INDENTATION RESISTANCE AND CORROSION BEHAVIOUR OF Fe-Mn MODIFIED Cu-Al ALLOYS IN SELECTED INDUSTRIAL AND BIOLOGICAL FLUIDS

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Abstract

The hardness, and corrosion behaviour of ferromanganese modified Cu-Al alloys in selected industrial and biological fluids has been investigated. Cu-Al alloys containing approximately 12wt% Al were produced by casting with varied lean additions of ferromanganese ranging from 0.1 – 0.4 wt% of the charge. The alloys were thermo-mechanically processed adopting a homogenization – cold rolling- annealing treatment as part of the alloy design schedule. Hardness measurement, weight loss corrosion testing and microstructural analysis were used to characterize the alloys produced. The results show that the addition of ferromanganese led to partial refinement of the grain structure with inequigranular recrystallized grains manifesting as dispersed phase in the Cu-Al alloy matrix. The hardness of the Cu-Al based alloys was observed to generally improve with the addition of Fe-Mn although it did not show sensitivity to increase with corresponding increase in the wt% of Fe-Mn. The mass loss of all grades of the alloy produced were observed to be less than $0.02g/cm^2$ in NaCl solution. In H_2SO_4 solution, it was observed that the addition Fe-Mn to the Cu-Al based alloys resulted in distinct improvement of the corrosion resistance of the alloys. The corrosion rates were also relatively lower in glucose and dextrose and saline solutions ($<0.006g/cm^2$) in comparison with NaCl solution ($<0.02g/cm^2$). It was noted that additions of 0.1-0.2wt% Fe-Mn to the Cu-Al based alloy yielded the best combination of properties in the study.

Keywords: Cu-Al based alloys, biomedical applications, ferromanganese, corrosion behaviour, grain refinement; industrial fluids

1 Introduction

Cu based alloys remain among the most competent low-cost engineered materials suitable for the design of components for harsh and many other sensitive environments [1-2]. This fact is corroborated from the assessment of the spectrum of applications where they are currently utilized. Cu based alloys have been used in the design of marine hardwares, shafts, pump and valve components for handling seawater; sour mine waters, non-oxidizing acids, and industrial process fluids [3-5]. They have also been used for manufacture of selected biomedical

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components and surgical tools[6].The material properties required for competent service performance for many of the afore-stated applications are a good combination of high strength, excellent corrosion and wear resistance, which are possessed by Cu-Al based alloys to a large extent [7]. Currently, their modest capacity for shape memory recovery after undergoing large deformation strains is being explored for the production of shape memory components [8-9]. This has buoyed hope that the possibility of low cost design of accessories for sensing devices such as thermostatic radiator valves, contact springs, and thermally actuated switches among others will soon be a commercial realization [10]. With the growing spectrum of applications and other potential uses of Cu based alloys, it is fathomable why there are many shades of studies on the processing – properties – performance characteristics of many Cu based alloys [11-12]. One notable observation from some of these studies is a seeming tendency for brittle fracture and cold formability difficulties of these alloys [10]. To some extent the use of microelements and thermomechanical processing has been adopted to address these challenges. The use of microelements such as Ti, B, Fe and thermomechanical treatment results in refinement of the grain structures of the Cu based alloys [13]. With the exception of Fe, some of the other microelements are quite scarce and expensive; and there has been interest to characterize the material behaviour of the alloys when other low-cost microelements are used. To date works with this processing concept have been very limited. In the present study, the influence of Fe-Mn addition on the indentation resistance and corrosion behaviour of Cu-Al based alloys in selected industrial and biological fluids is investigated. Fe-Mn was selected as microelement addition for the production of the Cu-Al based alloys because lean additions of both iron and manganese have very good solubility in Cu-Al based alloys [13]. This is also coupled with its relative cheap cost of purchase and lower melting point compared with the use of the pure forms of both iron and manganese.

2 Materials and Method

2.1 Alloy Design and Sample Preparation

Sand casting was adopted for the production of the Cu-12Al based alloys (in wt %). The first melt was produced without the addition of Fe-Mn, while subsequent melts produced with the same base Cu-12Al charge composition but with the addition of 0.1, 0.2, 0.3, and 0.4 wt % of Fe-Mn. The ferromanganese (Fe-Mn) used was a master alloy consisting of 30%Fe-70%Mn. 2.5 % additional Al provision was made for each melt during the casting process to accommodate potential Al losses during melting. The chemical compositions of the alloys produced are presented in **Table 1**.

Table 1 Chemical Composition of the Cu-Al based alloys produced

Sample designation	Cu	Al	FeMn
A0	87.96	12.04	0
A0.1	87.91	11.99	0.1
A0.2	87.78	12.02	0.2
A0.3	87.71	11.99	0.3
A0.4	87.66	12.04	0.4

Furtherance to the alloy design procedure, homogenization of the alloys in accordance with Alaneme et al [7] was carried out. The homogenization treatment was performed at 800 °C, for 4 h followed by water quenching. Cold rolling to approximately 10% of the original thickness of the ingots was done after which the alloys were annealed at 500^{o}C for two hours followed by air cooling. Samples for indentation test (hardness measurement), corrosion test, and microstructural analysis were then machined from the alloys. In order to eliminate potential machining induced stresses, the samples were subjected to a final annealing treatment at 500 °C for two hours before water quenching.

2.2 Hardness Measurement

The indentation resistance (hardness) of the Cu-Al based alloys produced was evaluated with an EmcoTEST DURASCAN Microhardness Tester equipped with ecos Workflow ultra modern software. Flat polished surfaces were produced on each sample before the test was carried out. A load of 100 g was applied on the specimens and the indentation resistance determined from the hardness value obtained from the Rockwell hardness scale A used for the measurement. Repeat hardness tests (a minimum of three) were performed on each sample and the mean of values within the range of ± 2% was taken as a measure of the indentation resistance (hardness) of the samples.

2.3 Microstructural Characterization

Microstructural analysis of the Cu-Al alloys produced was carried out using a Zeiss MetallurgicalMicroscope equipped with computer based software for image analysis. The samples were metallographically polished and etched by swabbing with 5g ferric chloride + 10ml HCl + 95ml ethanol solution before the microscopic examination.

2.4 Corrosion Test

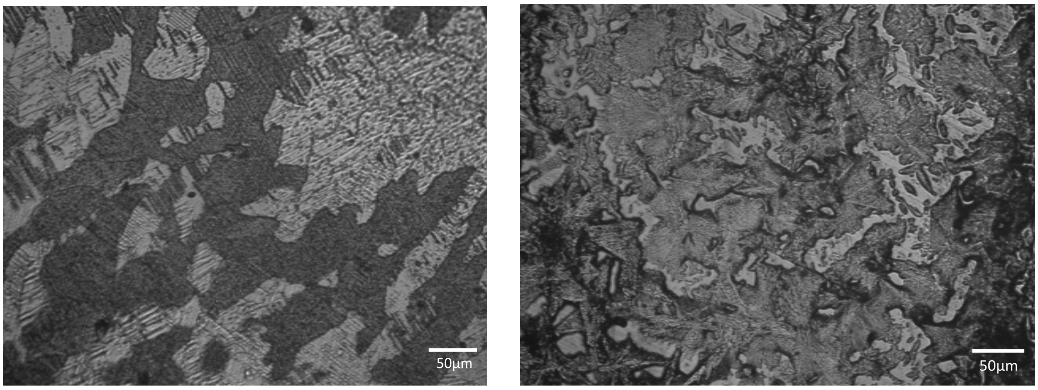
Mass loss and corrosion rate measurements were weight loss parameters used in evaluating the corrosion behaviour of the Cu-Al based alloys. The corrosion tests were performed by immersion of the Cu-Zn-Al alloy samples in 0.3M H_2SO_4 and 3.5wt% NaCl solutions which were considered as representative of industrial fluids. Complementary tests were performed in glucose and also dextrose and saline solutions to assess the alloy behaviour in typical biological fluids. The dextrose and saline solution consists of 5g of dextrose anhydrate and 0.9g sodium chloride in 100ml of water while the glucose solution contains 0.5g hydrous glucose in 100ml of water.

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 in the corrosion media. The solution-to-sample surface area ratio for each medium 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 42 days. The mass loss (g/cm^2) and the corrosion rate (mmy) for each sample was evaluated in accordance with ASTM G31 standards [14].

3 RESULTS AND DICUSSION

3.1 Microstructures

Optical photomicrographs of the unmodified Cu-Al alloy and the Cu-Al alloy modified with 0.1 wt% Fe-Mn (which has microstructural features representative of all modified Cu-Al alloy compositions) are presented in **Fig. 1**. The microstructure of the unmodified Cu-Al alloy is observed to be a dual phase Cu-Al structure with the average grain structure fairly coarse in size (**Fig. 1a**). The 0.1 wt% Fe-Mn modified grade of the Cu-Al alloy (**Fig. 1b**) shows inequigranular recrystallized grains which are dispersed within the matrix structure of the Cu-Al alloy. This is a clear indication that Fe-Mn addition alters the grain morphology of the Cu-Al alloys. Similar structural modifications with tendencies towards grain refinement have been recorded by the use of some other microelements notably Boron, Titanium, and Titanium-Boron additions [13].



(a) (b)

Fig. 1 Representative micrographs of (a) the Cu-Al alloy without Fe-Mn addition, and (b) the Cu-Al alloy modified with 0.1wt% Fe-Mn

3.2 Hardness Behaviour (Indentation Resistance)

The variation of hardness of the Cu-Al alloys with and without the addition of Fe-Mn is presented in **Fig. 2**. It is observed that the hardness of the alloys improved with the addition of Fe-Mn; however, the hardness values did not follow a consistent trend with respect to increase in the wt% of Fe-Mn. The improved hardness with the addition of Fe-Mn arises from the grain modification towards relatively less coarse sizes which as supported by the micrographs presented in **Fig. 1**. The less coarse structure helps in improving the strength of the alloy as explained by the Hall-Petch relations [15] thus improving the resistance of the alloys to indentation deformation.

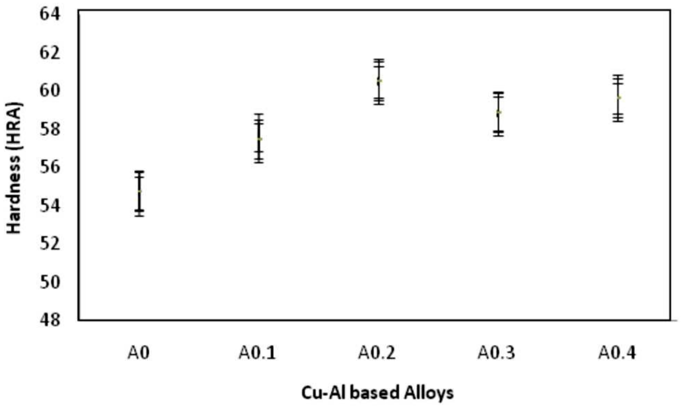
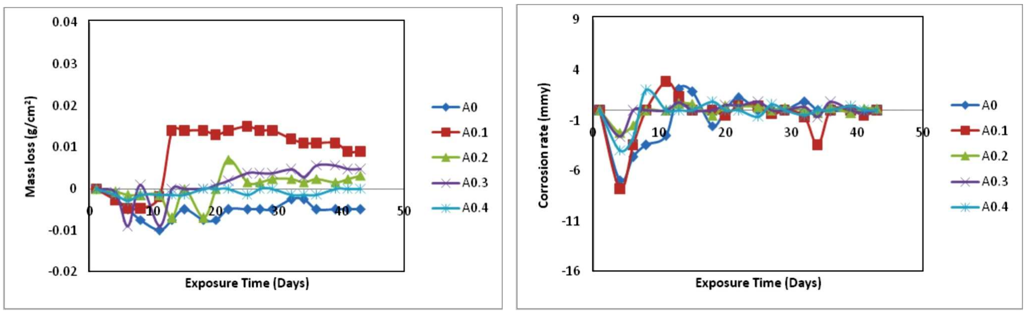


Fig. 2 Variation of hardness values for the Cu-Al based alloys produced

3.3 Corrosion Behaviour of the Cu-Al alloys

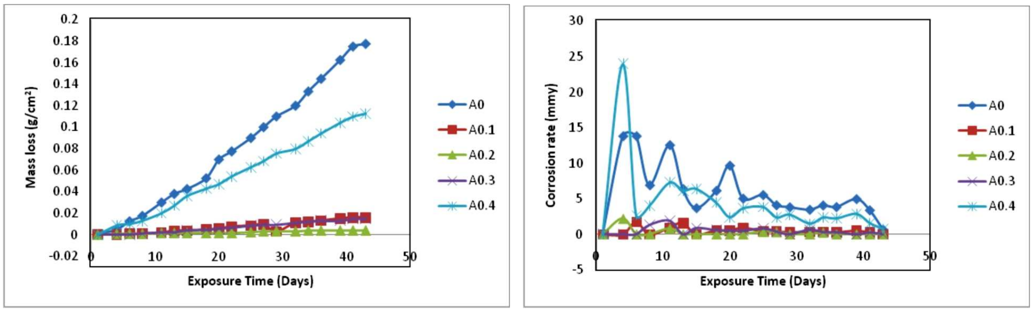
3.3.1 Representative Industrial Fluids

The variation of mass loss and corrosion rates of the Cu-Al based alloys in 3.5% NaCl and 0.3M H_2SO_4 solutions (taken as representative of typical industrial fluids) are presented in **Fig. 3** and **Fig. 4** respectively. From **Fig. 3(a)**, it is observed that the mass loss of all grades of the alloy produced were less than 0.02g/cm^2 in NaCl solution. Close observation show that the addition of Fe-Mn affects slightly the sensitivity of the alloy to corrosion in 3.5% NaCl solution. The addition of Fe-Mn resulted in slight increase in the corrosion susceptibility of the alloy in comparison with the composition without Fe-Mn. This sensitivity is more pronounced for the composition with 0.1wt% Fe-Mn. The other Fe-Mn modified Cu-Al alloys had lower mass loss values comparable with that of the alloy grade without Fe-Mn. **Fig. 3(b)** shows that the period where the alloys exhibited the highest resistance to corrosion was within the 1st and 6th day of immersion in the NaCl solution while peak corrosion rate for the period of the study was observed within the 8th and 13th day of immersion in the solution. The corrosion rate was relatively stable for most of the alloy compositions after the 15th day of immersion.



(a) (b)

Fig. 3 Variation of (a) mass loss, and (b) corrosion rate for the Cu-Al based alloys produced immersed in 3.5% NaCl solution.



(a) (b)

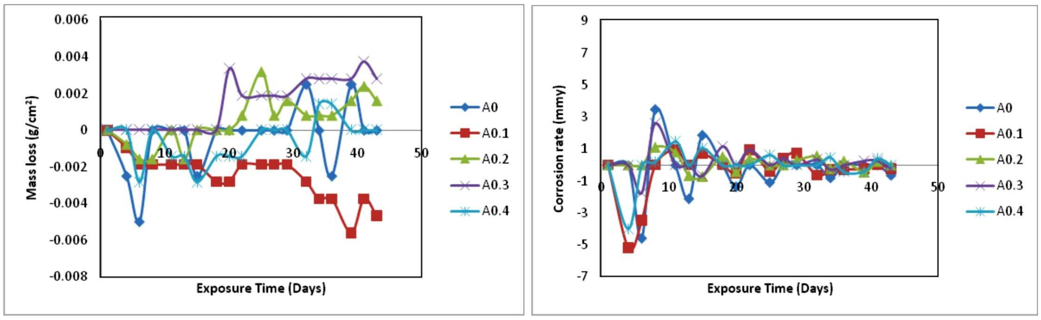
Fig. 4 Variation of (a) mass loss, and (b) corrosion rate for the Cu-Al based alloys produced immersed in 0.3MH_2SO_4 solution

In the case of exposure in 0.3M H_2SO_4 solution, the mass loss and corrosion rate plots are presented in **Fig. 4**. It is observed from **Fig. 4(a)** that the addition Fe-Mn to the Cu-Al based alloys resulted in significant improvement of the corrosion resistance of the Cu-Al alloys in 0.3MH_2SO_4 solution. The optimum corrosion resistance was obtained for the sample containing

0.2wt% Fe-Mn which was observed to have the least mass loss amongst all the alloy compositions produced. Further addition of Fe-Mn resulted in decrease in corrosion resistance (increase in mass loss) which was quite elevated with the addition of up to 0.4wt% Fe-Mn. This is a positive indicator that lean additions of Fe-Mn modified Cu-Al alloys can improve its corrosion resistance for applications in environments with moderate H_2SO_4 concentrations. **Fig.4(b)** confirms that the corrosion rates were more pronounced for the Cu-Al alloy without Fe-Mn and the alloy grade containing 0.4wt% Fe-Mn as their corrosion rates were the most elevated of all the alloy grades produced. The other alloy compositions containing Fe-Mn were stable in H_2SO_4 solution as minimal fluctuations in corrosion rate behaviour was observed from the plot.

3.3.2 Representative Biological Fluids

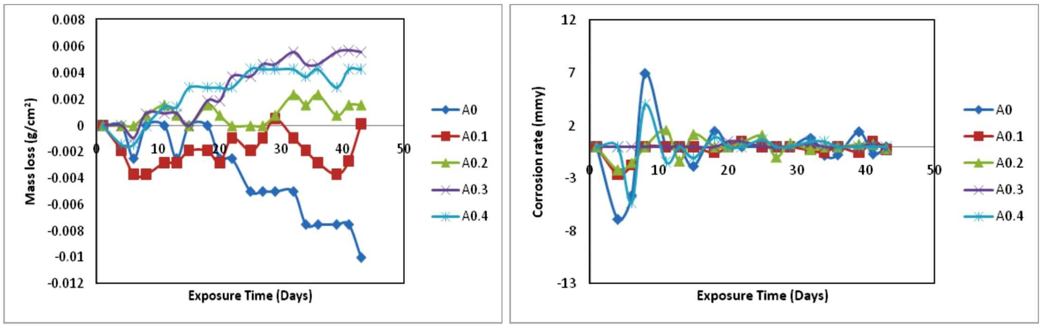
Further studies to ascertain the potential for use of the Cu-Al alloys produced in biological fluids was studied in glucose solution (**Fig. 5**) and dextrose and saline solution (**Fig. 6**) which are common body fluids. The mass loss and corrosion rate of the alloys in glucose solution are presented in **Fig. 5**. From **Fig. 5(a)**, it is observed that the alloys generally had mass loss values less than 0.006g/cm^2 in glucose solution in comparison with NaCl solution (**Fig. 3a**) which had mass loss within the range (<0.02g/cm^2). This is a strong indication that the dissolution rate of the alloy in glucose solution is lower than in NaCl solution. It is also observed from **Fig. 5(a)** that the alloy without Fe-Mn and that containing 0.1wt% Fe-Mn are the best suited for this environment. **Fig. 5(b)** shows that the least corrosion rate was observed within the 1st – 6th day of immersion while the peak corrosion rates during the experiment was within the 6th – 10th day. The corrosion rates on other days are observed to be less dramatic compared to the first 10 days of the immersion test.



(a) (b)

Fig. 5 Variation of (a) mass loss and (b) corrosion rate for the Cu-Al based alloys produced immersed in glucose solution

Similarly, in dextrose and saline solutions, there is also a high resistance to corrosion (<0.004g/cm^2) in comparison to the NaCl solution (**Fig. 3a**). From **Fig. 6(a)**, it is observed that maximum mass loss of the alloy is 0.004g/cm^2 - an indication that the alloys are less susceptible to attack by the dextrose and saline solution in comparison with NaCl solution. Close observation show that the alloy grade containing 0.1wt% Fe-Mn was the most stable in the solution compared with the other alloy grades. **Fig. 6(b)**, confirms that the alloy grade containing 0.1 wt% Fe-Mn was the most stable in the dextrose and saline solution compared with the other alloy grades.



(a) (b)

Fig. 6 Variation of (a) mass loss, and (b) corrosion rate for the Cu-Al based alloys produced immersed in dextrose and saline solution

Cu based alloys have been studied in similar biological fluids with consideration of their potentials for biomedical applications reported [16-17]. The problems of cytotoxicity and the link of Al to the cause of neurological disorders such as Alzheimer's disease have raised alot of concerns and limited their use as inplant [17]. Nonetheless, their behaviour in a number of bodily fluids has still continued to generate interest among researchers [17-19].

4 Conclusions

In this study, the hardness and corrosion behaviour of ferromanganese modified Cu-Al alloys in selected industrial and biological fluids was investigated. The results show that:

- The addition of ferromanganese led to partial refinement of the grain structure with inequigranular recrystallized grains manifesting as dispersed phase in the Cu-Al alloy matrix.
- The hardness of the Cu-Al based alloys generally improved with the addition of Fe-Mn although it did not show sensitivity to increases with corresponding increase in the wt% of Fe-Mn.
- The mass loss of all grades of the alloy produced were observed to be less than 0.02g/cm^2 in NaCl solution. In H_2SO_4 solution, it was observed that the addition Fe-Mn to the Cu-Al based alloys resulted in distinct improvement of the corrosion resistance of the alloys.
- The corrosion rates were also relatively lower in glucose and dextrose and saline solutions (<0.006g/cm^2) in comparison with NaCl solution (<0.02g/cm^2).
- It was noted that additions of 0.1-0.2wt% Fe-Mn to the Cu-Al based alloy yielded the best combination of properties in the study.

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