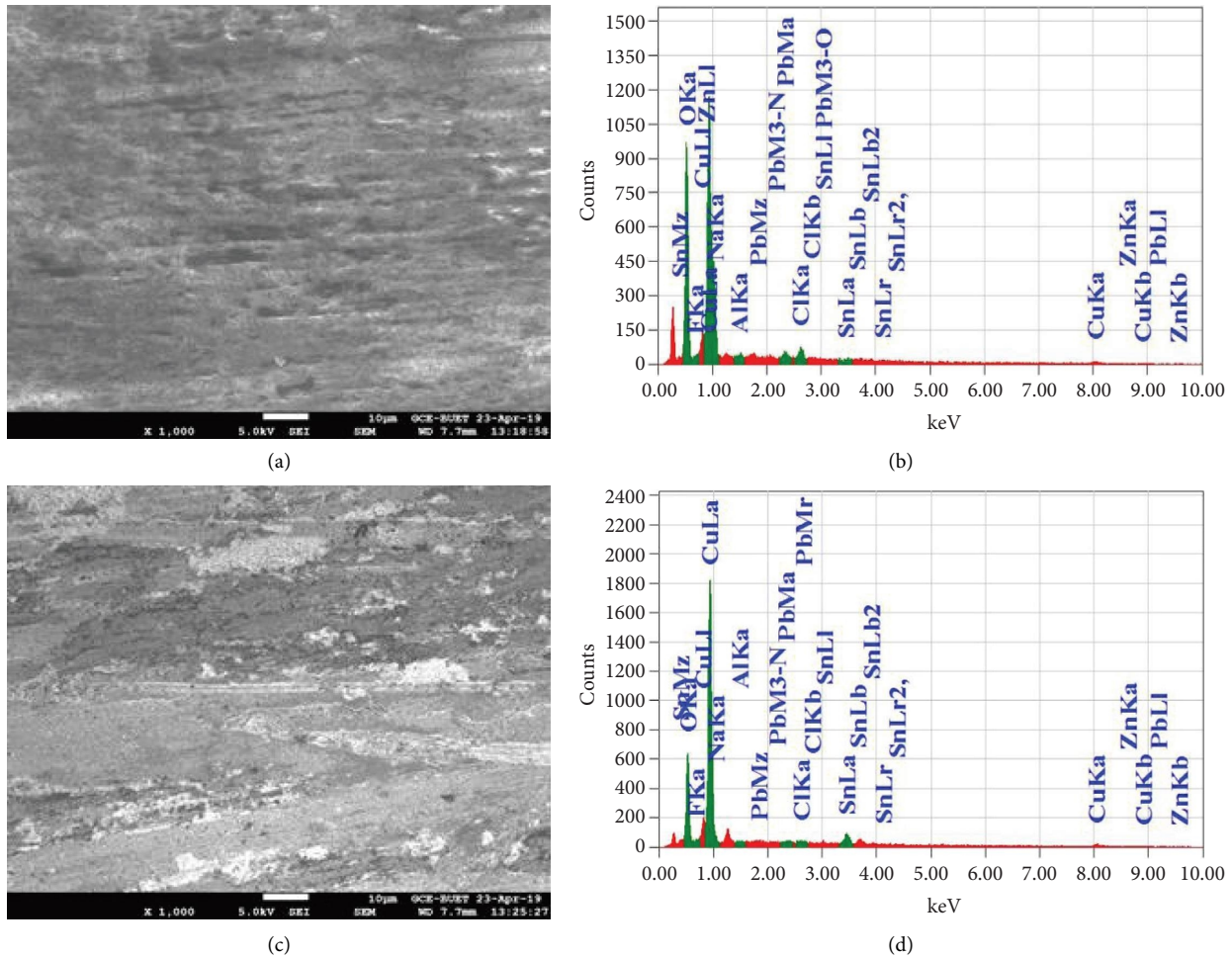
(a)

(b)

(c)

(d)

FIGURE 11: SEM images and EDX spectra after exposure in sea water for 36 days: (a) SEM of brass, (b) EDX of brass, (c) SEM of bronze, and (d) EDX of bronze.

of submerged materials resulting in significant percentage of oxygen along with certain amount of chlorine. The reason behind such happening is the oxidation effect and heterogeneous reactions taken place with diversified elements/compounds existing in sea water.

4. Conclusions

The corrosion investigation of copper and solder affected copper in the Bay of Bengal is summarized below:

(1) The corrosion rate of copper alloys can vary from ocean to ocean since the sea water is a complex solution. Moreover, it is severely affected by factors such as salinity, dissolved gases, conductivity.

(2) The water of BoB having pH 7.8 has confirmed that copper and its alloys are not immune from corrosion.

(3) Leaching losses are augmented for inclusion of tin and/or lead in copper over the whole immersion period in the water of BoB. The highest material degradation is observed for Cu-Pb alloy (Material III) amongst four copper based materials in sea water environment and it is followed by solder affected copper (Material IV), then Cu-Sn alloy (Material II), and the lowest loss is of pure copper (Material I).

(4) The alloying inclusion of tin and/or lead has reduced the corrosion resistance of copper for both cast and cold-rolled conditions. However, the solder affected copper is found to be more corrosion resistant than commercial copper alloys (brass and bronze), thereby, enhancing the reuse potentials of old/scraped copper.

(5) The electrical conductivity of copper and its alloys is affected very little in contact of sea water. However, the cold work effect on conductivity of copper and its alloys diminishes after the corrosion in sea water.

(6) The microstructures of the corroded surfaces have affirmed the moderate corrosiveness of copper and its alloys in contact of sea water. Moreover, the chemical compositions in the surfaces of all four copper based materials are changed as consequence of corrosion.

(7) Therefore, corrosion allowance needs to be taken into account for the design calculations for the products of copper and its alloys to be used in marine applications.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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