INVESTIGATION THE EFFECTS OF ZIRCONIUM ADDITION ON WEAR AND CORROSION BEHAVIOUR OF ALPHA-BRASS ALLOY (Cu-Zn30)

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ABSTRACT

Brass alloys have extensive engineering uses as condenser and heat exchanger structures in salty water. Pitting corrosion, dezincification and stress corrosion cracking of brass in water have been broadly considered. Dealloying or dezincification in brass may be cheerfully detected with bare eyes because the alloy changes a ruddy colour that differs with its yellowish colour in the previous period, various alloying elements have been used to reduce the dezincification and corrosion of brass alloys.

Current work is dedicated to investigate the effect of various amounts of zirconium additions (0.05, 0.10, 0.15 and 0.20) wt.% to a-brass alloy (Cu-Zn30) produced by die casting on mechanical and corrosion behaviour.

Several tests were conducted in this research includes XRF and XRD for the specimens after casting and heat treatment, microstructure test for specimens before and after addition of Zr, dry wear test with and without addition of Zr.

The results from optical microscope images show that Zr additions cause refinement of the original grains for a-brass alloy (Cu-Zn30).

Hardness test showed an increase of a-brass alloy (Cu-Zn30) hardness with increasing Zr amount, the average hardness of the specimen without Zr addition was (102HV) while the average hardness of specimen with (0.20%wt Zr) addition increased to (185 HV).

The wear rate for a-brass alloy (Cu-Zn30) specimen decreased after addition of Zr (0.05, 0.10, 0.15 and 0.20) wt.%. The wear rate of the a-brass alloy (Cu-Zn30) was (12.3*10^-6 cm^2/min) while the wear rate of specimen with (0.20%wt Zr) addition reduced to (5.66*10^-6 cm^2/min) under load 30N for 30 minutes.

The corrosion behavior of a-brass alloy (Cu-Zn30) with and without Zr has been studied by electrochemical test in salt solution (3.5% NaCl).
The corrosion rate for α-brass alloy (Cu-Zn30) specimen decreased after addition of Zr (0.05 , 0.10, 0.15 and 0.20)wt.%. The corrosion rate of the α-brass alloy (Cu-Zn30) was (203*10^{-4} mpy) while the wear rate of specimen with (0.20)%wt Zr) addition reduced to (2*10^{-4} mpy) under same conditions.

**Keywords:** α-Brass Alloy, Zirconium, Electrochemical Test, Dry Wear Test.

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**1. INTRODUCTION**

Brass has been widely used in many industrial fields and investigating brass corrosion has great importance. Various methods are used to decrease brass corrosion in different mediums. One of the most important methods in the protection of copper and copper alloys against the corrosion is use of alloying elements. In generally corrosion of brass tends to form a layer of zinc oxide which coats its surface. Insoluble film of cuprous chloride is adsorbed on the surface of the brass when dipping in chloride ion media.

Grain refinement is a well-established process for many cast and wrought alloys. The mechanical properties of various alloys could be enhanced by reducing the grain size. Refinement is also known to improve casting characteristics such as fluidity and hot tearing. Grain refinement of copper-base alloys is not widely used, especially in sand casting process [1]. However, in permanent mold casting of copper alloys it is now common to use alloying elements to counteract the problem of severe hot tearing which also improves the pressure tightness of plumbing components.

Early work on grain refinement of copper alloys showed various additions are effective with different copper alloys. For bronzes and gun metals, a) 0.3% Zr with C and or N in the absence of sulfur, b) 0.2% Ti with 0.03% B and C) 0.1% Fe or Co with 0.03% B are effective. Couture and Edwards found zirconium effective in tin bronzes and red brass, but not silicon bronze. Although sulfur destroys the grain refining effect of zirconium, it could be recovered by adding magnesium [2]. Ruddle indicated 0.05% Zr or 1% iron is effective for gun metals and red brass. Iron was effective as grain refiner for aluminum and manganese bronzes. Iron-free aluminum bronzes and beta brasses can be refined by a combination of 0.03% Zr and 0.02% B [3]. Zirconium (0.3%) and boron (0.02%) together were effective in Fe-free beta brass [4]. Wallace has also shown that for copper zinc alloys, 1% iron powder is effective, whereas for iron-free alloys such as Cu-33Zn4Al, combinations of 0.06% zirconium and 0.02% boron were effective. Zirconium alone had little effect, but boron alone could be effective. Nevertheless, the combination was not effective on 67Cu-33Zn [5]. Alpha-beta brasses will be refined if iron is added or they contain more than 1% iron. However, for alloys with low levels of iron, boron is the best additive.

Ali.et.al. [6] studied the addition of Al to alpha brass alloy. Yielded a significant improvement in the oxidation resistance. In this work, pure aluminum (1- 2wt%) added to alpha brass alloy. These alloys were prepared by melting and casting in a metallic mold. Cyclic oxidation tests were conducted on the alpha brass alloy with and without aluminum addition at a wide range of temperatures (500- 900 °C) in still air for 52 hrs. at 4 hrs. cycle .The oxidation kinetics followed breakaway behavior for alpha brass alloy at 800 and 900 °C.
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Claesson and Rod, O. [7] Studied the effect of alloying elements arsenic (As), antimony (Sb) and phosphorus (P) on the dezincification resistance of α-phase in brass. Samples alloyed with Sb showed a satisfactory resistance to dezincification and no grain boundary attack. Microalloying with both As and Sb is capable of providing good corrosion resistance for the commercial brass alloy CB772.

Ali, [8] improved the mechanical and corrosion properties by adding indium particles to CuZn30 alloy. He found that the addition of In with (0.5-2) wt% causes an increase in hardness of CuZn30 alloys. And improve corrosion resistance of α-brass in NaCl solution up to 99.4% for 2wt% In. further Indium addition led to improve wear resistance and the highest wear resistance is for 2wt%In .Hussien R [9] found that the addition of (2, 3 and 4)wt% cerium and 4wt% Aluminum to α-brass alloy improves the corrosion resistance in salt solution (3.5% NaCl).The corrosion rate reduced and reached (0.84067*10⁻⁷) mpy for the specimen (α-brass+4 wt% Ce+4wt% Al) in compared to (4.024 *10⁻⁷) mpy for reference alloy. Further The (α-brass+4 wt% Ce+4wt% Al) alloy showed more wear resistance than other α-brass alloys.

Current work aims to study the effects of zirconium addition (0.5,0.10,0.15 and 0.20) wt% on some properties including: (microstructure ,hardness, corrosion resistance and wear resistance) of (α-brass) alloys and discuss the results.

2. EXPERIMENTAL PROCEDURE

2.1. Materials
Table1 shows chemical composition of α-brass alloy (Cu-Zn30) without & with (0.05,0.1,0.15 and 0.2) wt% Zr additions.

Table 1 shows chemical composition α-brass alloy (Cu-Zn30) without & with (0.05,0.10,0.15 and 0.20) wt% Zr additions.

<table>
<thead>
<tr>
<th>Zn</th>
<th>Pb</th>
<th>Sn</th>
<th>P</th>
<th>Zr</th>
<th>Mn</th>
<th>Fe</th>
<th>Si</th>
<th>Sb</th>
<th>As</th>
<th>Cu</th>
</tr>
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<tbody>
<tr>
<td>32.56</td>
<td>2.54</td>
<td>0.675</td>
<td>0.019</td>
<td>-</td>
<td>0.0754</td>
<td>0.943</td>
<td>0.147</td>
<td>0.009</td>
<td>0.094</td>
<td>Bal.</td>
</tr>
<tr>
<td>32.45</td>
<td>2.87</td>
<td>0.643</td>
<td>0.016</td>
<td>0.06</td>
<td>0.0421</td>
<td>0.236</td>
<td>0.193</td>
<td>0.008</td>
<td>0.063</td>
<td>Bal.</td>
</tr>
<tr>
<td>33.56</td>
<td>2.54</td>
<td>0.721</td>
<td>0.018</td>
<td>0.13</td>
<td>0.0543</td>
<td>0.765</td>
<td>0.187</td>
<td>0.005</td>
<td>0.055</td>
<td>Bal.</td>
</tr>
<tr>
<td>32.57</td>
<td>2.92</td>
<td>0.654</td>
<td>0.012</td>
<td>0.17</td>
<td>0.0932</td>
<td>0.481</td>
<td>0.176</td>
<td>0.007</td>
<td>0.028</td>
<td>Bal.</td>
</tr>
<tr>
<td>33.87</td>
<td>2.54</td>
<td>0.698</td>
<td>0.013</td>
<td>0.24</td>
<td>0.0764</td>
<td>0.787</td>
<td>0.163</td>
<td>0.004</td>
<td>0.016</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

2.2. Preparation of Specimens
Electric furnace was used for melting and pouring in melting crucible. Addition (0.05,0.10,0.15 and 0.20 wt%) of zirconium to the α-brass alloy (Cu-Zn30),this alloy melting at 902°C. While the melting point of Zn is 419.6°C and the boiling point is 907 °C. Added 5wt % from zinc to compensate with lost zinc ratio during melting. Mixed molten by graphite rod to homogenous the melting alloy. The metal is poured into the cylindrical metallic mold(inner diameter 10 mm and height 60mm).Heat treatment was conducted at a temperature (580°C) for 8 hours then the furnace cooled in order to homogenize the composition.
2.3. Testing of Specimens

2.3.1. Microstructure Test
The specimens were imaged after grinding of up to (3000) grit and finally polished by 0.25μm diamond paste. To study the microstructure of the specimens, they were etched using (FeCl₃ 5gm+alcohol.95ml) [10].

2.3.2 X-Ray Fluorescent Analysis (XRF)
Handheld (XRF) analyzer type (DS-2000) American, is used to explain the chemical composition for powders and alloys.

2.3.3 X-Ray Diffraction Analysis
X-ray diffraction analysis have been conducted for the alloys using XRD instrument (Mini flex2). The XRD generator with Cu target at 40 KV, 30 mA and scanning speed 6° per minute was used. The scanning rate was (20° – 90°).

2.3.4. Microhardness Test
Microhardness test was used to measure hardness values by microhardness Vickers (HV) device (HVS-1000) using a load of (500 g for 10 sec), the hardness was recorded as an average of three hardness readings for each specimen.

2.3.5 Electrochemical Test.
The corrosion resistance of the specimens α-brass alloy (Cu-Zn30) with and without (0.05, 0.10, 15 and 2 wt.%) zirconium addition were studied in 3.5% NaCl solution at room temperature using polarization instrument type (WENKING M lap 0). Corrosion current density measurement is obtained by using the following equation [11]:

\[ i_{cor} = \frac{I_{cor}}{A} \]  

Where:  \( i_{cor} \) = corrosion current density, \( \mu A/cm^2 \),  
\( I_{cor} \) = total corrosion current, \( \mu A \), and  
\( A \) = exposed specimen area, \( cm^2 \). (3.4 cm²)

2.3. Dry Sliding Wear Test
The dry sliding wear were studied by using pin-on-disc concept using (400 rpm) and constant radius 5.25mm and the loads (10,20and 30)N. The specimen was weighted before test using (0.0001) accuracy electric balance. After a period of time (5,10,15,20,and 25 min) the test specimen was weight again. The wear schematic which used in this work is shown in Fig. 1 [12].

![Fig.1 Pin-on-disc concept [12]](http://www.iaeme.com/ IJMET/index.asp 847 editor@iaeme.com)
3. RESULTS & DISCUSSION

3.1. Microstructure Examination
Light optical microscope was used to examine the microstructure of etched specimens. Optical images of 40X magnification showed the microstructure was achieved of the α-brass alloy (Cu-Zn30) after addition (0.05, 0.10, 0.15 and 0.20 wt %) zirconium with compared to α-brass alloy (Cu-Zn30) (Fig. 2).

3.2. X-Ray Diffraction analysis
Fig. 3 showed X-ray diffraction for α-brass alloy (Cu-Zn30) with 0.20 wt% Zr alloy specimen and doesn't indicate any peak belong to zirconium. This is due to the very low content of zirconium that cannot be indicated by this analysis.

Fig. 2: Light optical microstructure for α-brass alloy (Cu-Zn30) (A) after heat treatment, (B) 0.05 wt % Zr, (C) 0.10 wt % Zr, (d) 0.15 wt % Zr and (E) 0.20 wt % Zr at (40X)
3.3. Microhardness Tests
In the current work the hardness of the specimens of all alloys was measured by using Vickers hardness test. From Fig.4, it can be observed α-brass alloy (Cu-Zn30) with zirconium presented higher hardness values in comparison with α-brass alloy (Cu-Zn30) and the hardness increased as the zirconium content increases. This is attributed to zirconium particles.

3.4. Dry Sliding Wear Test
All specimens of (10) mm in diameter subjected to wear test under different loads (10, 20 and 30)N and for different times (5, 10, 15, 20, 25 and 30)min at room temperature. The results have been presented in Figures (5-9).
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Fig. 5 Volume loose vs time for $\alpha$-brass alloy (Cu-Zn30) under (10, 20 and 30 N) load

Fig. 6: Volume loose vs time for ($\alpha$-brass alloy (Cu-Zn30- 0.05 wt.% Zr) under (10, 20 and 30N) load

Fig. 7 Volume loose vs time for ($\alpha$-brass alloy (Cu-Zn30-0.1 wt% Zr) under (10, 20 and 30 N) load
From the above figures, it can be noted that the wear rate of all tested specimens under 30N load is higher than that of 10N and 20N. This is due to increase in friction at the surface as the load on the material increases [13].

In addition, the volume loss increase as the time increase for all tested specimens. This is certainly because more time of friction tend to remove more material from the surface. Further it has been attributed to the increase in plastic deformation of the material on the surface, particles of the material pulled out [14,16]. In order to show the effect of zirconium addition on the wear rate of α- brass alloy (Cu-Zn30), the wear rate with zirconium content under 10, 20, and 30 N load at 30 min plotted in the following figure 10.
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![Graph showing wear rate vs zirconium content](image1)

**Fig.10:** Wear rate vs zirconium content for the specimens under (10, 20, and 30 N) load (30 min)time.

It can be noted from figure 10 that the wear rate decrease as the zirconium content increases. The reason behind these reduces in wear rate related to zirconium role in increasing the hardness then the wear rate will be reduced.

Figure 11 show by light optical microscope the worn surfaces of specimens, proof of abrasion wear which can be clear in tested specimens. The mentioned figures illustrated the effect of wear process on the surface of the specimen. The mechanism of wear during all the tests is abrasive wear is same for all samples, but the penetration depth is less for α-brass alloy (Cu-Zn30- 0.20 wt% Zr). The existence of zirconium lower the frictional force between the surface of specimens and the press indentor, i.e. lowering the coefficient of friction. The result small grooves aligned parallel to the sliding direction and lost in metal weight.

![Light optical microscopy for α-brass alloy (Cu-Zn30) and α-brass alloy (Cu-Zn30- 0.20 wt% Zr) after wear test](image2)

**Fig. 11** Light optical microscopy for (A) α-brass alloy (Cu-Zn30) (B) α-brass alloy (Cu-Zn30- 0.20 wt % Zr) after wear test under 30 N load for 30 minute. (40X)

### 3.5. Electrochemical Tests

The corrosion behavior of all used specimens in 3.5%NaCl solution has been studied to give estimation about the corrosion behavior of all alloys. Polarization curves for α-brass alloy (Cu-Zn30) specimens without and with Zr addition are illustrated in Figures (12-17) respectively. The corrosion parameters are corrosion current (Icorr.), corrosion potential (Ecorr.) and (corrosion rate) resulted from corrosion test for the specimens in mentioned solution were illustrated in table 2. From this table it can be seen that there is significant improvement in corrosion resistance of the alloys with different additives of zirconium. Icorr. for the specimens were graded from 1.101 (μA/cm²) for α-brass alloy (Cu-Zn30- 0.05% Zr) to 0.048 (μA/cm²) for α-brass alloy (Cu-Zn30- 0.20 Zr) which were lower than Icorr. For Cu-
Zn30 alloy which was 4.05 (μA/cm²). This improvement in corrosion resistance can be attributed to the behavior of zirconium element as grain refiner and as noble element which enhanced the corrosion resistance of α-brass alloy (Cu-Zn30). Finally the corrosion rates were calculated based on following equation [15]:

\[
\text{Corrosion rate} = \frac{0.13 \times \text{i}_{\text{corr}}(\text{E}w)}{\rho} \quad \text{..........(2)}
\]

Where:

- \(E.W\) = equivalent weight (g/eq.)
- \(\rho\) = density (g/cm³)
- 0.13 = metric and time conversion factor
- \(i_{\text{corr}}\) = current density (μA/cm²).
- \(\text{mpy}\) = Corrosion rate (mils per year)

Fig. 12: Polarization curve for α-brass Cu-Zn30 alloy in 3.5%NaCl solution.

Fig. 13: Polarization curve for α-brass Cu-Zn30-0.05Zr alloy in 3.5%NaCl solution.
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**Fig. 14:** Polarization curve for α-brass Cu-Zn30-0.10 Zr alloy in 3.5% NaCl solution.

**Fig. 15:** Polarization curve for α-brass Cu-Zn30-0.15 Zr alloy in 3.5% NaCl solution.

**Fig. 16:** Polarization curve for α-brass Cu-Zn30-0.20 Zr alloy in 3.5% NaCl solution.
Table 2: Shows the corrosion current (Icorr.), corrosion potential (Ecorr.) and corrosion rate for all used samples in NaCl Solution.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Icorr. (µA/cm²)</th>
<th>Ecorr. (mV)</th>
<th>Corrosion Rate (mpy)</th>
<th>Improvement percentage%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Zn30</td>
<td>4.050</td>
<td>-553.1</td>
<td>0.0203</td>
<td></td>
</tr>
<tr>
<td>Cu-Zn30-0.05%Zr</td>
<td>1.995</td>
<td>-433.9</td>
<td>0.0100</td>
<td>50.73</td>
</tr>
<tr>
<td>Cu-Zn30-0.10%Zr</td>
<td>1.101</td>
<td>-478.9</td>
<td>0.0055</td>
<td>72.90</td>
</tr>
<tr>
<td>Cu-Zn30-0.15%Zr</td>
<td>0.259</td>
<td>-257</td>
<td>0.0013</td>
<td>93.59</td>
</tr>
<tr>
<td>Cu-Zn30-0.20%Zr</td>
<td>0.048</td>
<td>-532</td>
<td>0.0002</td>
<td>99.01</td>
</tr>
</tbody>
</table>

Fig. 17: Corrosion rate vs Zr content for the specimens in NaCl solution.

4. CONCLUSIONS

Zirconium addition to α-brass Cu-Zn30 alloy with 0.05, 0.10, 0.15, and 0.20 wt.% via casting process enhanced significantly mechanical and corrosion properties as following:

- Hardness increased with increasing the amount of zirconium. Whereas wear and corrosion rate are decreased with increasing the amount of Zr.
- The hardness enhanced by (45%) when added 0.20% wt.% Zr to α-brass Cu-Zn30 alloy
- Wear rate is increased in general with increasing the applied load.
- The wear rate decreased by (54%) under conditions of 0.20% wt. % Zr addition to α-brass Cu-Zn30 alloy.
- The corrosion rate in 3.5%NaCl was reduced by (99%) under addition of 0.20% wt.% Zr to α-brass Cu-Zn30 alloy.

REFERENCES


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