MECHANICAL AND CORROSION BEHAVIOUR OF IRON MODIFIED Cu-Zn-Al ALLOYS

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Abstract
The mechanical and corrosion behaviour of iron modified Cu-Zn-Al alloys has been investigated. Cu-Zn-Al alloys containing 20 and 25 wt. % Zn was produced by casting method with and without the addition of 0.1wt. % iron. The alloys were subjected to a homogenization – cold rolling- annealing treatment schedule, before the alloys were machined to specifications for tensile test, fracture toughness, hardness measurement, corrosion test and microstructural analysis. From the test results, it was observed that the structures of the Cu-Zn-Al alloys were modified by iron addition with near equi-axed grain morphologies developed. There was no significant difference in the hardness of the iron modified and the unmodified Cu-Zn-Al alloys, but the tensile strength, strain to fracture, and fracture toughness of the alloys improved with iron addition. The Cu-Zn-Al alloys also exhibited good corrosion resistance in 3.5 wt. % NaCl and 0.3M H_2SO_4 solutions. It was however observed that irrespective of iron addition, the mechanical properties and corrosion resistance of the Cu-20Zn-4Al-xFe alloy compositions where better in comparison with the Cu-25Zn-4Al-xFe alloy grades (where x=0,0.1wt. %).

Keywords: Cu-Zn-Al shape memory alloys, shape memory properties, mechanical properties, corrosion behaviour, grain refinement

1 Introduction

The development of low cost metallic alloys involving good combination of shape memory capacity and material properties has continued to draw the attention of materials scientists [1]. Shape memory alloys (SMAs) are characterized by the capacity to recover its original shape after undergoing large deformation strains. The ‘shape recovery’ is usually triggered by heating (above a transition temperature) or stress removal. This unique material behaviour has made SMAs a very important class of metallic materials [2]. Shape memory properties such as pseudo elasticity, one way- and two way- shape memory effects [3] have served as the basis for the design of components/devices such as self actuating fasteners, heat-shrinkable couplings and switches, thermally actuated switches, thermostatic radiator valves, cooling fans for automobiles, thermal protection devises, and contact springs [4-5]. It has also been applied in the development of flexible glass frames, bra under wires, and many biomedical applications as a result of their

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good corrosion resistance and biocompatibility [6]. The high damping capacity of SMAs has made them suitable for applications where reduced noises and vibrations are required [7]. Thus considering the current areas of application of SMAs and its potential for wider use, it is expected that studies on how to improve their overall material properties will remain of interest in the years ahead.

The major setback in the development and application of SMAs remains that a substantial number of available low cost options do not exhibit satisfactory combination of mechanical and shape memory properties [8]. The most successful and commercially applied SMA, Ni-Ti, possesses very good strength, formability and shape memory properties but is very expensive to produce [9]. The relatively cheaper Cu based SMAs (Cu-Zn-Al, Cu-Al-Ni, Cu-Al-Mn) which are reported to be second to Ni-Ti in terms of shape memory properties also have some limitations [9]. Most Cu based exhibit poor cold formability and tendency towards brittle fracture by virtue of their coarse grain structures. Also, they show a tendency to undergo natural ageing which affects its shape memory behaviour by raising the austenite/martensite transition temperature [10].The adoption of procedures to refine the grain structures of Cu-based SMAs by thermomechanical treatment and the use of microelements such as Boron, Iron, Titanium among others has been projected to be the best option in improving its properties [10]. To date the results available are still not exhaustive, and considering that Cu based SMAs remains the most attractive long term option for replacing Ni-Ti as a result of its relatively lower cost; research in Cu based SMAs will still continue to attract attention. In the present work, the influence of Iron addition on the microstructure, mechanical and corrosion behaviour of Cu-Zn-Al alloy SMAs is investigated. Cu-Zn-Al alloys are developed from relatively cheap metals using conventional metallurgical processes and are the least costly commercial SMAs available]. They have been noted to offer modest shape memory properties and recoverable strain of about 5% [11] but still have the potentials for improved mechanical properties particularly strength - ductility levels and fracture toughness while maintaining its high corrosion resistance.

2 Materials and Method

2.1 Alloy and Sample Preparation

The Cu-25.5Zn-4.0Al and Cu-20Zn-4.0Al alloys (in wt %) were initially produced without iron addition. The same alloys were produced with 0.1wt% iron addition with the intention of minimizing grain growth and stabilizing the Cu-Zn-Al alloys microstructure [10]. Supplemental 2.5% Zinc was added during charge calculations to account for potential losses by evaporation during melting. The alloys were melted in a crucible furnace; and the melted alloys were cast into sand moulds inserted with metallic chills. The chemical composition of the Cu-Zn-Al shape memory alloys determined by EDS analysis is presented in **Table 1**. After casting, the ingots with 25mm diameter and 30cm length, approximately, were homogenized at 800 °C, for 4 h and then water quenched. The ingots were then cold-rolled (10%, approximately), after which the alloys were annealed at 500^{o}C for two hours followed by air cooling. The samples for tensile test, fracture toughness, hardness measurement, corrosion test, and microstructural analysis were then machined from the alloys. The machined samples were all subjected to a final annealing treatment at 500 °C for two hours before water quenching to remove stresses induced in them during the machining operation.

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Table 1 Chemical Composition of the Cu-Zn-Al alloys

Sample Designation	Cu	Zn	Al	Fe
A1	71.01	25.03	3.96	-
A2	70.91	25.03	3.96	0.1
B1	75.94	20.05	4.01	-
B2	75.84	20.05	4.01	0.1

2.1 Hardness Measurement

The hardness of the Cu-Zn-Al alloys was determined using an EmcoTEST DURASCAN Microhardness Tester equipped with ecos Workflow ultra modern software. The samples for the hardness test were polished to obtain a flat and smooth surface finish before testing was conducted. A load of 100 g was applied on the specimens and the hardness was determined following standard procedures. Multiple hardness tests were performed on each sample and the mean of values within the range of ± 2% was taken as the hardness of the specimen.

2.2 Tensile Testing

The tensile strength and strain to fracture of the Cu-Zn-Al alloys were evaluated at room temperature with the aid of tensile testing performed in accordance with the ASTM 8M-91 standards [12]. The test was carried out using an Instron universal testing machine operated at a strain rate of 10^{-3}/s; and the samples for the test were machined to round specimen configuration with 6 mm diameter and 30 mm gauge length. Three repeat tests were performed for each Cu-Zn-Al composition to ensure repeatability and reliability of the data generated.

2.3 Fracture Toughness Evaluation

The fracture toughness of the Cu-Zn-Al alloys was evaluated using circumferential notch tensile (CNT) specimens [13]. The CNT testing was also performed at room temperature using an Instron universal testing machine. The samples for the test were machined having gauge length, specimen diameter (D), and notch diameter (d) of 30, 6, and 4.5 in mm respectively; and notch angle of 60^o. The specimens were subjected to tensile loading to fracture and the fracture load (P_f) obtained from the load – extension plots were used to evaluate the fracture toughness using the equation [14]:

$$K_{1C}=P_f/(D)^{3/2}[1.72(D/d)-1.27] \quad (2.1)$$

where, D and d are respectively the specimen diameter and the diameter of the notched section. Plane strain conditions and by extension, the validity of the fracture toughness values obtained was determined using the relations in accordance with Nath and Das [15]:

$$D \geq (K_{1C}/\sigma_y)^2 \quad (2.2)$$

Three repeat tests were performed for each Cu-Zn-Al composition to ensure repeatability and reliability of the data generated.

2.4 Microstructural Analysis

The microstructure of the Cu-Zn-Al alloy samples was observed using a Zeiss Metallurgical Microscope with accessories for image analysis. The samples were metallographically polished

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and etched with 5g ferric chloride + 10ml HCl + 95ml ethanol solution before the microscopic examination. A JSM 7600F Jeol ultra-high resolution field emission gun scanning electron microscope (FEG-SEM) equipped with an EDS was also used for chemical compositional analysis and in-depth microstructural study of the alloys.

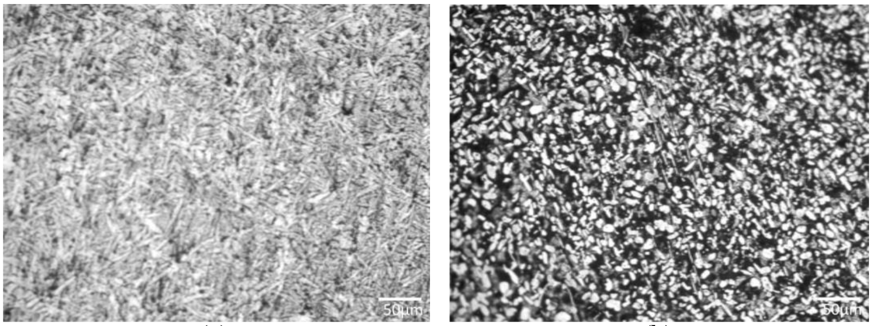
2.5 Corrosion Test

The corrosion behaviour of the Cu-Zn-Al alloys was studied using mass loss and corrosion rate measurements. The corrosion tests were performed by immersion of the Cu-Zn-Al alloy samples in 0.3M H_2SO_4 and 3.5wt% NaCl solution were both prepared following standard procedures [16]. The 0.3M H_2SO_4 and 3.5wt% NaCl solutions are both reported in literature as representative of acidic and marine environments which are among typical service environments where the Cu-Zn-Al alloys are utilized [17-18]. The specimens for the test were cut to size 10×10×10 mm and where mechanically polished with emery papers in order to produce a smooth surface finish. The samples were de-greased with acetone and then rinsed in distilled water before immersion both corrosion media. The solution-to-sample surface area ratio was about 150 ml cm^{-2}, and the corrosion setups were exposed to atmospheric air for the duration of the corrosion test. Weight loss readings were monitored on two day intervals for a period of 40 days. The mass loss (g/cm^2) and the corrosion rate (mmy^{-1}) for each sample was evaluated following recommendations in accordance with ASTM G31 standards [19].

3 Results and Discussion

3.1 Microstructures of the Cu-Zn-Al Alloys

Representative optical photomicrographs of all the Cu-Zn-Al alloys are presented in **Fig. 1** and **2**. The needle-like structure that characterizes the martensitic phase [9] is clearly visible in the unmodified Cu-Zn-Al alloy containing 25wt% Zn (A1) (Fig. 1a), while the iron modified grade of the same Cu-Zn-Al alloy composition (A2) shows a refined structure with near equi-axed grain morphology with little signs of the needle-like structure (Fig. 1b). Similar but less conspicuous modification in the grain structure is observed for the unmodified and iron modified Cu-Zn-Al alloys containing 20wt% Zn (**Fig. 2**). This is a clear indication that iron addition alters the grain morphology of the Cu-Zn-Al alloys. A similar structural modification which is characterized by grain refinement has been reported by the use of some other microelements notably Boron, Titanium, and Titanium-Boron additions [10]. However, Iron remains a very good candidate addition considering its lower cost and availability.



(a) (b)

Fig. 1 Optical Micrograph of (a) unmodified Cu-25Zn-4Al alloy (A1) showing needle-like structures of the martensitic phase, and (b) iron modified Cu-25Zn-4Al-0.1Fe alloy (A2) showing near equi-axed grain structure.

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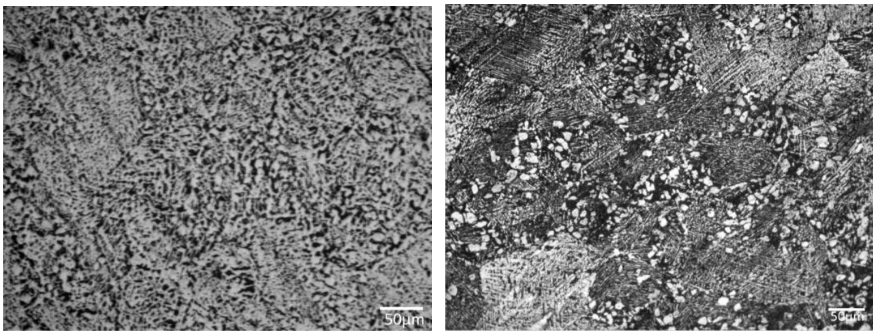

(a) (b)

Fig. 2 Optical Micrograph of (a) unmodified Cu-20Zn-4Al alloy (B1), and (b) iron modified Cu-20Zn-4Al-0.1Fe alloy (B2).

3.2 Mechanical Behaviour of the Cu-Zn-Al Alloys

The hardness values of the Cu-Zn-Al alloys are presented in **Fig. 3**. It is observed that there is no significant difference in the hardness of the iron modified and the unmodified Cu-Zn-Al alloys, although the B series Cu-Zn-Al alloys containing 20 wt% Zn exhibited slightly higher hardness values in comparison with the A series Cu-Zn-Al alloys containing 25 wt% Zn.

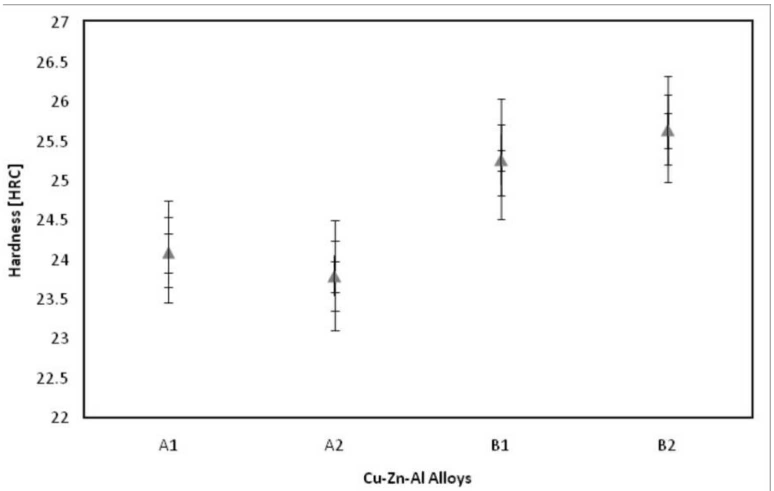

Fig. 3 Hardness values for the unmodified and iron added Cu-Zn-Al alloys.

The tensile strength (**Fig. 4**) is however observed to be lower for the unmodified alloys (A1, B1) in comparison with the iron modified samples (A2, B2). For the A series, it is observed that 3.72 % increase in tensile strength is achieved by iron modification while for the B series 3.43 % increase in tensile strength was observed. The improved tensile of the iron modified Cu-Zn-Al alloys is attributed to its relatively refined grain structures (Fig. 1b and 2b) which results in increased number of grain boundaries which serves as barriers to dislocation movement thus resulting in significant improvement in strength [10, 20]. It is however noted that the Cu-Zn-Al alloys with 20wt% Zn (B series) had relatively higher tensile strength values in comparison with the A series Cu-Zn-Al alloys which had 25wt% of Zn. This is quite encouraging from an

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economic perspective as Zn is relatively the most expensive of the three elements used in the development of the Cu-Zn-Al ternary alloy system.

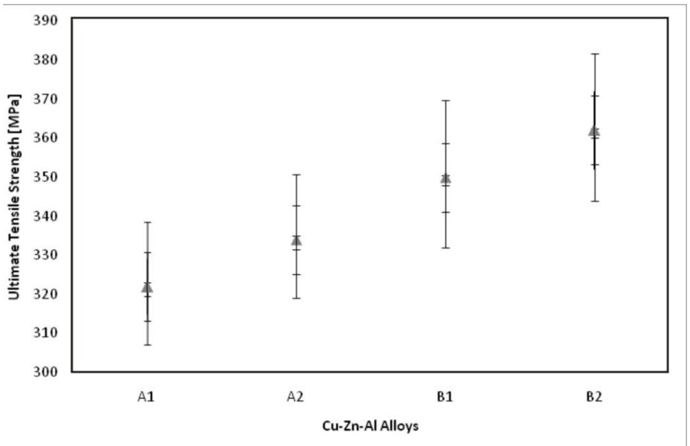

Fig. 4 Ultimate Tensile Strength values for the unmodified and iron added Cu-Zn-Al alloys.

The strain to fracture (**Fig. 5**) is also observed to improve with iron modification. Strain increments well over 25.5% for the unmodified Composition A and 18.5% for unmodified composition B was achieved with iron addition to the Cu-Zn-Al alloys. This is a clear indicator that the capacity of Cu-Zn-Al alloys to sustain plastic deformation and by extension its cold workability, improves with iron modification.

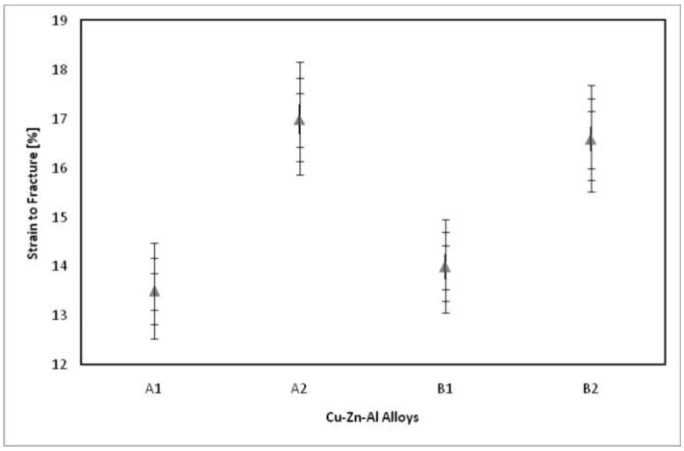

Fig. 5 Strain to Fracture values for the unmodified and iron added Cu-Zn-Al alloys.

The fracture toughness of the Cu-Zn-Al alloys is presented in **Fig. 6**. It is observed that the fracture toughness of the Cu-Zn-Al alloys increases with iron addition. 11.85% increase in fracture toughness was achieved for composition A while 13% increase was obtained for composition B with iron addition. This shows that there is improved capacity of the Cu-Zn-Al alloys to resist crack propagation by addition of iron into the alloy composition. This is due to the grain refining and stabilizing effect induced by iron addition on the Cu-Zn-Al alloys thereby increasing its toughness and hence resistance to crack propagation [10]. The SEM

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photomicrographs presented in **Fig. 7** shows that the fracture mechanism of the Cu-Zn-Al alloys is ductile fracture as there are predominantly spherical dimples (which characterizes the fracture mode of ductile materials) observable from the fractured surface of the alloys [21].

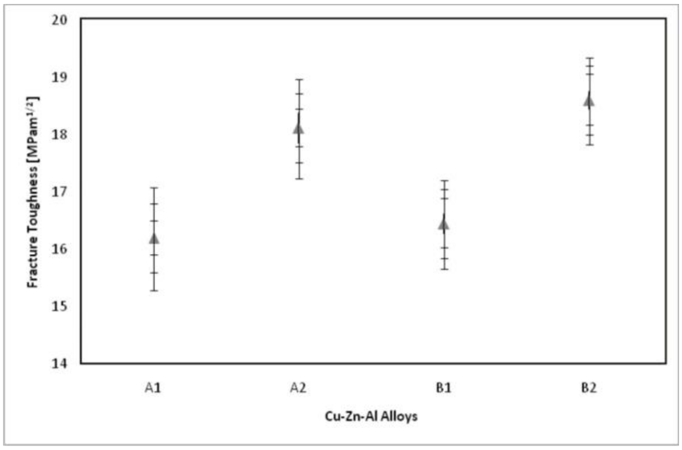

Fig. 6 Fracture Toughness values for the unmodified and iron added Cu-Zn-Al alloys.

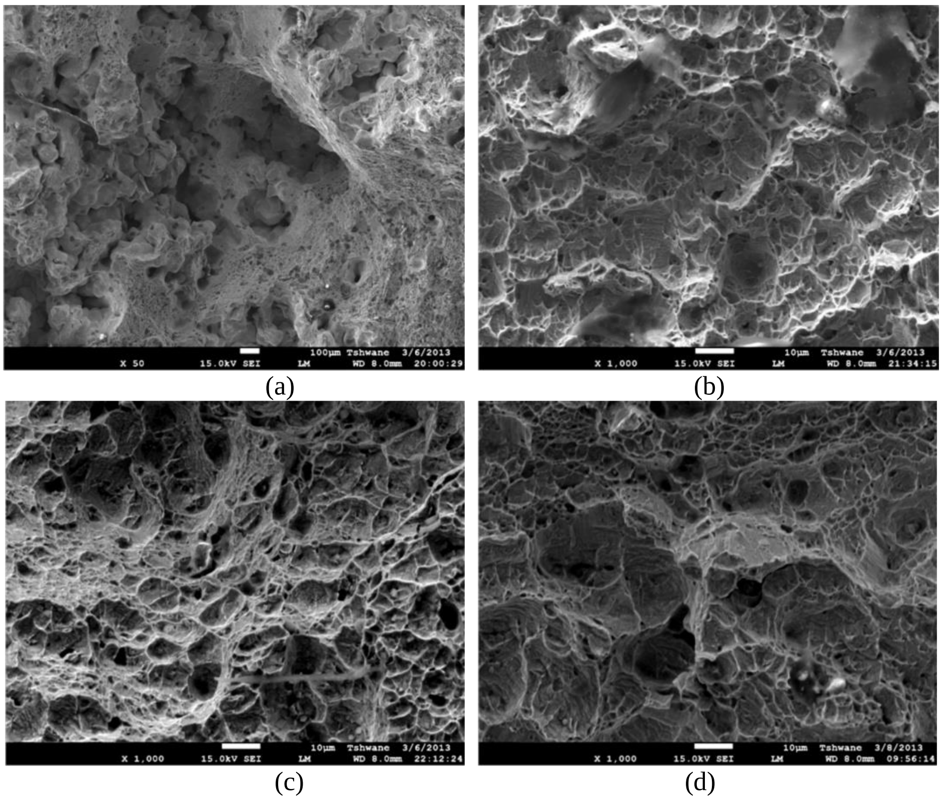

Fig. 7 SE image of the fracture surfaces of (a) unmodified Cu-25Zn-4Al alloy (A1), (b) iron modified Cu-25Zn-4Al alloy (A2), (c) unmodified Cu-20Zn-4Al alloy (B1), and (d) iron modified Cu-20Zn-4Al alloy (B2).

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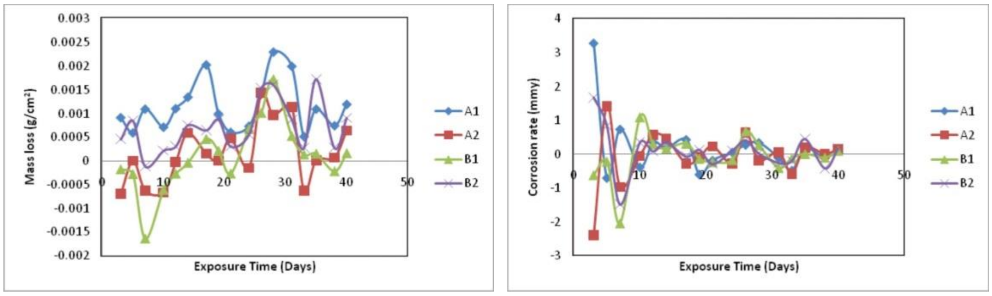
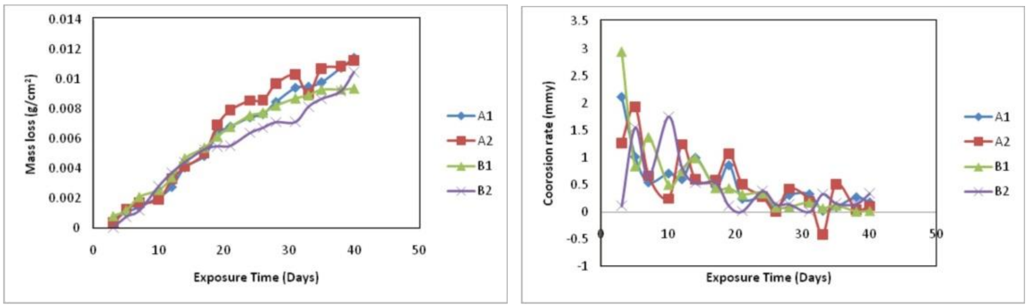
3.3 Corrosion behaviour of the Cu-Zn-Al alloys

The variation of mass loss and corrosion rates for the Cu-Zn-Al alloys immersed in 3.5 wt% NaCl and 0.3M H_2SO_4 solutions are presented in **Figs. 8-9**. From figure 8(a) it is observed that the mass loss of all the Cu-Zn-Al alloys were very low (< 0.0025g/cm^2). This is a good indication that the Cu-Zn-Al alloys can be used in the design of components for marine/saline environments. It is however noted that the corrosion trend fluctuates with exposure time as there appears to be a continuum of passive film formation, film breakdown, and repassivation as accounted for by the intermittent increase and decrease in mass loss of all the samples. It is also noted that Iron addition to the Cu-Zn-Al alloys (A2 and B2) did not increase the tendency for corrosion of the alloys in 3.5 wt% NaCl solution. The corrosion rate plots, Figure 8(b), supports the observations from Figure 8(a) as it is seen that corrosion rates were very low (apart from the initial period of immersion). Similar high corrosion resistance has been reported for quenched Cu-Zn-Al alloys exposed to marine environments [17].



(a) (b)

Fig. 8 showing (a) Mass loss for the unmodified and iron added Cu-Zn-Al alloys immersed in 3.5% NaCl solution, and (b) Corrosion rate for the unmodified and iron added Cu-Zn-Al alloys immersed in 3.5% NaCl solution.



(a) (b)

Fig. 9 showing (a) Mass loss for the unmodified and iron added Cu-Zn-Al alloys immersed in 0.3M H_2SO_4 solution, and (b) Corrosion rate for the unmodified and iron added Cu-Zn-Al alloys immersed in 0.3M H_2SO_4 solution.

From **Fig. 9**(a) it is observed that the mass loss of the Cu-Zn-Al alloys is low in 0.3MH_2SO_4 solution (< 0.012g/cm^2); which shows that the Cu-Zn-Al alloys has good corrosion resistance in sulphuric acid media and can be used in such environments. It is noted that the mass loss increases with exposure time although the rate decreases sharply with exposure time (Figure 9b).

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It has been reported that the addition of Aluminium to Cu-based alloys is effective in improving the corrosion resistance when the alloys are exposed to a sulfide-containing or high temperature environments [18]. It is however observed from Figure 9(a) that the B series Cu-Zn-Al alloy composition (which has 20 wt% Zn) exhibited a relatively lower corrosion tendency but there appeared not to be adverse effect of iron addition on the corrosion behaviour.

4 Conclusion

The influence of iron addition on the microstructure, mechanical and corrosion behaviour of Cu-Zn-Al alloys was investigated. The results show that:

1. The structures of the Cu-Zn-Al alloys are modified with iron addition with near equi-axed grain morphologies developed.
2. There was no significant difference in the hardness of the iron modified and the unmodified Cu-Zn-Al alloys, the tensile strength, strain to fracture, and fracture toughness of the alloys improved with iron addition.
3. The Cu-Zn-Al alloys exhibited good corrosion resistance in 3.5wt% NaCl and 0.3M H_2SO_4 solutions.
4. Irrespective of Iron addition, the mechanical properties and corrosion resistance of the Cu-20Zn-4Al-xFe alloy compositions where better in comparison with the Cu-25Zn-4Al-xFe alloy grades (where x=0,0.1wt. %).

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